oxid addn eta 2 refs

Research Topic task started on Fri Jan 4, 2008 at 4:17 PM

5 Research Topic candidates were identified in CAPLUS and MEDLINE.

using the phrase "oxidative addition and mechanism"

Selected 2 of 5 candidate topics.

5 references were found containing **"oxidative addition and mechanism"** as entered.

11860 references were found containing both of the concepts **"oxidative addition"** and **"mechanism"**.

Research Topic Refine started

154 references were found when refined using the phrase **"benzene and complex"**

Connected to ChemPort: document

* Liu, Weijun, Welch, Kevin, Trindle, Carl O., Sabat, Michal, Myers, William H., Harman, W. Dean. Facile Intermolecular Aryl-F Bond Cleavage in the Presence of Aryl C-H Bonds: Is the ?2-Arene Intermediate Bypassed?. Organometallics (2007), 26 (10), 2589-2597.

Connected to ChemPort: document

* Green, Jennifer C., Herbert, Benjamin J., Lonsdale, Richard. Oxidative addition of aryl chlorides to palladium N-heterocyclic carbene complexes and their role in catalytic arylamination. Journal of Organometallic Chemistry (2005), 690 (24-25), 6054-6067.

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Answer 1:

Bibliographic Information

Activation of carbon-hydrogen bonds via 1,2-addition across M-X (X = OH or NH2) bonds of d6 transition metals as a potential key step in hydrocarbon functionalization: a computational study. Cundari, Thomas R.; Grimes, Thomas V.; Gunnoe, T. Brent. Department of Chemistry and Center for Advanced Scientific Computing and Modeling (CASCaM), University of North Texas, Denton, TX, USA. Journal of the American Chemical Society (2007), 129(43), 13172-13182. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 148:33871 AN 2007:1141297 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Potential energy surfaces for oxidative addn. of benzene C-H-bonds to triazoborate d6-transition metal complexes [[HB(N:NH-?-N)3]M(X)(PH3)2]q (X = OH, NH2; M = Tc, Re, q = -1; M = Ru, q = 0; M = Co, Ir, q = +1; M = Ni, Pt, q = +2) were calcd. at DFT B3LYP level. The benzene activation started by formation of active species [[HB(N:NH-?-N)3]M(X)(PH3)]q (B) and proceeds via formation of the benzene ?-complexes [[HB(N:NH-?-N)3]M(X)(PH3)(?-C6H6)]q (C), oxidative addn. to form Ph complexes [[HB(N:NH-?-N)3]M(X)(PH3)(Ph)(XH)] (E) and ligand substitution to give the products [[HB(N:NH-?-N)3]M(X)(PH3)2(Ph)] (F). For the benzene C-H activation reaction steps, kite-shaped transition states were located and found to have relatively little metal-hydrogen interaction. The C-H activation process is best described as a metal-mediated proton transfer in which the metal center and ligand X function as an activating electrophile and intramol. base, resp. While the metal plays a primary role in controlling the kinetics and thermodn. of the reaction coordinate for C-H activation/functionalization, the ligand X also influences the energetics. On the basis of three thermodn. criteria characterizing salient energetic aspects of the proposed catalytic cycle and the detailed computational studies reported herein, late transition metal complexes (e.g., Pt, Co, etc.) in the d6 electron configuration, esp. the [[HB(N:NH-?-N)3]Co(PH3)2(OH)]+ complex and related Co(III) systems, are predicted to be the most promising for further catalyst investigation.

Answer 2:

Bibliographic Information

Competitive O-H and C-H oxidative addition of CH3OH to rhodium(ii) porphyrins. Li, Shan; Cui, Weihong; Wayland, Bradford B. Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA. Chemical Communications (Cambridge, United Kingdom) (2007), (39), 4024-4025. Publisher: Royal Society of Chemistry, CODEN: CHCOFS ISSN: 1359-7345. Journal written in English. CAN 148:23211 AN 2007:1108142 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Rhodium(ii) porphyrins react with CH3OH in benzene by alternate mechanisms that give H-CH2OH and H-OCH3 bond activation in different methanol concn. regimes which is a rare example of transition metal reactivity with methanol.

Answer 3:

Bibliographic Information

Carbon-Hydrogen Bond Activation in Hydridotris(pyrazolyl)borate Platinum(IV) Complexes: Comparison of Density Functionals, Basis Sets, and Bonding Patterns. Vastine, Benjamin Alan; Webster, Charles Edwin; Hall, Michael B. Department of Chemistry, Texas A&M University, College Station, TX, USA. Journal of Chemical Theory and Computation (2007), 3(6), 2268-2281. Publisher: American Chemical Society, CODEN: JCTCCE ISSN: 1549-9618. Journal written in English. CAN 147:522379 AN 2007:1033046 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reaction mechanism for the cycle beginning with the reductive elimination (RE) of methane from ?3-TpPtIV(CH3)2H (1) (Tp = hydridotris(pyrazolyl)borate) and subsequent oxidative addn. (OA) of benzene to form finally ?3-TpPtIV(Ph)2H (19) was investigated by d. functional theory (DFT). Two mechanistic steps are of particular interest, namely the barrier to C-H coupling (barrier 1 - Ba1) and the barrier to methane release (barrier 2 - Ba2). For 31 d. functionals, the calcd. values for Ba1 and Ba2 were benchmarked against the exptl. reported values of 26 (Ba1) and 35 (Ba2) kcal?mol-1, resp. Specifically, the values for Ba1 and Ba2, calcd. at the B3LYP/double-? plus polarization level of theory, are 24.6 and 34.3 kcal?mol-1, resp. Overall, the best performing functional was BPW91 where the mae assocd. with the calcd. values of the two barriers is 0.68 kcal?mol-1. The calcd. B3LYP values of Ba1 ranged between 20 and 26 kcal?mol-1 for 12 effective core potential basis sets for platinum and 29 all-electron basis sets for the first row elements. Polarization functions for the first row elements were important for accurate values, but the addn. of diffuse functions to non-hydrogen (+) and hydrogen atoms (++) had little effect on the calcd. values. Basis set satn. was achieved with APNO basis sets utilized for first-row atoms. Bader's "Atoms in Mols." was used to analyze the electron d. of several complexes, and the electron d. at the Pt-Nax bond crit. point (trans to the active site for C-H coupling) varied over a wider range than any of the other Pt-N bonds.

Answer 4:

Bibliographic Information

Investigations Directed at Catalytic Carbon-Carbon and Carbon-Oxygen Bond Formation via C-H Bond Activation.
Blackmore, Ian J.; Semiao, Christopher J.; Buschhaus, Miriam S. A.; Patrick, Brian O.; Legzdins, Peter. Department of Chemistry, The University of British Columbia, Vancouver, BC, Can. Organometallics (2007), 26(20), 4881-4889. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 147:427460 AN 2007:921226 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A potential catalytic cycle for the arom. C-H-bond activation by molybdenum and tungsten half-sandwich nitrosyl complexes Cp'M(NO)(L) (M = Mo, W; Cp' = ?5-C5Me5, ?5-C5H5; L = Lewis base) was explored by NMR monitoring, isolation and structural characterization of intermediates. The cycle is based on three steps: (1) oxidative addn. of the hydrocarbon substrate to the metal center, (2) subsequent hydrometalation of the olefin or the ketone, and (3) final reductive elimination of the coupled product. Of the various Cp'M(NO)(L) groups examd., the Cp*W(NO)(PPh3) fragment has been found to be the best candidate for mediating these catalytic steps since it is not prone to form unreactive Cp*W(NO)(PPh3)2 as are some of the other fragments that readily decomp. to 18e Cp'M(NO)L2 complexes. Hence, Cp*W(NO)(PPh3) has been utilized to det. if the oxidative addn. and hydrometalation steps can occur sequentially under one-pot exptl. conditions. However, olefins are too ?-acidic and readily form stable 18e Cp*W(NO)(PPh3)(?2-olefin) adducts, which prevent oxidative addn. of the hydrocarbon substrate to the tungsten center. Similarly, benzophenone, Ph2CO, and diisopropyl ketone, iPr2CO, also form 1:1 ?2-C:O adducts with the ?-basic tungsten center in the 16e fragment. Nevertheless, oxidative addn. and hydrometalation do occur sequentially to form the desired aryl alkoxide complex, Cp*W(NO)(OCHiPr2)(Ph), in addn. to the Cp*W(NO)(?2-OCiPr2)(PPh3) adduct, when benzene and diisopropyl ketone are employed as the two substrates. The solid-state mol. structures of cis-Cp*W(NO)[?2-(CH2NMe)P(NMe2)2](H), Cp*W(NO)(OCHiPr2)(Ph), and Cp*W(NO)(?2-OCiPr2)(PPh3) have been established by single-crystal x-ray crystallog. analyses.

Answer 5:

Bibliographic Information

Transition metal-catalyzed olefin arylation via C-H bond activation of arenes. Matsumoto, Takaya. Central Technical Research Laboratory, Nippon Oil Corporation, 8 Chidoricho, Naka-ku, Yokohama, Kanagawa, Japan. Catalysis Surveys from Asia (2007), 11(1/2), 31-48. Publisher: Springer Science+Business Media, Inc., CODEN: CSAABF ISSN: 1571-1013. Journal; General Review written in English. CAN 147:541308 AN 2007:905527 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A review. In this article, two kinds of our transition metal-catalyzed olefin arylations are summarized and discussed. The first one is Ir-catalyzed novel anti-Markovnikov hydroarylation of olefins with benzene. Using this reaction catalyzed by [Ir(?-acac-O,O',C3)(acac-O,O')(acac-C3)]2 (acac = acetylacetonato), straight-chain alkylarenes, which were not obtainable by the conventional Friedel-Crafts arom. alkylation with olefins, were able to be successfully synthesized directly from arenes and olefins with the higher selectivity than that of branched alkylarenes. This is the first efficient catalyst which shows the desirable high regioselectivity. The reaction of benzene with propylene gave n-propylbenzene and cumene in 61% and 39% selectivities, resp., and the reaction of benzene and styrene afforded 1,2-diphenylethane in 98% selectivity. The reaction of alkylarene and olefin showed meta and para orientations. A wide range of olefins and arenes can be employed for the synthesis of alkylarenes. The mechanism of the reaction involves C-H bond activation of benzene by Ir center to form Ir-Ph species. The second reaction is Rh-catalyzed oxidative arylation of ethylene with benzene to directly produce styrene, namely one-step synthesis of styrene. The reaction of benzene with ethylene catalyzed by Rh(ppy)2(OAc) (ppyH = 2-phenylpyridine, OAc = acetate) with Cu oxidizing agent gave styrene and vinyl acetate in 77% and 23% selectivities, resp., in contrast to those by Pd(OAc)2, 47% of styrene and 53% of vinyl acetate. The mechanism of the reaction involves Rh-mediated C-H bond activation of benzene, which appears to be a rate-detg. step. Furthermore, Rh complexes in a Rh(I) oxidn. state at the beginning of the reaction work as catalysts for the reaction by addn. of acacH and O2 without any oxidizing agent, like Cu salt.

Answer 6:

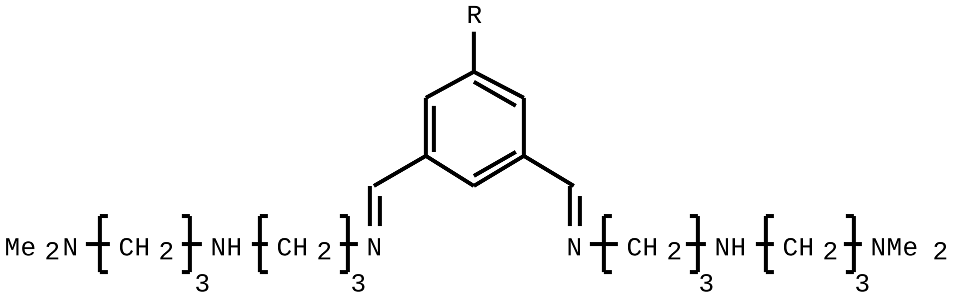
Bibliographic Information

Fast O2 Binding at Dicopper Complexes Containing Schiff-Base Dinucleating Ligands. Company, Anna; Gomez, Laura; Mas-Balleste, Ruben; Korendovych, Ivan V.; Ribas, Xavi; Poater, Albert; Parella, Teodor; Fontrodona, Xavier; Benet-Buchholz, Jordi; Sola, Miquel; Que, Lawrence, Jr.; Rybak-Akimova, Elena V.; Costas, Miquel. Departament de Quimica and Institut de Quimica Computacional, Universitat de Girona, Girona, Spain. Inorganic Chemistry (Washington, DC, United States) (2007), 46(12), 4997-5012. Publisher: American Chemical Society, CODEN: INOCAJ ISSN: 0020-1669. Journal written in English. CAN 147:156566 AN 2007:521274 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A new family of dicopper(I) complexes [CuI2RL](X)2 (R = H, 1X, R = tBu, 2X and R = NO2, 3X, X = CF3SO3, ClO4, SbF6, or BArF, BArF = [B{3,5-(CF3)2C6H3}4]-), where RL is a Schiff-base ligand (I) contg. two tridentate binding sites linked by a xylyl spacer, was prepd. and characterized, and its reaction with O2 was studied. The complexes were designed with the aim of reproducing structural aspects of the active site of type 3 dicopper proteins; they contain two three-coordinate copper sites and a rather flexible podand ligand backbone. The solid-state structures of 1ClO4?2CH3CN, 2CF3SO3, 2ClO4, and 3BArF?CH3CN were established by single-crystal x-ray diffraction anal. 1ClO4 adopts a polymeric structure in the solid state while 2CF3SO3, 2ClO4, and 3BArF?CH3CN are monomeric. The complexes were studied in soln. by 1H and 19F NMR spectroscopy, which put forward the presence of dynamic processes. 1-3BArF and 1-3CF3SO3 in acetone react rapidly with O2 to generate metastable [CuIII2(?-O)2(RL)]2+ 1-3(O2) and [CuIII2(?-O)2(CF3SO3)(RL)]+ 1-3(O2)(CF3SO3) species, resp., that were characterized by UV-visible spectroscopy and resonance Raman anal. Instead, reaction of 1-3BArF with O2 in CH2Cl2 results in intermol. O2 binding. DFT methods were used to study the chem. identities and structural parameters of the O2 adducts, and the relative stability of the CuIII2(?-O)2 form with respect to the CuII2(?-?2:?2-O2) isomer. The reaction of 1X, X = CF3SO3 and BArF, with O2 in acetone was studied by stopped-flow UV-visible exhibiting an unexpected very fast reaction rate (k = 3.82(4) ? 103 M-1 s-1, ?H.thermod. = 4.9 ? 0.5 kJ mol-1, ?S.thermod. = -148 ? 5 J K-1 mol-1), nearly 3 orders of magnitude faster than in the parent [CuI2(m-XYLMeAN)]2+. Thermal decompn. of 1-3(O2) does not result in arom. hydroxylation. The mechanism and kinetics of O2 binding to 1X (X = CF3SO3 and BArF) are discussed and compared with those assocd. with selected examples of reported models of O2-processing copper proteins.

A synergistic role of the copper ions in O2 binding and activation is clearly established from this anal.



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Answer 7:

Bibliographic Information

Facile Intermolecular Aryl-F Bond Cleavage in the Presence of Aryl C-H Bonds: Is the ?2-Arene Intermediate Bypassed?
Liu, Weijun; Welch, Kevin; Trindle, Carl O.; Sabat, Michal; Myers, William H.; Harman, W. Dean. Department of Chemistry, University of Virginia, Charlottesville, VA, USA. Organometallics (2007), 26(10), 2589-2597. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 147:52993 AN 2007:408263 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Tungsten ?2-benzene complex [TpW(NO)(PMe3)(?2-C6H6)] (1) undergoes clean insertion of C-F bonds of fluorobenzene to form the seven-coordinate complex [TpW(NO)(PMe3)(F)(Ph)] (2), while no C-H insertion is detected. Structure of 2 was confirmed by x-ray crystallog. Treatment of the complex 2 with triethyl- or phenyldimethylsilane results in liberation of benzene and the corresponding silyl fluoride. Reaction of 1 with PhCF3 and C6F6 and 1-fluoronaphthalene gave the benzene substitution products, [TpW(NO)(PMe3)(3,4-?-C6H5CF3)], [TpW(NO)(PMe3)(?2-C6F6)] and [TpW(NO)(PMe3)(?2-1-C10H7F)] (4, 5 and 6a-d, resp.), while reaction of 1-fluoro-3-(trifluoromethyl)benzene afforded the oxidn. addn. product, [TpW(NO)(PMe3)(F)(3-CF3C6H3)] (5). DFT calcns. suggest a low-energy reaction pathway for C-F activation involving a fluorine-bound ?-complex that does not require the presence of an ?2-arene intermediate. As the fluorine content of the benzene increases, or the benzene is replaced by fluoronaphthalene, C-F addn. is no longer obsd., and either C-H addn. or ?2-coordination dominates. Two species thought to be ?2-silanes, [TpW(NO)(PMe3)(H,Si-?-HSiEt3)] (9) and [TpW(NO)(PMe3)(H,Si-?-HSiPhMe2)] (10), are also reported.

Answer 8:

Bibliographic Information

Theoretical Elucidation of the Platinum-Mediated Arene C-H Activation Reactions. Li, Ji-Lai; Geng, Cai-Yun; Huang, Xu-Ri; Zhang, Xiang; Sun, Chia-Chung. State Key Laboratory of Theoretical and Computational Chemistry Institute of Theoretical Chemistry, Jilin University, Changchun, Peop. Rep. China. Organometallics (2007), 26(9), 2203-2210. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 146:521915 AN 2007:342169 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The complete reaction mechanism of the platinum diimine complex-mediated arene C-H activation was investigated by using the B3LYP d. functional theory method. The calcns. show that the protonation should occur at the metal center, giving a coordinately unsatd. five-coordinate Pt(IV) hydride which is trapped by acetonitrile; otherwise monophenyl solvento cations (N-N)Pt(Ph)(NCMe)+

should be isolated and characterized spectroscopically. Potential energy surface, transition state structures and geometry optimization for the possible reaction intermediates, (N-N)PtPh2 (N-N = ArN:CMeCMe:NAr, where Ar = 2,6-Me2C6H3), [(N-N)PtPh(?2-C6H6)]+, [(N-N)Pt(H)Ph2]+, [(N-N)Pt(H)Ph2(MeCN)]+, [(N-N)PtPh(MeCN)]+ were calcd. Oxidative addn.-reductive elimination and ?-bond metathesis mechanisms (including direct ?-bond metathesis and indirect ?-bond metathesis) are considered as possible mechanisms for H-D-exchange. The indirect ?-bond metathesis, which goes through a two-step H migration, is dramatically higher in energy than that of the direct one, and may be safely rule it out. The barrier assocd. with direct ?-bond metathesis is 14.70 kcal/mol, to be compared with 20.56 kcal/mol found in oxidative addn. So, unlike the methane C-H activation, the direct ?-bond metathesis pathway is predicted to take place predominantly. Furthermore, the solvent-induced associative elimination of benzene is also confirmed by the current theor. studies for the first time. The trigonal bipyramidal transition states offer substantial evidence for this process, and the principle of microscopic reversibility then implies that benzene coordination will also be a solvent-assisted, associative process for a C-H activation reaction. For the different rates of benzene elimination, our calcns. show that nucleophiles with higher electron-donating abilities and small steric effects of the diimine ligands will favor elimination greatly.

Answer 9:

Bibliographic Information

Comprehensive Theoretical Study on the Mechanism of Regioselective Hydroformylation of Phosphinobutene Catalyzed by a Heterobinuclear Rhodium(I)-Chromium Complex. Tang, Dianyong; Qin, Song; Su, Zhishan; Hu, Changwei. Key Laboratory of Green Chemistry and Technology, Sichuan University, Chengdu, Peop. Rep. China. Organometallics (2007), 26(1), 33-47. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 146:206452 AN 2006:1281875 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A concerted mechanism for the hydroformylation of phosphinobutene catalyzed by heterobinuclear (CO)4Cr(?-PH2)2RhH(CO)(PH3) was elucidated by d. functional theory (DFT), with particular emphasis on the catalytic cycle, the regioselectivity, the cooperativity of Cr with Rh, and the interpretation of exptl. observations. Four possible mechanisms were studied, and the results were compared. The introduction of the Cr(CO)4 moiety remodels the mechanism. The Rh-Cr-catalyzed hydroformylation mechanism includes the following:(a) formation of the chelate acyl species through a chelate associative mechanism including olefin addn., olefin insertion, and carbonyl insertion steps, (b) CO addn. to the chelate acyl species with the formation of a monodentate acyl species, and (c) the conversion of the monodentate acyl species to the product aldehyde through H2 coordination, H2 oxidative addn., and aldehyde elimination. Carbonyl insertion is predicted to be the rate-limiting step, with a free energy barrier of 86.76 kJ/mol in benzene soln. at 353.15 K and 27.15 atm. The favorability of the branched product is predicted to be nearly 100% both kinetically and thermodynamically. The Cr serves as an orbital reservoir in olefin addn. and insertion steps via the variation of the orbital interaction between Rh and Cr atoms. The catalytic activity of the Rh(I)-Cr bimetallic complex is higher than that of the monometallic Rh catalysts. These could explain satisfactorily the reported exptl. observations.

Answer 10:

Bibliographic Information

Reactivity of Pd(0)(NHC)2 (NHC: N-heterocyclic carbene) in oxidative addition with aryl halides in Heck reactions. Roland, Sylvain; Mangeney, Pierre; Jutand, Anny. Laboratoire de Chimie Organique, UMR CNRS 7611, Universite Pierre et Marie Curie, Paris, Fr. Synlett (2006), (18), 3088-3094. Publisher: Georg Thieme Verlag, CODEN: SYNLES ISSN: 0936-5214. Journal written in English. CAN 146:163252 AN 2006:1263070 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Pd(0)(NHC)2 complexes (satd. or unsatd. NHC) may react in oxidative addn. of aryl halides by two mechanisms: a dissociative mechanism involving Pd(0)(NHC) as reactive complex formed after dissocn. of one carbene or an associative mechanism involving

Pd(0)(NHC)2 as the reactive complex. The mechanism of the oxidative addn. of aryl halides with Pd(0)(2)2 (2: 1,3-di-benzyl-4,5-di-tert-butylimidazolidin-2-ylidene) is established in this work (associative mechanism) and compared to that of Pd(0)(1)2 (1: 1,3-di-tert-butylimidazolin-2-ylidene) which reacts via Pd(0)(1) in a dissociative mechanism, as reported by Cloke et al. Both complexes activate aryl chlorides at room temp. The more reactive complex with aryl chlorides is Pd(0)(2)2 which directly reacts in an associative mechanism. Pd(0)(2)2 is even more reactive than Pd(0)(1). Consequently, the reactivity of Pd(0)(NHC)2 complexes in oxidative addns. is not connected to the structure of the reactive species, i.e., Pd(0)(NHC)2 vs. Pd(0)(NHC) but is more relevant to the electronic and steric properties of the carbene ligand.

Answer 11:

Bibliographic Information

Intermolecular Arene C-H Activation by Nickel(II). Liang, Lan-Chang; Chien, Pin-Shu; Huang, Yu-Lun. Department of Chemistry and Center for Nanoscience Nanotechnology, National Sun Yat-sen University, Kaohsiung, Taiwan. Journal of the American Chemical Society (2006), 128(49), 15562-15563. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 146:122118 AN 2006:1193543 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Intermol. arene C-H activation mediated by a divalent nickel bis(2-diphenylphosphinophenyl)amine PNP-pincer complexes proceeds in solns. under mild conditions is described. Reactions of benzene, toluene and m-xylene with [R-PNP]NiH an 1 equiv of B(C6F5)3 gave the corresponding aryl complexes [R-PNP]NiAr [R-PNP = N(C6H4PR2-2)2-?N,?P,?P'; R = iPr, Cy; Ar = Ph, 3- or 4-MeC6H4, 3,5-Me2C6H3, resp.]. The starting complexes [R-PNP]NiH were prepd. by reactions of either Ni(COD)2 with H[N(C6H4-2-PR2)2] or [R-PNP]NiCl with LiBHEt3 in THF at -35? in high yield. The mechanism of the arene C-H-activation comprise formation of zwitterionic [R-PNP]Ni(?-H)B(C6F5)3 complexes which then undergo oxidative C-H-addn. Reaction of [R-PNP]NiH with AlMe3 in benzene at room temp. afforded exclusively the corresponding [R-PNP]NiPh. The remarkable reactivity of inexpensive Ni(II) species established in this study is attractive, particularly from an economic viewpoint, as compared to the current alternatives of 4d and 5d metals.

Answer 12:

Bibliographic Information

Oxidative addition of methane and benzene C-H bonds to rhodium center: A DFT study. Bi, Siwei; Zhang, Zhenwei; Zhu, Shufen. College of Chemistry Science, Qufu Normal University, Shandong, Qufu, Peop. Rep. China. Chemical Physics Letters (2006), 431(4-6), 385-389. Publisher: Elsevier B.V., CODEN: CHPLBC ISSN: 0009-2614. Journal written in English. CAN 146:81465 AN 2006:1190216 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A d. functional theory study on mechanisms of the oxidative addn. of methane and benzene C-H bonds to the rhodium center contg. Cp and PMe3 ligands has been performed. Our calcd. results confirm that the C-H bond cleavage from a sigma complex to a hydride alkyl complex is the rate-detg. step. Compared with the case of methane C-H bond, the oxidative addn. of benzene C-H bond is more favorable kinetically and thermodynamically. Stronger back-donation from metal center to the ?* antibonding orbital of benzene C-H bond is responsible for the observations.

Answer 13:

Bibliographic Information

Mechanistic study of cyclohexene oxidation and its use in modification of industrial waste organics. Mukherjee, Sanghamitra; Samanta, Sujit; Bhaumik, Asim; Ray, Bidhan Chandra. Department of Chemistry, Jadavpur University, Kolkata, India. Applied Catalysis, B: Environmental (2006), 68(1-2), 12-20. Publisher: Elsevier B.V., CODEN: ACBEE3 ISSN: 0926-3373. Journal written in English. CAN 146:46721 AN 2006:1052930 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Mechanistic study of oxidn. of cyclohexene was carried out over a copper complex and its immobilized analog supported on organically modified silica. The immobilized complex has been characterized by using at. absorption spectrophotometry (AAS), FT-IR, EPR and UV-vis spectroscopic studies and SEM image anal. Catalytic oxidn. of cyclohexene was carried out over this copper complex and the immobilized analog with different oxidants like dil. aq. hydrogen peroxide and tert-Bu hydroperoxide at ambient conditions. Acetonitrile and water was used as solvent and dispersion medium, resp., with or without addnl. acid in different sets of oxidn. reactions. The mechanism of hydride shift initiated the study of benzene oxidn., which gave quinone as major product. The activity of the immobilized catalyst remains nearly the same after four cycles, suggesting the true heterogeneous nature of the catalyst.

Answer 14:

Bibliographic Information

Reactivity of V(V) peroxo complexes. Bonchio, Marcella; Conte, Valeria; Modena, Giorgio. Dipartimento di Scienze Chimiche, Universita di Padova, Italy. Chimica e l'Industria (Milan, Italy) (2006), 88(6), 44-49. Publisher: Promedia Publishing, CODEN: CINMAB ISSN: 0009-4315. Journal; General Review written in Italian. CAN 145:300340 AN 2006:970029 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A review; the mechanism of oxygen transfer by peroxometal complexes depends on several factors with the prominent role of the metal itself and of its coordination sphere. In addn. to the most-known polar electrophilic oxidn., the occurrence of S.E.T pathways have been delineated which are responsible for radical chain oxidns. Within the frame of a joint project, key results obtained in collaboration with Prof. John Edwards at Brown University (R.I., USA), have traced the formation of competent intermediates involved in the direct benzene hydroxylation by vanadium(V) peroxocomplexes and their fate along the radical chain process.

Answer 15:

Bibliographic Information

Solvent polarity effect on CH activation by platinum with N and O-donor ligands. Ziatdinov, Vadim R.; Periana, Roy A. Department of Chemistry, Loker Hydrocarbon Institute, University of Southern California, Los Angeles, CA, USA. Abstracts of Papers, 232nd ACS National Meeting, San Francisco, CA, United States, Sept. 10-14, 2006 (2006), INOR-786. Publisher: American Chemical Society, Washington, D. C CODEN: 69IHRD Conference; Meeting Abstract; Computer Optical Disk written in English. AN 2006:861174 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The potential to achieve facile C-H activation rates in protic solvents has attracted a significant attention from the scientific community. Recently, we reported a novel picolinate, (NO)Pt(II) complex for the C-H activation of benzene that was 300 times more reactive than dichloro(f--2-{2,2'-bipyrimidyl})platinum(II). Theor. (DFT) and exptl. studies of the effect of solvent polarity on the reaction rates of platinum(II) with N and O-donor ligands are presented. We report DFT results on a solvent assisted electrophilic transition state as well as alternative mechanisms, such as electrophilic substitution, oxidative addn. and oxidative hydrogen migration (OHM). In each case, the role of solvent have been established and exptl. confirmed for a no. of a model systems.

Answer 16:

Bibliographic Information

Ortho C-H activation of haloarenes and anisole by an electron-rich iridium(I) complex: mechanism and origin of regio- and chemoselectivity. An experimental and theoretical study. Ben-Ari, Eyal; Cohen, Revital; Gandelman, Mark; Shimon, Linda J. W.; Martin, Jan M. L.; Milstein, David. Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel. Organometallics (2006), 25(13), 3190-3210. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 145:145850 AN 2006:458988 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Iridium(I) pincer PNP-complex undergoes facile C-H-activation with benzene, haloarenes and anisole, forming stable hydrido-aryl Ir(III) complexes; the origin of ortho-chemoselectivity of the reaction was explored exptl. and by quantum-chem. calcns. Reaction of (PNP)Ir(COE)+PF6- (1; PNP = 2,6-bis(di-tert-butylphosphinomethyl)pyridine; COE = cyclooctene) with benzene yields a stable unsatd. square pyramidal Ir(III) hydrido-aryl complex, [(PNP)Ir(H)(Ph)] (2), which undergoes arene exchange upon reaction with other arenes at 50?. Upon reaction of 1 with haloarenes (chlorobenzene and bromobenzene) and anisole at 50?, selective ortho C-H activation takes place. No C-halogen bond activation was obsd., even in the case of the normally reactive bromobenzene and despite the steric hindrance imposed by the halo substituent. The ortho-activated complexes [(PNP)Ir(H)(Ar)](8a, 9a, 10a; Ar = 2-ClC6H4, 2-BrC6H4, 2-MeOC6H4) exhibited a higher barrier to arene exchange; i.e., no exchange took place when heating at a temp. as high as 60?. These complexes were more stable, both thermodynamically and kinetically, than the corresponding meta- and para-isomers. The obsd. selectivity is a result of coordination of the heteroatom to the metal center, which kinetically directs the metal to the ortho C-H bond and stabilizes the resulting complex thermodynamically. Upon reaction of complex 1 with fluorobenzene under the same conditions, no such selectivity was obsd., due to low coordination ability of the fluorine substituent. Competition expts. showed that the ortho-activated complexes 8a, 9a, and 10a have similar kinetic stability, while thermodynamically the chloro and methoxy complexes 8a and 10a are more stable than the bromo complex 9a. Computational studies, using the DFT mPW1K exchange-correlation functional and a variety of basis sets for PNP-based systems, provide mechanistic insight. The rate-detg. step for the overall C-H activation process of benzene is COE dissocn.

to form a reactive 14e complex, followed by formation of a ?2C-C intermediate, which is converted into an ?2C-H complex, both being important intermediates in the C-H activation process. In the case of chlorobenzene, bromobenzene, and anisole, ?1-coordination via the heteroatom to the 14e species followed by formation of the ortho ?2C-H complex leads to selective activation. The unobserved C-halide activation process was shown computationally in the case of chlorobenzene to involve the same Cl-coordinated intermediate as in the C-H activation process, but it experiences a higher activation barrier. The ortho C-H activation product is also thermodynamically more stable than the C-Cl oxidative addn. complex.

Answer 17:

Bibliographic Information

Oxidative addition of aryl chlorides to palladium N-heterocyclic carbene complexes and their role in catalytic arylamination. Green, Jennifer C.; Herbert, Benjamin J.; Lonsdale, Richard. Chemistry Department, University of Oxford, Inorganic Chemistry Laboratory, Oxford, UK. Journal of Organometallic Chemistry (2005), 690(24-25), 6054-6067. Publisher: Elsevier B.V., CODEN: JORCAI ISSN: 0022-328X. Journal written in English. CAN 144:129091 AN 2005:1245718 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

D. functional theory was used to study various solvated species that may be formed from Pd bis N-heterocyclic carbene complexes, [Pd(cyclo-C{NRCH}2)2], (PdL2) in benzene soln. Formation of an ?2-arene complex is shown to stabilize a monocarbene species, PdL(?2-C6H5X), where the arene is either the solvent or a reacting aryl halide. Oxidative addn. of an aryl chloride was modeled, and the most likely transition state was established as a PdL(aryl chloride) species, with just one carbene ligand coordinated to the Pd. The catalytic cycle for aryl amination was studied and the oxidative addn. of the aryl halide shown to be the rate detg. step. Reductive elimination of the aryl amine has a lower activation energy. Oxidative addn. of alkyl halides is less favorable because of the absence of an unsatd. group, such as the aryl ring, to bond to the Pd.

Answer 18:

Bibliographic Information

The F/Ph Rearrangement Reaction of [(Ph3P)3RhF], the Fluoride Congener of Wilkinson's Catalyst. Macgregor, Stuart A.; Roe, D. Christopher; Marshall, William J.; Bloch, Karen M.; Bakhmutov, Vladimir I.; Grushin, Vladimir V. Central Research & Development, E. I. DuPont de Nemours and Company, Inc., Wilmington, DE, USA. Journal of the American Chemical Society (2005), 127(43), 15304-15321. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 143:459676 AN 2005:1080520 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The fluoride congener of Wilkinson's catalyst, [(Ph3P)3RhF] (1), has been synthesized and fully characterized. Unlike Wilkinson's catalyst, 1 easily activates the inert C-Cl bond of ArCl (Ar = Ph, p-tolyl) under mild conditions (3 h at 80 ?C) to produce trans-[(Ph3P)2Rh(Ph2PF)(Cl)] (2) and ArPh as a result of C-Cl, Rh-F, and P-C bond cleavage and C-C, Rh-Cl, and P-F bond formation. In benzene (2-3 h at 80 ?C), 1 decomps. to a 1:1 mixt. of trans-[(Ph3P)2Rh(Ph2PF)(F)] (3) and the cyclometalated complex [(Ph3P)2Rh(Ph2PC6H4)] (4). Both the chloroarene activation and the thermal decompn. reactions have been shown to occur via the facile and reversible F/Ph rearrangement reaction of 1 to cis-[(Ph3P)2Rh(Ph)(Ph2PF)] (5), which has been isolated and fully characterized. Kinetic studies of the F/Ph rearrangement, an intramol. process not influenced by extra phosphine, have led to the detn. of Ea = 22.7 ? 1.2 kcal mol-1, ?H .thermod. = 22.0 ? 1.2 kcal mol-1, and ?S .thermod. = -10.0 ? 3.7 eu. Theor. studies of F/Ph exchange with the [(PH3)2(PH2Ph)RhF] model system pointed to two possible mechanisms: (i) Ph transfer to Rh followed by F transfer to P (formally oxidative addn. followed by reductive elimination, pathway 1) and (ii) F transfer to produce a metallophosphorane with subsequent Ph transfer to Rh (pathway 2). Although pathway 1 cannot be ruled out completely, the metallophosphorane mechanism finds more support from both our own and previously reported observations. Possible involvement of metallophosphorane intermediates in various P-F, P-O, and P-C bond-forming reactions at a metal center is discussed.

Answer 19:

Bibliographic Information

Oxidative Addition of Methyl Iodide to a New Type of Binuclear Platinum(II) Complex: a Kinetic Study. Jamali, Sirous; Nabavizadeh, S. Masoud; Rashidi, Mehdi. Chemistry Department, Persian Gulf University, Bushehr, Iran. Inorganic Chemistry (2005), 44(23), 8594-8601. Publisher: American Chemical Society, CODEN: INOCAJ ISSN: 0020-1669. Journal written in English. CAN 143:354003 AN 2005:1065655 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A new organodiplatinum(II) complex cis,cis-[Me2Pt(?-NN)(?-dppm)PtMe2] (1), in which NN = phthalazine and dppm = bis(diphenylphosphino)methane, is synthesized by the reaction of cis,cis-[Me2Pt(?-SMe2)(?-dppm)PtMe2] with 1 equiv of NN. Complex 1 has a 5d?(Pt) ? ?*(imine) metal-to-ligand charge-transfer band in the visible region, which was used to easily follow the kinetics of its reaction with MeI. Meanwhile, the complex contains a robust bridging dppm ligand that holds the binuclear integrity during the reaction. A double MeI oxidative addn. was obsd., as shown by spectrophotometry and confirmed by a low-temp. 31P NMR study. The classical SN2 mechanism was suggested for both steps, and the involved intermediates were suggested. Consistent with the proposed mechanism, the rates of the reactions at different temps. were slower in benzene than in acetone and large neg. ?S.thermod. values were found in each step. However, some abnormalities were obsd. in the related rate consts. and ?S.thermod. values, which were demonstrated to be due to the associative involvement of the polar acetone mols. in the reactions. The rates are almost 6 times slower in the second step as compared to the first step because of the electronic effects transmitted through the ligands and the steric effects.

Answer 20:

Bibliographic Information

Mechanism of the Mild Functionalization of Arenes by Diboron Reagents Catalyzed by Iridium Complexes. Intermediacy and Chemistry of Bipyridine-Ligated Iridium Trisboryl Complexes. Boller, Timothy M.; Murphy, Jaclyn M.; Hapke, Marko; Ishiyama, Tatsuo; Miyaura, Norio; Hartwig, John F. Department of Chemistry, Yale University, New Haven, CT, USA. Journal of the American Chemical Society (2005), 127(41), 14263-14278. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 143:460266 AN 2005:1037114 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Mechanism of iridium-catalyzed direct boration of arenes by bis-pinacolatodiboron mediated by tris-boryl Ir(III) bipyridine complex was evaluated by kinetic and NMR spectral data. Iridium(III) tris-boryl complex fac-[Ir(4,4'-tBu2-2,2'-bpy)(?2-cyclooctene)(Bpin)3] (1, Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborol-2-yl), isolated earlier from the boronation of arenes in the presence of [(cod)IrCl]2, was prepd. in high yield by reaction of [(cod)IrOMe]2 with HBpin and 4,4'-di-tert-butyl-2,2'-bipyridine. Stoichiometric boronation of arenes by 1 gives 3 equiv of arylboronate at room temp.; low-temp. reactions yield the iridium hydrido-boryl complexes and proceed with second-order kinetics, the rate consts. decreasing with increasing nucleophilicity of the arene. Catalytic boronation of arenes by B2pin2 exhibits inverse first order on cyclooctene concn., proving the rapid pre-dissocn. of alkene ligand; the complex 1 being the catalyst resting state. The complex 1 is also formed in low yield from [Ir(COD)(OMe)]2, dtbpy, COE, and B2pin2. An alternative mechanism in which the arene reacts with the Ir(I) complex [Ir(dtbpy)Bpin] after dissocn. of COE and reductive elimination of B2pin2 does not occur to a measurable extent. Both the stoichiometric and catalytic boronation reactions occur faster with the electron-rich heteroarenes thiophene and furan than with arenes, perhaps because ?2-heteroarene complexes are more stable than the ?2-arene complexes and the ?2-heteroarene or arene complexes are intermediates that precede oxidative addn. Kinetic studies on the catalytic reaction show that [Ir(dtbpy)(COE)(Bpin)3] enters the catalytic cycle by dissocn. of COE, and a comparison of the kinetic isotope effects of the catalytic and stoichiometric reactions shows that the reactive intermediate [Ir(dtbpy)(Bpin)3] cleaves the arene C-H bond. The barriers for ligand exchange and C-H activation allow an exptl. assessment of several conclusions drawn from computational work.

The obtained kinetic results corroborate the conclusion that C-H bond cleavage is turnover-limiting, but the exptl. barrier for this bond cleavage is much lower than the calcd. barrier.

Answer 21:

Bibliographic Information

Mechanism of C-H Bond Activation of Alkyl-Substituted Benzenes by Cationic Platinum(II) Complexes. Driver, Tom G.; Day, Michael W.; Labinger, Jay A.; Bercaw, John E. Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, CA, USA. Organometallics (2005), 24(15), 3644-3654. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 143:229968 AN 2005:535454 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Methylplatinum diimine complexes undergo oxidative addn. of 1,4-diethylbenzene, forming ?3-benzyl complexes via ?-2,5-diethylphenyl intermediates; the reaction products with deuterated alkylarom. hydrocarbons were examd. for evaluation of the reaction mechanism. Protonolysis of [(ArN:CMeCMe:NAr-?N,?N')PtMe2] by CF3CD2OD gave [(ArN:CMeCMe:NAr-?N,?N')PtMe(DOCD2CF3-?O)]+, which forms [(ArN:CMeCMe:NAr-?N,?N')[(1,2,?-?)-MeCHC6H4Et-4]Pt]+ (9a-c; Ar = 2,4,6-Me3C6H2, 3,5-Me2C6H3, 3,5-tBu2C6H3) and methane. In the case of 9b,c, the intermediate ?-2,5-diethylphenyl complexes [(ArN:CMeCMe:NAr-?N,?N')Pt(C6H3Et2-2,5)(DOCD2CF3-?O)]+ (8) were detected by 1H NMR. For toluene and p-xylene, isotopic labeling shows that initial activation occurs at aryl positions with subsequent intermol. conversion to the benzyl product. For ethylbenzene and 1,4-diethylbenzene, initial activation takes place exclusively at aryl C-H bonds, and conversion to the ?3-benzyl product takes place via intramol. isomerization. Only in the most extreme case of steric demanding diimine ligands (Ar =

2,4,6-Me3C6H2) the reaction with triethylbenzene proceeds as direct activation of the Et group rather than the aryl activation.

Answer 22:

Bibliographic Information

Cooperative Friedel-Crafts Catalysis in Heterobimetallic Regime: Alkylation of Aromatics by ?-Activated Alcohols.
Choudhury, Joyanta; Podder, Susmita; Roy, Sujit. Organometallics & Catalysis Laboratory, Chemistry Department, Indian Institute of Technology, Kharagpur, India. Journal of the American Chemical Society (2005), 127(17), 6162-6163. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 142:463247 AN 2005:291826 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The highly active Friedel-Crafts alkylation (FCA) catalyst, [Ir(COD)Cl(SnCl3)(SnCl4)(arene)]+Cl- (1-SnCl4), is easily generated in one-pot from [Ir(COD)Cl]2 or [Ir(COD)(?-Cl)Cl(SnCl3)]2 (1) and SnCl4. The reaction of arenes, heteroarenes with benzyl, and allyl alcs. is promoted by 1-SnCl4 (1 mol %) with high turnover frequency. Kinetic evidence is presented to establish FCA pattern. From dual-catalyst combination studies varying the transition metal and main group metal partner, the efficiency of the present catalysts is attributed to the electrophilic "IrIII-SnIV" core.

Answer 23:

Bibliographic Information

Supramolecular Triruthenium Cluster-Based Benzene Hydrogenation Catalysis: Fact or Fiction? Hagen, Collin M.; Vieille-Petit, Ludovic; Laurenczy, Gabor; Suess-Fink, Georg; Finke, Richard G. Department of Chemistry, Colorado State University, Ft. Collins, CO, USA. Organometallics (2005), 24(8), 1819-1831. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 142:430415 AN 2005:208101 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The question is addressed of whether the triruthenium cluster cation [Ru3(?2-H)3(?6-C6H6)(?6-C6Me6)2(?3-O)]+ (1) is a supramol., outer-sphere benzene hydrogenation catalyst or is a precatalyst to known Ru(0)n catalysis of benzene hydrogenation. This question of is it homogeneous or heterogeneous catalysis is esp. important in the present case since if 1 is a supramol., homogeneous catalyst as postulated in the literature-i.e., if 1 can in fact accomplish catalysis of reactions as difficult as benzene redn. with no inner-sphere, d-orbital-mediated ligand dissocn., oxidative addn., migratory insertion, or reductive elimination-then that finding holds promise of rewriting the rules of organometallic-based catalysis. The identity of the true catalyst derived from 1 is, therefore, addressed by a collaborative effort between research groups at the Universite de Neuchatel and Colorado State University. The methodol. employed is that worked out previously for addressing the historically vexing question of is it homogeneous or heterogeneous catalysis (Y. Lin and R. G. Finke (1994)). A combination of the following classes of expts. were employed:(i) Ru metal product studies; (ii) kinetic studies; (iii) Hg(0) and quant. poisoning expts., (iv) NMR studies of H/D exchange rates; (v) other data, plus (vi) the principle that the correct mechanism will explain all of the data. The results provide a compelling case that 1 is not the true benzene hydrogenation catalyst as previously believed; instead, all the authors' evidence is consistent with, and supportive of, trace Ru(0) derived from 1 under the reaction conditions as the true, active catalyst. Nine addnl. conclusions are also presented as part of the summary and take-home messages, as well as a citation of Halpern's rules for catalysis.

Answer 24:

Bibliographic Information

Mechanism of benzene CH activation by bpymPt complex. Ziatdinov, Vadim R.; Mironov, Oleg A.; Periana, Roy A. Department of Chemistry, Loker Hydrocarbon Institute, University of Southern California, Los Angeles, CA, USA. Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, United States, March 13-17, 2005 (2005), INOR-649. Publisher: American Chemical Society, Washington, D. C CODEN: 69GQMP Conference; Meeting Abstract written in English. AN 2005:191037 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The selective, low temp., conversion of benzene to phenol continues to be an important goal in the field of catalysis. We have been recently interested in exploring the use of homogenous, bipyrimidine Platinum complexes for this transformation. Methane to methanol conversion has been reported previously in sulfuric acid. However, sulfonation reaction limits the use of strong acid media for aryls. The first step of catalytic cycle assumes CH activation. The mechanism of benzene CH activation by bipyrimidine Pt complex is reported in weaker than sulfuric acid media, trifluoroacetic acid. Important phenyl-Platinum intermediate is characterized. Interestingly, that the electrophilic mechanism of CH activation vs. oxidn. addn. remains dominant even in weaker acidic media. DFT calcns. support importance of acidic media and electrophilic character of CH activation.

Answer 25:

Bibliographic Information

Intermolecular Activation of Hydrocarbon C-H Bonds Initiated by the Tungsten Hydrocarbyl Hydrido Complexes CpW(NO)(R)(H)(PMe3) (R = Alkyl, Aryl). Lee, Kajin; Legzdins, Peter; Pamplin, Craig B.; Patrick, Brian O.; Wada, Kenji. Department of Chemistry, The University of British Columbia, Vancouver, BC, Can. Organometallics (2005), 24(4), 638-649. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 142:280278 AN 2005:20576 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Oxidative addn. reactions of benzene, neopentane and tetramethylsilane with half-sandwich tungsten nitroso complexes gave tungsten Ph and alkyl derivs., resp. Trans-[Cp*W(NO)(CH2EMe3)(H)(PMe3)] (Cp* = ?5-C5Me5; E = C, Si) complexes can be prepd. by the hydrogenation at 1 atm of the appropriate [Cp*W(NO)(CH2EMe3)2] precursor in the presence of a slight excess of PMe3 (cis- and trans-descriptors define the relative positions of the hydrocarbyl and the hydrido ligands in a four-legged piano-stool mol. structure). The use of D2 in place of H2 affords the corresponding trans-[Cp*W(NO)(CH2EMe3)(D)(PMe3)] complexes. The cis-[Cp*W(NO)(CH2EMe3)(H)(PMe3)] isomers are obtainable by C-H bond-activation reactions of the trans precursors. Thus, activation of SiMe4 by trans-[Cp*W(NO)(CH2CMe3)(H)(PMe3)] under ambient conditions produces cis-[Cp*W(NO)(CH2SiMe3)(H)(PMe3)]. Similarly, activation of C6H6 and C6D6 at 20-27? by the trans-[Cp*W(NO)(CH2EMe3)(H)(PMe3)] complexes produce cis-[Cp*W(NO)(Ph)(H)(PMe3)] and cis-[Cp*W(NO)(C6D5)(D)(PMe3)], resp.; the solid-state mol. structure of the latter complex was detd. by a single-crystal x-ray crystallog. Kinetic, mechanistic, and theor. investigations of these benzene C-H activation processes are consistent with initial trans to cis isomerization of the reactants followed by intramol. reductive elimination of EMe4 to form the 16-electron Cp*W(NO)(PMe3) intermediate. Subsequent oxidative addn. of the incoming benzene substrate to this coordinatively unsatd. intermediate produces the final cis hydrido Ph complex. These single C-H activation processes are the requisite first steps in the development of these organometallic complexes as catalysts for the selective functionalization of hydrocarbons.

Answer 26:

Bibliographic Information

Electronic and Steric Effects in the Insertion of Alkynes into an Iridium(III) Hydride. Li, Xingwei; Vogel, Tiffany; Incarvito, Christopher D.; Crabtree, Robert H. Department of Chemistry, Yale University, New Haven, CT, USA. Organometallics (2005), 24(1), 62-76. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English.

CAN 142:198184 AN 2004:1048270 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Insertion of a variety of alkynes into the Ir-H bond of trans-[IrH(PPh3)2(C(Ph):CHC(O)Me)(acetone)]+ (1) follows three different routes depending on the alkyne structures. For relatively electron-rich alkynes (PhC?CH, PhCH2C?CH, and p-OMeC6H4C?CH), double insertion occurs stepwise, each alkyne undergoing rearrangement to a vinylidene intermediate independently to afford an iridium(III) ?2-butadienyl. In the first alkyne insertion, deuterium labeling and crossover expts. confirm that the alkyne to vinylidene rearrangement is intraligand. Both a vinyl and a vinylidene intermediate were trapped and isolated during this first insertion. In the second alkyne insertion, a C-H agostic intermediate was isolated. Electron-poor alkynes (p-CF3C6H4C?CH and p-NO2C6H4C?CH) also undergo double insertion into 1, but deuterium labeling expts. using p-CF3C6H4C?CD indicate reversible C(sp)-H oxidative addn. Insertion of highly polarized alkynes [R1C?CC(O)R2] to 1 occurs only once and involves no vinylidene intermediates, even when R1 = H. The regio- and stereochem. in this case are mainly controlled by the steric effects of R1. In this series, rare cis-(PPh3)2 intermediates were isolated for HC?CC(O)R (R = Me, OMe). X-ray crystal structures of representative products trans-bis(triphenylphosphine)(2-o-pyridylphenyl)(1,4-diphenylbuta-1,4-dien-2-yl)iridium hexafluoroantimonate, cis-bis(triphenylphosphine)(?2-{O,C1}-1-phenylbut-1-en-3-on-1-yl)(?2-{O,C1}-methylprop-1-enoat-1-yl)iridium hexafluoroantimonate, and trans-bis(triphenylphosphine)(?2-{O,C1}-1-phenylbut-1-en-3-on-1-yl)(?2-{O,C2}-1-phenylbut-1-(E)-en-3-one-2-yl) iridium tetrafluoroborate are reported.

Answer 27:

Bibliographic Information

Experimental and Computational Studies of Ruthenium(II)-Catalyzed Addition of Arene C-H Bonds to Olefins. Lail, Marty; Bell, Christen M.; Conner, David; Cundari, Thomas R.; Gunnoe, T. Brent; Petersen, Jeffrey L. Department of Chemistry, North Carolina State University, Raleigh, NC, USA. Organometallics (2004), 23(21), 5007-5020. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 141:395645 AN 2004:736799 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Hydroarylation reactions of olefins are catalyzed by the octahedral Ru(II) complex TpRu(CO)(NCMe)(Ph) (1) (Tp = hydridotris(pyrazolyl)borate). Exptl. studies and d. functional theory calcns. support a reaction pathway that involves initial MeCN/olefin ligand exchange and subsequent olefin insertion into the Ru-Ph bond. Metal-mediated C-H activation of arene to form a Ru-aryl bond with release of alkyl arene completes the proposed catalytic cycle. The cyclopentadienyl complex CpRu(PPh3)2(Ph) produces ethylbenzene and styrene from a benzene/ethylene soln. at 90?; however, the transformation is not catalytic. A benzene soln. of (PCP)Ru(CO)(Ph) (PCP = 2,6-(tBu2PCH2)2C6H3) and ethylene at 90? produces styrene in 12% yield without observation of ethylbenzene. Computational studies (DFT) suggest that the C-H activation step does not proceed through the formation of a Ru(IV) oxidative addn. intermediate but rather occurs by a concerted pathway. The crystal and mol. structures of TpRu(CO)(NCMe)(CH2CH2Ph) were detd. by x-ray crystallog.

Answer 28:

Bibliographic Information

Alkane C-H bond activation by O-donor Ir complexes. Bhalla, Gaurav; Liu, Xiang Yang; Wong-Foy, Antek; Jones, C. J.; Periana, Roy A. Department of Chemistry, Loker Hydrocarbon Institute, University of Southern California, Los Angeles, CA, USA. ACS Symposium Series (2004), 885(Activation and Functionalization of C-H Bonds), 105-115. Publisher: American Chemical Society, CODEN: ACSMC8 ISSN: 0097-6156. Journal written in English. CAN 142:56495 AN 2004:676908 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Alkane activation by methyliridium acetylacetonato-pyridine complex gave corresponding alkyl complexes and methane. Reaction of Ir(acac)3 with Me2Zn or Me2Hg in the presence of pyridine gave trans-[IrMe(py)(acac)2] (1-Me), which undergoes alkyl exchange reaction with RH affording trans-[IrR(py)(acac)2] (R = CH2C6H3-3,5-Me2, cyclo-C6H11, Ph, CH2COMe). Deuterium- and 13C-labeling expts. reveal, that ?-elimination of alkene from iridium-alkyl complexes proceeds with lower rates, than alkyl exchange. The O-donor complexes exhibit thermal and protic stability and are efficient catalysts for H/D exchange reactions with alkanes. Somewhat surprisingly, the O-donor Ir alkyl complexes with ?-CH bonds are stable to generation of coordinated or uncoordinated olefinic products. Mechanistic studies suggest that while these O-donor Ir-alkyl complexes undergo ?-hydride elimination reactions these reactions are reversible and unproductive. Crystal structure of trans-[Ir(cyclo-C6H11)(py)(acac)2] is reported.

Answer 29:

Bibliographic Information

Unexpected Formation of an ortho-Palladated Diphenylthioether. Vicente, Jose; Abad, Jose-Antonio; Lopez-Nicolas, Rosa-Maria; Jones, Peter G. Grupo de Quimica Organometalica, Departamento de Quimica Inorganica, Facultad de Quimica Universidad de Murcia, Murcia, Spain. Organometallics (2004), 23(18), 4325-4327. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 141:277752 AN 2004:600448 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Reaction of [Ph4P][SC6H4Br-2] with [Pd(dba)2] (dba = dibenzylideneacetone) in the presence of PPh3 gave trans-[Pd(2-(SPh)C6H4)Br(PPh3)2]. A sequence of reactions consisting of oxidative addn. of the tetraphenylphosphonium cation to palladium(0), reductive C-S coupling giving 2-(SPh)C6H4Br, and, again, an oxidative addn. of the latter to palladium(0), seems to constitute the pathway for formation of the final palladium complex. Some exptl. evidence supporting this pathway is provided. The crystal structure of trans-[Pd(2-(SPh)C6H4)Br(PPh3)2] has been solved by an X-ray diffraction study.

Answer 30:

Bibliographic Information

Multiple active oxidants in competitive epoxidations catalyzed by porphyrins and corroles. Collman, James P.; Zeng, Li; Decreau, Richard A. Department of Chemistry, Stanford University, Stanford, CA, USA. Chemical Communications (Cambridge, United Kingdom) (2003), (24), 2974-2975. Publisher: Royal Society of Chemistry, CODEN: CHCOFS ISSN: 1359-7345. Journal written in English. CAN 140:128203 AN 2003:964461 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The existence of multiple active oxygenating species in porphyrin and corrole-catalyzed competitive epoxidns. of styrene and cis-cyclooctene was demonstrated. Catalysts used in this study included meso-chloro[5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphinato(2-)-?N21,?N22,?N23,?N24]iron, chloro[5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphinato(2-)-?N21,?N22,?N23,?N24]manganese and [1,2,3,7,8,12,13,17,18,19-decadehydro-21,22-dihydro-5,10,15-tris(pentafluorophenyl)corrinato(3-)-?N21,?N22,?N23,?N24]manganese. In the case of an iron catalyst it was proposed that in addn. to a discrete iron-oxo intermediate, a complex between the iron catalyst and iodosylarene exists as second active oxidant. This second oxidant effects the epoxidn. reactions via a bifurcated mechanism.

Answer 31:

Bibliographic Information

cis-trans Isomerisation of CpRe(CO)2(H)(ArF) (ArF = C6FnH5-n; n = 0-5) is the rate determining step in C-H activation of fluoroarenes: a DFT study. Clot, Eric; Oelckers, Beatriz; Klahn, A. Hugo; Eisenstein, Odile; Perutz, Robin N. Universite Montpellier 2, LSDSMS (UMR 5636), Montpellier, Fr. Dalton Transactions (2003), (21), 4065-4074. Publisher: Royal Society of Chemistry, CODEN: DTARAF ISSN: 1477-9226. Journal written in English. CAN 140:321467 AN 2003:830021 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

D. functional calcns. were used to examine the reaction of [CpRe(CO)2] with fluorobenzenes C6FnH6-n (n = 0-5). Two classes of product were obsd. exptl. (using Cp or Cp*): (a) coordination of the arene in an ?2 fashion and (b) C-H activation to form a hydrido-aryl complex. Increasing the no. of fluorines on the arene ring favors C-H activation. The thermodn. and kinetic (reaction path) aspects of these transformations were examd. with DFT (B3PW91) calcns. For a given arene, the Re moiety is shown to exhibit the following order of thermodn. preference for coordination: HC:CH site > HC:CF site > FC:CF site. Binding energies to the different arenes do not follow a clear trend and span .apprx.20 kJ mol-1. The Re-C bond energies in CpRe(CO)(H)(C6FnH5-n) span 55 kJ mol-1. Calcd. structural parameters agree with the crystal structure of coordination of C6H6 and C6F6. Likewise the binding energy of C6H6 is in good agreement with exptl. data. The calcd. free energy difference between CpRe(CO)2(?2-C6FnH6-n) and CpRe(CO)2(H)(C6FnH5-n) shows that preference for the hydrido-aryl complex is detd. principally by the bond dissocn. energy of the C-H bond of the free arene. The binding energy to the ?2-arene appears to be only a secondary factor. Three families of complexes are apparent. If there is no F on the C ortho to the Re-C bond that is formed, the ?2-arene complex is energetically preferred. If there is one F at the ortho position, the energies of the products are similar. In the case of two ortho F substituents, the product of oxidative addn. is significantly favored. In agreement with the calcns., exptl. evidence shows that benzene only coordinates to Cp*Re(CO)2, whereas 1,4-C6F2H4 gives a mixt. of products and 1,3-C6F2H4 gives only the hydrido-aryl complex. The arene with the stronger C-H bond is the one which gives more oxidative addn. product because the Re-C bond energy increases with F substitution (and in particular with ortho F) more than twice as fast as the C-H bond dissocn. energy.

The reaction path for the overall transformation was detd. The ? C-H complex is identified as an intermediate on the pathway for the oxidative addn. The initial product of oxidative addn. is the cis hydrido-aryl isomer which subsequently isomerizes to the trans isomer. The rate detg. step is the cis-trans isomerization process and not the oxidative addn. step. The cis-trans isomerization proceeds via an unconventional concerted motion of H and the two CO's. The variation of the Re-C bond energy is the dominant factor in detg. the changes in the energy barrier between the different fluoroarenes, resulting in strong correlation between the thermodn. and kinetics of reaction. The activation barriers are therefore also grouped in three families (0 F ortho, 1 F ortho, 2 F ortho).

Answer 32:

Bibliographic Information

Generation of [Tp*Rh(?4-1,3-COD)] (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate, 1,3-COD = cyclooctadiene) and its potential in C-H bond activation. Boaretto, Rita; Paolucci, Gino; Sostero, Silvana; Traverso, Orazio. Dipartimento di Chimica, Universita di Ferrara, Ferrara, Italy. Journal of Molecular Catalysis A: Chemical (2003), 204-205 253-258. Publisher: Elsevier Science B.V., CODEN: JMCCF2 ISSN: 1381-1169. Journal written in English. CAN 140:321488 AN 2003:697996 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Photolysis of [Tp*Rh(?4-1,5-COD)] (1) (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate; 1,5-COD = cyclooctadiene) in benzene at 400 nm gives a quant. yield of the new compd. [Tp*Rh(?4-1,3-COD)] (2). Selected photolysis of 2 at 336 nm can be used to produce (a) hydrido-phenyl-phosphite [Tp*Rh(H)(C6H5)P(OMe)3], (b) hydrido-carbonyl [Tp*Rh(H)2(CO)], and (c) chelate [Tp*Rh(C6H5)(CH2CH2COOtBu)] when the photoreactions were made in the presence of P(OMe)3, CH3OH, and tBu-acrylate, resp. These results are interpreted in terms of oxidative addn. reactions by the reactive intermediates photogenerated in the Rh system 2.

Answer 33:

Bibliographic Information

Reductive Elimination/Oxidative Addition of Carbon-Hydrogen Bonds at Pt(IV)/Pt(II) Centers: Mechanistic Studies of the Solution Thermolyses of TpMe2Pt(CH3)2H. Jensen, Michael P.; Wick, Douglas D.; Reinartz, Stefan; White, Peter S.; Templeton, Joseph L.; Goldberg, Karen I. Department of Chemistry, University of Washington, Seattle, WA, USA. Journal of the American Chemical Society (2003), 125(28), 8614-8624. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 139:164880 AN 2003:463778 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Reductive elimination of methane occurs upon soln. thermolysis of ?3-TpMe2PtIV(CH3)2H (1, TpMe2 = hydridotris(3,5-dimethylpyrazolyl)borate). The platinum product of this reaction is dependent on the solvent used. C-D bond activation occurs after methane elimination in benzene-d6, to yield ?3-TpMe2PtIV(CH3)(C6D5)D (2-d6), which undergoes a second reductive elimination/oxidative addn. reaction to yield isotopically labeled methane and ?3-TpMe2PtIV(C6D5)2D (3-d11). In contrast, ?2-TpMe2PtII(CH3)(NCCD3) (4) was obtained in the presence of acetonitrile-d3, after elimination of methane from 1. Reductive elimination of methane from these Pt(IV) complexes follows first-order kinetics, and the obsd. reaction rates are nearly independent on the solvent. Virtually identical activation parameters (?H.thermod.obs = 35.0 ? 1.1 kcal/mol, ?S.thermod.obs = 13 ? 3 eu) were measured for the reductive elimination of methane from 1 in both benzene-d6 and toluene-d8. A lower energy process (?H.thermod.scr = 26 ? 1 kcal/mol, ?S.thermod.scr = 1 ? 4 eu) scrambles hydrogen atoms of 1 between the Me and hydride positions, as confirmed by monitoring the equilibration of ?3-TpMe2PtIV(CH3)2D (1-d1) with its scrambled isotopomer, ?3-TpMe2PtIV(CH3)(CH2D)H (1-d1'). The ?-methane complex ?2-TpMe2PtII(CH3)(CH4) is proposed as a common intermediate in both the scrambling and reductive elimination processes. Kinetic results are consistent with rate-detg. dissociative loss of methane from this intermediate to produce the coordinatively unsatd. intermediate [TpMe2PtII(CH3)], which reacts rapidly with solvent. The difference in activation enthalpies for the H/D scrambling and C-H reductive elimination provides a lower limit for the binding enthalpy of methane to [TpMe2PtII(CH3)] of 9 ? 2 kcal/mol.

Answer 34:

Bibliographic Information

Synthesis and Reactivity of Silyl Ruthenium Complexes: The Importance of Trans Effects in C-H Activation, Si-C Bond Formation, and Dehydrogenative Coupling of Silanes. Dioumaev, Vladimir K.; Procopio, Leo J.; Carroll, Patrick J.; Berry, Donald H. Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA, USA. Journal of the American Chemical Society (2003), 125(26), 8043-8058. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 139:149741 AN 2003:440026 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A series of octahedral ruthenium silyl hydride complexes, cis-[(PMe3)4Ru(SiR3)H] (SiR3 = SiMe3, 1a; SiMe2CH2SiMe3, 1b; SiEt3, 1c; SiMe2H, 1d), were prepd. by the reaction of hydrosilanes with [(PMe3)3Ru(?2-CH2PMe2)H] (5), cis-[(PMe3)4RuMe2] (6), or [(PMe3)4RuH2] (9). Reaction with 6 proceeds via an intermediate product, cis-[(PMe3)4Ru(SiR3)Me] (SiR3 = SiMe3, 7a; SiMe2CH2SiMe3, 7b). Alternatively, 1 and 7 were prepd. via a fast hydrosilane exchange with another cis-[(PMe3)4Ru(SiR3)H] or cis-[(PMe3)4Ru(SiR3)Me], which occurs at a rate approaching the NMR time scale. Compds. 1a, 1b, 1d, and 7a adopt octahedral geometries in soln. and the solid state with mutually cis silyl and hydride (or silyl and methyl) ligands. The longest Ru-P distance within a complex is always trans to Si, reflecting the strong trans influence of silicon. The aptitude of phosphine dissocn. in these complexes was probed in reactions of 1a, 1c, and 7a with PMe3-d9 and CO. The dissocn. is regioselective in the position trans to a silyl ligand (trans effect of Si), and the rate approaches the NMR time scale. A slower secondary process introduces PMe3-d9 and CO in the other octahedral positions, most likely via non-dissociative isomerization. The equil. concn. of dissocd. phosphine in the soln. of

7a is .apprx.5% due to strong trans-effect of the silyl group. Compds. 1a-c also react with dihydrogen via regioselective dissocn. of phosphine from the site trans to Si, but the final product, fac-[(PMe3)3Ru(SiR3)H3] (SiR3 = SiMe3, 4a; SiMe2CH2SiMe3, 4b; SiEt3, 4c), features hydrides cis to Si. Alternatively, 4a-c were prepd. by photolysis of [(PMe3)4RuH2] in the presence of a hydrosilane or by exchange of fac-[(PMe3)3Ru(SiR3)H3] with another HSiR3. The reverse reaction, H2 elimination from 4a and trapping with PMe3 or PMe3-d9 is also regioselective, but is very unfavorable. At 70?, a slower but irreversible SiH elimination also occurs and furnishes (PMe3)4RuH2.

The structure of 4a exhibits a tetrahedral P3Si environment around the metal with the three hydrides adjacent to silicon and capping the P2Si faces. Although strong Si??HRu interactions are not indicated in the structure or by IR, the HSi distances (2.13-2.23(5) .ANG.) suggest some degree of nonclassical SiH bonding in the H3SiR3 fragment. Thermolysis of 1a in C6D6 at 45-55? leads to an intermol. C-D activation of C6D6. In an even slower intramol. CH activation process, (PMe3)3Ru(?2-CH2PMe2)H (5) is also produced. The structure of intermediates, mechanisms, and aptitudes for PMe3 dissocn. and addn./elimination of H-H, Si-H, C-Si, and C-H bonds in these systems are discussed with a special emphasis on the trans effect and trans influence of silicon and ramifications for SiC coupling catalysis.

Answer 35:

Bibliographic Information

Synthesis, Structure, and Reactivity of an Unusual Platinum Olefin Carbene Complex, [(?4-cod)Pt{:C(Ph2P:NSiMe3)2-?C,?N}]. Jones, Nathan D.; Lin, Guanyang; Gossage, Robert A.; McDonald, Robert; Cavell, Ronald G. Department of Chemistry, University of Alberta, Edmonton, AB, Can. Organometallics (2003), 22(14), 2832-2841. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 139:149739 AN 2003:439003 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The organolithium dimer [Li2C(Ph2P:NSiMe3)2]2 ([Li2-1]2) reacts with 2 equiv. of [PtCl2(cod)] (cod = 1,5-cyclooctadiene) in Et2O soln. to give the novel Pt-carbene complex [(?4-cod)Pt{:C(Ph2P:NSiMe3)2-?C,?N}] (2), which is characterized by a relatively long Pt-C(carbene) bond and relatively short Pt-C(olefin) interactions indicative of an electron-rich Pt center. Under oxygen- and moisture-free conditions, 2 is remarkably inert; the cod ligand is not displaced by either monodentate or bidentate phosphines, phosphine sulfide, phosphite, or pyridine at room temp., nor is the four-membered C,N-chelate ring opened by these reagents. However, 2 reacts with the electrophiles MeOTf (OTf = trifluoromethanesulfonate) and CO2. In the former case, the uncoordinated N atom of 2 is methylated to form [(?4-cod)Pt{:C(Ph2P:N(Me)SiMe3)(Ph2P:NSiMe3)-?C,?N}][OTf] (3). In the latter, initial nucleophilic attack by the uncoordinated N atom on CO2, followed by trimethylsilyl group migration from N to O, gives [(?4-cod)Pt{:C(Ph2P:NSiMe3)(Ph2P:NC(O)OSiMe3)-?C,?N}] (4). Heating a benzene soln. of 2 to 100? in a sealed tube for several hours, or to 60? for 10 min in the presence of H2O, yields the ortho-metalated complex [(?4-cod)Pt{CH(Ph(C6H4)P:NSiMe3)(Ph2P:NSiMe3)-?C,?C'}] (5), which is characterized by Pt-C distances that are in the typical range for Pt-C(alkyl) and Pt-C(arene) interactions. The diastereoselectivity of the ortho metalation is consistent with an oxidative addn. (nucleophilic) reaction mechanism for the ortho metalation. In contrast to 2, 5 displays typical cod substitution reactivity with chelating phosphines. The reaction between [Li2-1]2 and [PtCl2(cod)] in C6H6 soln. proceeds only very slowly and gives [Li][Pt{CH(Ph(C6H4)P:NSiMe3)(Ph2P:NSiMe3)-?C,?C'}{CH(Ph2P:NSiMe3)2-?C,?N}] (7) in low yield. The crystal structure of 2, 5, and 7 were detd.

Answer 36:

Bibliographic Information

Mechanistic study on the cross-coupling of alkynyl stannanes with aryl iodides catalyzed by ?2-(dimethyl fumarate)palladium(0) complexes with iminophosphine ligands. Crociani, Bruno; Antonaroli, Simonetta; Beghetto, Valentina; Matteoli, Ugo; Scrivanti, Alberto. Dipartimento di Scienze e Tecnologie Chimiche, Universita di Roma "Tor Vergata", Rome, Italy. Dalton Transactions (2003), (11), 2194-2202. Publisher: Royal Society of Chemistry, CODEN: DTARAF ISSN: 1477-9226. Journal written in English. CAN 140:42284 AN 2003:415704 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reactions of [Pd(?2-dmfu)(P-N)] [dmfu = di-Me fumarate; P-N = 2-(PPh2)C6H4-1-CH:NR, R = 4-MeOC6H4 (1a), iPr (2a)] and [Pd(?2-dmfu)(P-N)2] with IC6H4CF3-4, ISnBu3 and PhC?CSnBu3 were studied under pseudo-first-order conditions. The oxidative addn. of IC6H4CF3-4 yields [PdI(4-CF3C6H4)(P-N)] (1b or 2b). No reaction takes place with PhC?CSnBu3 and also with ISnBu3 in the presence of an excess of PhC?CSnBu3. In the presence of fumaronitrile (fn), 1b and 2b undergo transmetalation by PhC?CSnBu3 followed by fast reductive elimination to yield [Pd(?2-fn)(P-N)]. The same reaction sequence occurs for the system [PdI(4-CF3C6H4)(P-N)]/P-N (1:1 molar ratio) to give [Pd(?2-fn)(P-N)2]. The palladium(0) complexes are active catalysts in the cross-coupling of PhC?CSnBu3 with aryl iodides ArI (Ar = 4-CF3C6H4, Ph). The catalytic efficiency depends on the complex: [Pd(?2-dmfu)(P-N)2] > [Pd(?2-dmfu)(P-N)], and on the substituent R: 4-MeOC6H4 > iPr. The reactivity and spectroscopic data suggest a catalytic cycle involving initial oxidative addn. of ArI to a palladium(0) species, followed by transmetalation of the product and by fast reductive elimination to regenerate the starting palladium(0) compd. For [Pd(?2-dmfu)(P-N)] as catalyst, the oxidative addn. is the rate-detg. step, while for [Pd(?2-dmfu)(P-N)2] the oxidative addn. and the transmetalation steps occur at comparable rate.

Answer 37:

Bibliographic Information

Preparation and Characterization of Osmium-Stannyl Polyhydrides: d4-d2 Oxidative Addition of Neutral Molecules in a Late Transition Metal. Esteruelas, Miguel A.; Lledos, Agusti; Maseras, Feliu; Olivan, Montserrat; Onate, Enrique; Tajada, Maria A.; Tomas, Jaume. Departamento de Quimica Inorganica, Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-CSIC, Zaragoza, Spain. Organometallics (2003), 22(10), 2087-2096. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 139:7012 AN 2003:267296 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Complex OsH2Cl2(PiPr3)2 (1) reacts with 2.0 equiv of HSnPh3 to give the tetrahydride-stannyl deriv. OsH4Cl(SnPh3)(PiPr3)2 (2) and ClSnPh3. The structure of 2 was detd. by x-ray diffraction anal. In the solid state and in soln. at temps. <298 K, the coordination geometry around the Os atom can be rationalized as derived from a distorted dodecahedron. In the presence of diphenylacetylene, complex 2 gives [cyclic] OsH3(SnClPh2){?2-CH2:CMePiPr2}(PiPr3) (3), cis-stilbene, and benzene. In the solid state, the structure of 3 as detd. by x-ray diffraction anal. can be described as a very distorted pentagonal bipyramid, with the P atom of the triisopropylphosphine ligand and the midpoint of the olefinic bond of the isopropenyl group of the dehydrogenated phosphine occupying axial positions. In soln., at temps. >233 K, the coordinated olefin is released. Complex 3 reacts with H2 to afford the pentahydride OsH5(SnClPh2)(PiPr3)2 (4), as a result of the hydrogenation of the coordinated olefinic bond and the d4-d2 oxidative addn. of H. The structure of 4 in the solid state also was detd. by x-ray diffraction. The coordination geometry around the Os atom can be rationalized as a distorted dodecahedron. In soln., complex 4 does not have a rigid structure even at 193 K. DFT calcns. in model systems of 2, 3, and 4, in which the bulky ligands were replaced by small models, followed by QM/MM optimizations with the real ligands have allowed the complete detn. of the hydride positions and of the role played by steric effects in the exptl. structures.

Answer 38:

Bibliographic Information

C-H bond activation by a hydrotris(pyrazolyl)borato ruthenium hydride complex. Ng, Siu Man; Lam, Wai Han; Mak, Chi Chuen; Tsang, Chun Wai; Jia, Guochen; Lin, Zhenyang; Lau, Chak Po. Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, Peop. Rep. China. Organometallics (2003), 22(4), 641-651. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 138:238276 AN 2003:29231 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The ruthenium complex TpRu(PPh3)(CH3CN)H (Tp = hydrotris(pyrazolyl)borate) catalyzes H/D exchange between CH4 and some deuterated org. solvents (benzene-d6, tetrahydrofuran-d8, di-Et ether-d10, and dioxane-d8). Preferential cleavage of the ?-C-D and the ?-C-D bonds of THF-d8 and di-Et ether-d10, resp., is obsd. The H/D exchange processes were investigated by d. functional theory calcns. at the B3LYP level. Theor. study on the reaction mechanism suggests that ?-complexes TpRu(PPh3)(?2-H-R)H are active species in the exchange processes. During the exchange processes, the reversible transformations of TpRu(PPh3)(?2-H-R)H to TpRu(PPh3)(?2-H2)R are the crucial steps. The barriers for the transformations are in the range 10-13.4 kcal/mol. Interestingly, the transition states for the transformations correspond to the seven-coordinate TpRu(PPh3)(R)(H)(H), which are species derived from the oxidative addn. of H-R to the metal center. The exchange processes involve transformations of the (?2-H-R) species to the (?2-H2) species followed by H-H rotation in the latter. The rotation barriers are calcd. to be in the range 2-4 kcal/mol. The exchange process having an arom. R group is found to be most favorable due to the strong Ru-C(sp2) bonding, which stabilizes the (?2-H2) species and lowers the transformation barrier. The complex TpRu(PPh3)(CH3CN)H catalyzes H/D exchange between H2 and the deuterated solvents, too.

Answer 39:

Bibliographic Information

Rhodium-antimony linkages in coordination chemistry as revealed in X-ray structural studies. Cini, Renzo. Department of Chemical and Biosystem Sciences and Technologies, University of Siena, Siena, Italy. Trends in Inorganic Chemistry (2001), 7 57-75. Publisher: Research Trends, CODEN: TIICEB Journal; General Review written in English. CAN 139:197513 AN 2002:950055 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A review. The articles which report on the crystal structures of compds. which contain at least a Rh-Sb covalent linkage are critically reviewed and analyzed as regard as preparative strategies and structural, characteristics. The compds. are presented in the order of their publication date, unless comparative reasons required a different order. The no. of coordination compds. in which Sb atoms act as donors to Rh are quite scarce when compared to the legions of complexes which have lighter Group 15 donors (i.e. N, P, As) and the total of crystallog. investigated structures is around twenty. The reported compds. contain either Rh(I), Rh(II) or Rh(III) centers. Mixed-valence poly-nuclear species have not been reported, so far. The Sb atoms of the free ligands are usually trivalent and SbR3 (R = Ph, iPr) are the most frequent bases. The anal. reveals that new and unexpected Rh-C types of bonds form at least when [RhICl(SbPh3)3] reacts with (CF3)C?C(CF3) to produce [RhIIICl{?2-C2,C5-CF3CC(CF3)C(CF3)C(CF3)}(SbPh3)2]; when [RhI(DPD)(CO)2] (see the list of abbreviations) reacts with SbPh3 in methanol to produce [RhI(CO){C(O)CH3}(SbPh3)3] and in hexane to produce [RhIII(?2-O,O-DPD)(?1-Ph)2(SbPh3)2]?2C6H6; when [RhICl(CO)(SbPh3)3] reacts with HC?CCH2Cl to produce [Rh111Cl{?2-C1,C4-C(=O)CH=C(Cl)CH2}(SbPh3)3]; and when RhCl3?3H2O reacts with SbPh3 to produce [RhIIICl2(Ph)(SbPh3)3]. The latter compd. proved to be a versatile starting compd. for prepg. a variety of new complexes such as [RhIIICl2(Ph)(PY)3], [RhIIICl2(Ph)(PY)2(MePYM)], [RhIIICl2(Ph)(PYR)2(SbPh3)], and the triphenylphosphine derivs. [RhIIICl2(Ph)(PPh3)2] and [Rh(Ph)(H2TP)2(PPh3)] [Rh(Ph)(H2TP)(HTP)(PPh3)]Cl3?HCl?6H2O. The detailed reaction mechanisms which bring to the formation of such organometallic linkages are mostly unknown. The Rh(I)-Sb complexes were made from the reaction of Rh(I)-complexes as starting materials.

?2-C2H4 is replaced by carbene CPh2, when [Rh1Cl(?2-C2H4)(SbiPr3)2] reacts with CPh2N2 in pentane and [RhICl(=CPh2)(SbiPr3)2] is then formed. On heating the latter compd. at 60?C in benzene for 4h the binuclear compd. [RhI2Cl2(?-CPh2)2(?-SbiPr3)] forms; it is stabilized by a metal-metal linking interaction, and most interestingly, by an unusual bridging SbiPr3 ligand. This bridge can then be removed by phosphine ligands. The Rh(II)-Sb complexes (three over a total of twenty-two) have the common binuclear structure with four bridging chelating ligands; they were prepd. by starting from analogous binuclear Rh(II) compds. by displacing the apical ligands with SbPh3. The Rh(III)-Sb complexes were prepd. from Rh(III)-complexes by substitution reactions (see for instance, the prepn. of [RhIIICl2(S6,N7-H2TP)(Ph)(SbPh3)] from [RhIIICl2(Ph)(SbPh3)3]) or from Rh(I)-complexes via complicate oxidative-addn. reactions (see for instance, the prepn. of [RhIII(?5-C5H5){?2-C1,C3-C(=NCH3)C(Ph)=C(Ph)}(SbiPr3)] from [RhI(?5-C5H5)(?2-PhC?CPh)(SbiPr3)] and CNCH3, in pentane).

Answer 40:

Bibliographic Information

Dinuclear Oxidative Addition of N-H and S-H Bonds at Chromium. Reaction of .bul.Cr(CO)3(C5Me5) with {o-(HA)C6H4S-Cr(CO)3(C5Me5)} (A = S, NH) Yielding [?2-o-(?-A)C6H4S-Cr(C5Me5)]2 and H-Cr(CO)3(C5Me5). Sukcharoenphon, Kengkaj; Ju, Telvin D.; Abboud, Khalil A.; Hoff, Carl D. Department of Chemistry, University of Miami, Coral Gables, FL, USA. Inorganic Chemistry (2002), 41(25), 6769-6774. Publisher: American Chemical Society, CODEN: INOCAJ ISSN: 0020-1669. Journal written in English. CAN 138:89882 AN 2002:872969 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Reaction of the 17-electron radical .bul.Cr(CO)3Cp* (Cp* = C5Me5) with 0.5 equiv of 2-aminophenyl disulfide [(o-H2NC6H4)2S2] results in rapid oxidative addn. to form the initial product (o-H2N)C6H4S-Cr(CO)3Cp*. Addn. of a second equiv. of .bul.Cr(CO)3Cp* to this soln. results in the formation of H-Cr(CO)3Cp* as well as 1/2[{?2-o-(?-NH)C6H4S}CrCp*]2. Spectroscopic data show that (o-H2N)C6H4S-Cr(CO)3Cp* loses CO to form {?2-(o-H2N)C6H4S}Cr(CO)2Cp*. Attack on the N-H bond of the coordinated amine by .bul.Cr(CO)3Cp* provides a reasonable mechanism consistent with the observation that both chelate formation and oxidative addn. of the N-H bond are faster under argon than under CO atm. The N-H bonds of uncoordinated aniline do not react with .bul.Cr(CO)3Cp*. Reaction of the 2 mol. of .bul.Cr(CO)3Cp* with 1,2-benzene dithiol [1,2-C6H4(SH)2] yields the initial product (o-HS)C6H4S-Cr(CO)3Cp* and 1 mol. of H-Cr(CO)3Cp*. Addn. of 1 equiv. more of .bul.Cr(CO)3Cp* to this soln. also results in the formation of 1 equiv. of H-Cr(CO)3Cp*, as well as the dimeric product 1/2[{?2-o-(?-S)C6H4S}CrCp*]2. This reaction also occurs more rapidly under Ar than under CO, consistent with intramol. coordination of the second thiol group prior to oxidative addn. The crystal structures of [{?2-o-(?-NH)C6H4S}CrCp*]2 and [{?2-o-(?-S)C6H4S}CrCp*]2 are reported.

Answer 41:

Bibliographic Information

Barriers for Arene C-H Bond Activation in Platinum(II) ?2-Arene Intermediates. Norris, Cynthia M.; Reinartz, Stefan; White, Peter S.; Templeton, Joseph L. Department of Chemistry, University of North Carolina, Chapel Hill, NC, USA. Organometallics (2002), 21(25), 5649-5656. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 138:73366 AN 2002:850393 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Protonation of Pt(IV) complexes Tp'Pt(Ar)(H)(R) [Tp' = hydridotris(3,5-dimethylpyrazolyl)borate; Ar = aryl; R = H, C6H5] with [H(OEt2)2][BAr'4] [BAr'4 = tetrakis(3,5-trifluoromethylphenyl)borate] gave cationic Pt(II) ?2-arene complexes [?2-(HTp')Pt(?2-HAr)(R)][BAr'4] [Ar = C6H5, R = H (2); Ar = MeC6H4, R = H (4); Ar = 3,6-Me2C6H3, R = H (6); Ar = R = C6H5 (8)]. A barrier of 9.4 kcal/mol for Pt migration around the ?2-p-xylene ring was calcd. for complex 6 at 183 K following variable-temp. NMR measurements. Eyring anal. of H exchange between the bound benzene and the hydride ligand for cationic benzene complex 2 indicates ?H.thermod. = 11.7 ? 0.5 kcal mol-1 and ?S.thermod. = -3.8 ? 2 cal mol-1 K-1. This process is assumed to proceed via arene C-H oxidative addn. to give a five-coordinate Pt(IV) Ph dihydride intermediate. Isolation of ground state ?2-arene adducts with adjacent hydride ligands has allowed the barrier to oxidative addn. for arene C-H bonds (?G.thermod.) to be measured as 13.3 kcal/mol for the p-hydrogen and 13.6 kcal/mol for the m-hydrogens in the toluene adduct 4 and 14.2 kcal/mol for the p-xylene adduct 6. Averaging of the environments for two Tp' arms is an NMR observable feature for the C1 sym. ?2-benzene Ph adduct 8. This dynamic process, which presumably occurs via a five-coordinate Pt(IV) di-Ph hydride intermediate with Cs symmetry, allows the barrier for arene C-H oxidative addn. to be calcd. as 12.9 kcal/mol. Kinetic isotope effects for oxidative addn. of the arene C-H(D) bond in the benzene hydride adduct 2 and the benzene Ph adduct 8 are kH/kD = 3.0 at 259 K and 4.7 at 241 K, resp. These data provide insight into the energetics of arene C-H bond activation.

Answer 42:

Bibliographic Information

Electrophilic (Li+) acceleration of C-H reductive elimination and oxidative addition reactions of Os(II)/Os(0) nitrosyl complexes. Yandulov, Dmitry V.; Caulton, Kenneth G. Department of Chemistry, Indiana University, Bloomington, IN, USA. New Journal of Chemistry (2002), 26(5), 498-502. Publisher: Royal Society of Chemistry, CODEN: NJCHE5 ISSN: 1144-0546. Journal written in English. CAN 137:232750 AN 2002:390942 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reductive elimination of methane from cis,trans-Os(H)2Me(NO)L2 (L = PiPr3) in benzene is accelerated by added LiN(SiMe3)2, with 1H NMR and IR evidence for binding of the Li electrophile to NO O. Oxidative addn. of benzene to the transient OsH(NO)L2, to give cis,trans-Os(H)2Ph(NO)L2, is also accelerated by LiN(SiMe3)2. DFT calcns. of the reaction path with and without LiNMe2 show the rate acceleration is due to preferential stabilization of the oxidative addn./reductive elimination transition state, due to the greater back donation to NO in the TS. This is traced, in turn, to the relief of the filled-filled repulsion between the occupied Os d and C-H ?-orbitals by the Li electrophile on NO O.

Answer 43:

Bibliographic Information

Five-Coordinate Platinum(IV) Complex as a Precursor to a Novel Pt(II) Olefin Hydride Complex for Alkane Activation. Fekl, Ulrich; Goldberg, Karen I. Department of Chemistry, University of Washington, Seattle, WA, USA. Journal of the American Chemical Society (2002), 124(24), 6804-6805. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 137:109364 AN 2002:378107 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The five-coordinate Pt(IV) complex (nacnac)PtMe3 (nacnac- = [(2,6-iPr2C6H3N:CMe)2CH]-) thermally eliminates ethane and methane in C6D6 to produce a novel olefin(hydrido)platinum(II) complex (1; [DPt(2,6-((CD3)2CD)2C6H3N:CMeCHCMe:NC6H3(CD(CD3)2)-2-(C(CD3):CD2)-6)]), where the ?2-coordinating olefin is part of the nacnac-type ligand. This Pt(II) product regioselectively activates hydrocarbons, including alkanes under mild conditions, as indicated by scrambling of H and D between the hydrocarbon solvent and selected positions on the ligand of the Pt complex. A mechanism in which olefin insertion into the metal hydride bond opens a site to allow hydrocarbon coordination and C-H bond oxidative addn. is proposed. The crystal and mol. structures of 1 were detd. by x-ray crystallog.

Answer 44:

Bibliographic Information

Synthesis of Stereoregular and Optically Active Poly[{methyl(1-naphthyl)silylene}(o-phenylene)methylene] by Platinum-Catalyzed Ring-Opening Polymerization. Uenishi, Kazuya; Imae, Ichiro; Shirakawa, Eiji; Kawakami, Yusuke. Graduate School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), Tatsunokuchi, Ishikawa, Japan. Macromolecules (2002), 35(7), 2455-2460. Publisher: American Chemical Society, CODEN: MAMOBX ISSN: 0024-9297. Journal written in English. CAN 136:325955 AN 2002:138077 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Reaction of 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene (I) with platinum 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (PDT) as catalyst (0.1 mol%) gave a polymer, possibly cyclic, with Mn = 1,210,000, polydispersity index (PDI) = 1.77, and cyclic dimer produced via a reductive-elimination. Reaction of I with PDT in the presence of Et3SiH (1:Et3SiH = 1:1) gave 1-triethylsilyl-2-{methyl(1-naphthyl)silylmethyl}benzene (II), a dimer, 1-{methyl(1-naphthyl)(2'-triethylsilylphenylmethyl)silyl}-2-{methyl(1-naphthyl)silylmethyl}benzene (III), and a trimer,

1-{methyl(1-naphthyl)(2'-triethylsilylphenylmethyl)silyl}-2-[methyl(1-naphthyl)[2'-{methyl(1-naphthyl)silylmethylphenyl}]silylmethyl]benzene, in 54, 18, and 11% yield, resp., through a regioselective ring-opening reaction, followed by the ?-bond metathesis process. The mol. wt. of the formed polymers can be controlled by the amt. of Et3SiH. When optically pure (+)-I was used, II and III are proved to have enantiomer excess (ee) or optical purity (op) higher than 99%. These products are considered to be formed from the intermediate cyclic Pt complexes, which were formed by a regio- and stereoselective oxidative-addn. of silicon-aryl bond of (+)-I to Pt, followed by a stereoselective ?-bond metathesis process. Pt-catalyzed ring-opening polymn. (ROP) of optically pure (+)-I provided an isotactic and optically pure polymer [Mn = 356 000, PDI = 1.73, [?]27D = -33.5, c 1.11, CHCl3].

Answer 45:

Bibliographic Information

Electronic and Medium Effects on the Rate of Arene C-H Bond Activation by Cationic Ir(III) Complexes. Tellers, David M.; Yung, Cathleen M.; Arndtsen, Bruce A.; Adamson, Dan R.; Bergman, Robert G. Division of Chemical Sciences, Center for New Directions in Synthesis,Department of Chemistry, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA, USA. Journal of the American Chemical Society (2002), 124(7), 1400-1410. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 136:279551 AN 2002:73516 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A detailed mechanistic study of arene C-H activation in CH2Cl2 soln. by Cp*(L)IrMe(X) [L = PMe3, P(OMe)3; X = OTf, (CH2Cl2)BArf; (BArf = B[3,5-C6H3(CF3)2]4)-] is presented. Triflate dissocn. in Cp*(L)IrMe(OTf), to generate tight and/or solvent-sepd. ion pairs contg. a cationic Ir complex, precedes C-H activation. Consistent with the ion-pair hypothesis, the rate of arene activation by Cp*(L)IrMe(OTf) is unaffected by added external triflate salts, but the rate is strongly dependent upon the medium. Thus the reactivity of Cp*(PMe3)IrMe(OTf) can be increased by almost 3 orders of magnitude by addn. of (n-Hex)4NBArf, presumably because the added BArf anion exchanges with the OTf anion in the initially formed ion pair, transiently forming a cation/borate ion pair in soln. (special salt effect). In contrast, addn. of (n-Hex)4NBArf to [Cp*PMe3Ir(Me)CH2Cl2][BArf] does not affect the rate of benzene activation; here there is no initial covalent/ionic preequil. that can be perturbed with added (n-Hex)4NBArf. An anal. of the reaction between Cp*(PMe3)IrMe(OTf) and various substituted arenes demonstrated that electron-donating substituents on the arene increase the rate of the C-H activation reaction. The rate of C6H6 activation by [Cp*(PMe3)Ir(Me)CH2Cl2][BArf] is substantially faster than [Cp*(P(OMe)3)Ir(Me)CH2Cl2][BArf]. D. functional theory computations suggest that this is due to a less favorable preequil. for dissocn. of the CH2Cl2 ligand in the tri-Me phosphite complex, rather than to a large electronic effect on the C-H oxidative addn. transition state. Because of these combined effects, the overall rate of arene activation is increased by electron-donating substituents on both the substrate and the Ir complex.

Answer 46:

Bibliographic Information

Investigation of the Mechanism of Alkane Reductive Elimination and Skeletal Isomerization in Tp'Rh(CNneopentyl)(R)H Complexes: The Role of Alkane Complexes. Northcutt, Todd O.; Wick, Douglas D.; Vetter, Andrew J.; Jones, William D. Department of Chemistry, University of Rochester, Rochester, NY, USA. Journal of the American Chemical Society (2001), 123(30), 7257-7270. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 135:227097 AN 2001:481472 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Expts. are described that provide indirect evidence for the involvement of alkane ?-complexes in oxidative addn./reductive elimination reactions of Tp'Rh(L)(R)H complexes (Tp' = tris-3,5-dimethylpyrazolylborate, L = CNCH2CMe3). Reductive elimination rates in benzene-d6 were detd. for loss of alkane from Tp'Rh(L)(R)H, where R = Me, Et, Pr, Bu, pentyl, and hexyl, to generate RH and

Tp'Rh(L)(C6D5)D. The iso-Pr hydride complex Tp'Rh(L)(CHMe2)H was found to rearrange to the Pr hydride complex Tp'Rh(L)(CH2CH2CH3)H in an intramol. reaction. The sec-Bu complex behaves similarly. These same reactions were studied by prepg. the corresponding metal deuteride complexes, Tp'Rh(L)(R)D, and the scrambling of the deuterium label into the ?- and ?-positions of the alkyl group monitored by 2H NMR spectroscopy. Inverse isotope effects obsd. in reductive elimination are the result of an inverse equil. isotope effect between the alkyl hydride(deuteride) complex and the ?-alkane complex. A kinetic model has been proposed using alkane complexes as intermediates and the selectivities available to these alkane complexes have been detd. by kinetic modeling of the deuterium scrambling reactions.

Answer 47:

Bibliographic Information

Formation of aryl- and benzylboronate esters by rhodium-catalyzed C-H bond functionalization with pinacolborane.
Shimada, Shigeru; Batsanov, Andrei S.; Howard, Judith A. K.; Marder, Todd B. Department of Chemistry, University of Durham, Durham, UK. Angewandte Chemie, International Edition (2001), 40(11), 2168-2171. Publisher: Wiley-VCH Verlag GmbH, CODEN: ACIEF5 ISSN: 1433-7851. Journal written in English. CAN 135:195590 AN 2001:447155 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

[RhCl(PiPr3)2(N2)] (1) catalyzed the borylation of arom. and benzylic C-H bonds with pinacolborane (HBpin), with high selectivity for benzylic C-H functionalization with PhMe, p-xylene and mesitylene. Borylated toluenes were obtained in yields of 21-69%, with PhCH2Bpin the major product in ratios of 81-87%. A diborylated side product, PhCH(Bpin)2, was obtained in ?7% yield, and its structure was detd. by x-ray crystallog. (space group P21/n, Z = 4, wR(F2) = 0.165). Reaction of HBpin with C6H6 in presence of 1.0 mol % 1 at 140? for 58 h gave 86% PhBpin, via arom. C-H functionalization. Oxidative addn. of HBpin to 1 in C6H6 at 120? gave 79% trans-[Rh(Cl)(H)(Bpin)(PiPr3)2] (2), the structure of which was detd. by x-ray crystallog. (space group P21/n, Z = 4, wR(F2) = 0.052). A mechanism for the catalytic formation of PhCH2Bpin from PhMe and HBpin in presence of 1 is proposed, involving formation of 2 as an intermediate.

Answer 48:

Bibliographic Information

Meta, para and meta, ortho double exo nucleophilic additions of trimethylsilylester enolates derived from saturated and unsaturated carboxylic acids to tricarbonylchromium complexes of aryl ethers: dearomatizing cyclization to lactones.
Rudler, Henri; Comte, Virginie; Garrier, Eva; Bellassoued, Moncef; Chelain, Evelyne; Vaissermann, Jacqueline. Laboratoire de Synthese Organique et Organometallique, UMR 7611, Universite Pierre et Marie Curie, Paris, Fr. Journal of Organometallic Chemistry (2001), 621(1-2), 284-298. Publisher: Elsevier Science S.A., CODEN: JORCAI ISSN: 0022-328X. Journal written in English. CAN 135:19729 AN 2001:194210 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

K enolates derived from satd. and unsatd. bis(trimethylsilyl) ketene acetals react with tricarbonylchromium complexes of anisole and di-Ph ether to give, in addn. to ?-arylcarboxylic acids, the mono adducts, lactones, arising from a double exo nucleophilic addn. The latter were not obsd. in the case of benzenetricarbonylchromium. The intermediate dienol ethers could be isolated and fully characterized by x-ray crystallog. The influence of the nature of the substituents on the ketene acetals, of the nature of the oxidant, and of the nature of the ester enolates on the reaction was established and is discussed in terms of the reaction mechanism.

Answer 49:

Bibliographic Information

Palladium chemistry related to benzyl bromide carbonylation: mechanistic studies. Trzeciak, Anna M.; Ziolkowski, Jozef J. Faculty of Chemistry, University of Wroclaw, Wroclaw, Pol. Monatshefte fuer Chemie (2000), 131(12), 1281-1291. Publisher: Springer-Verlag Wien, CODEN: MOCMB7 ISSN: 0026-9247. Journal written in English. CAN 134:353383 AN 2001:148294 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Palladium(II) complexes of the general formula PdCl2(PR3)2 with PR3 = P(OPh)3, P(OC6H4Me-4)3, P(OC6H4Me-2)3, and PPh2(OBu) were reduced by NEt3 in chloroform or benzene to Pd(0) complexes Pd(PR3)4 and Pd(PR3)x(NEt3)4-x. The same reaction performed in the presence of air gave CH3CHO or CH3CH2CHO when NPr3 was used instead of NEt3. Pd(P(OPh)3)4 reacted with benzyl bromide affording the oxidative addn. product cis-PdBr(CH2Ph)(P(OPh)3)2. The reaction of PdCl2(P(OPh)3)2 with benzyl bromide was obsd. only in the presence of NEt3, and a dimeric complex of [PdBr(CH2Ph)(P(OPh)3)]2 was identified as the reaction product. Both benzyl complexes reacted fast with CO (1 atm) to form acyl complexes exhibiting v(CO) bands at 1709 and 1650 cm-1.

Answer 50:

Bibliographic Information

Organic chemistry of subvalent transition metal complexes, 20. Mechanistic comparison of the nickel(0)-catalyzed homo-oligomerization and co-oligomerization of alkynes and nitriles. Eisch, John J.; Ma, Xin; Han, Kyoung I.; Gitua, John N.; Kruger, Carl. Department of Chemistry, The State University of New York at Binghamton, Binghamton, NY, USA. European Journal of Inorganic Chemistry (2001), (1), 77-88. Publisher: Wiley-VCH Verlag GmbH, CODEN: EJICFO ISSN: 1434-1948. Journal written in English. CAN 134:237123 AN 2001:30462 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A comparative mechanistic study of the Ni(0)-catalyzed homo-oligomerization and co-oligomerization of alkynes and of nitriles was undertaken, with diphenylacetylene and benzonitrile, towards an array of Ni(0) reagents, such as finely divided Ni, (COD)2Ni, (Bpy)(COD)Ni, (Et3P)4Ni, (Bpy)(PhC?CPh)Ni and (COD)2Ni-MeAlCl2 combinations in donor (THF) and nondonor (PhMe or neat substrate) solvents. Special attention was given to the detailed mol. structures of the initial 1:1 adducts, (Bpy)(PhC?CPh)Ni, (Ph3P)3(PhC?CPh)Ni and [(Ph3P)(PhC?N)Ni]4 by a consideration of XRD and IR data. Data from the single crystal XRD anal. of (Bpy)(PhC?CPh)Ni, reported here for the 1st time, are in excellent accord with the presence of a 2,3-diphenylnickelacyclopropene ring for the (PhC?CPh)Ni moiety with almost coplanar chelating coordination of the bipyridyl ligand, rather than with the presence of simple side-on coordination of the alkyne with the metal center. A parallel anal. of XRD and IR data for the two benzonitrile-Ni(0) complexes, which were drawn from previous publications, concluded that the Ni in (Ph3P)3(PhC?N)Ni is coordinated in an end-on fashion and the Ni centers in [(Ph3P)(PhC?N)Ni]4 are coordinated as bridges between nitrile units in both an end-on and side-on manner. The stereochem. of the acid hydrolysis of the nickelacyclopropene complex to (E)- or (Z)-alkene depends on the structure of the cleaving acid; parallel hydrolysis of nitrile-Ni complexes showed that end-on complexes regenerate the nitrile, while side-on complexes lead to the aldehyde. In homo-oligomerization of diphenylacetylene or other alkyne the clean cyclotrimerization to the benzene deriv. proceeds by way of a nickelacyclopentadiene intermediate, as was evident by chem. trapping. The homo-oligomerization of benzonitrile by Ni(0) was found not to lead to 2,4,6-triphenyl-1,3,5-triazine, as claimed in the literature, but rather solely to benzyl Ph ketone, the dimeric hydrolysis product.

The attempted co-oligomerization of diphenylacetylene and benzonitrile with ordinary Ni(0) complexes led only to the homocyclotrimer of the alkyne. Only when the alkyne was prebonded to the Ni, as in (Bpy)(PhC?N)Ni, could significant amts. of a codimerization product with the nitrile be obsd. The origin of the triazine, claimed in a previous report to form from benzonitrile and Raney Ni, was traced to the presence of adventitious moisture and air. Other unexpected products formed from Ni(0) complexes and benzonitrile arise from oxidative addn. reactions of Ni(0) with various ? C-E bonds. The crystal and mol. structures of (Bpy)(PhC?CPh)Ni were detd. by x-ray crystallog.

Answer 51:

Bibliographic Information

Mechanistic Features of Boron-Iodine Bond Activation of B-Iodocarboranes. Marshall, William J.; Young, Robert J., Jr.; Grushin, Vladimir V. Central Research and Development, E. I. DuPont de Nemours & Co. Inc., Wilmington, DE, USA. Organometallics (2001), 20(3), 523-533. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 134:237531 AN 2001:27838 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Oxidative addn. of the B-I bond of 9-iodo-m-carborane to [(Ph3P)nPd] (n = 3, 4) is reversible, the equil. being shifted to the Pd(0) and the iodocarborane. In the presence of [(Ph3P)4Pd] and [Bu4N]Br in THF, 9-iodo-m-carborane undergoes halide exchange to produce 9-bromo-m-carborane. Coordinatively unsatd. Pd(0) and hydrido Pd(II) species generated upon thermal decompn. of [(Ph3P)2Pd(Ph)(O2CH)] and [(Ph3P)2Pd2(Ph)2(?-O2CH)2] reduce 9-iodo-m-carborane to m-carborane with 100% selectivity. The thermal decompn. of [(Ph3P)2Pd2(Ph)2(?-O2CH)2] in the presence of excess 9-iodo-m-carborane and PhI (1:1) gave m-carborane (3%) and [(Ph3P)2Pd2(Ph)2(?-I)2] (97%), whose structure was confirmed by single-crystal x-ray diffraction. X-ray anal. of 9-iodo-m-carborane and m-carboran-9-yl(phenyl)iodonium tetrafluoroborate shows that in the iodonium salt the B-I bond is longer by .apprx.0.03 .ANG. than in the iodocarborane. In contrast, the C-I bond distances in carboran-9-yl(phenyl)iodonium tetrafluoroborate (2.111(2) .ANG.) and in iodobenzene (2.098(4) .ANG.) are only marginally different. The elongation of the B-I bond, not the C-I bond, likely contributes to (i) the enhanced reactivity of B-carboranyl(phenyl)iodonium cations toward nucleophiles and (ii) the remarkably high selectivity of these SN reactions that occur exclusively at the B atom. A new crystallog. form of 9,10-diiodo-m-carborane is reported.

Answer 52:

Bibliographic Information

Oxidative-Addition of Organic Monochloro Derivatives to Dinuclear Rhodium Complexes: Mechanistic Considerations. Tejel, Cristina; Ciriano, Miguel A.; Edwards, Andrew J.; Lahoz, Fernando J.; Oro, Luis A. Departamento de Quimica Inorganica Instituto de Ciencia de Materiales de Aragon, Universidad de Zaragoza-CSIC, Zaragoza, Spain. Organometallics (2000), 19(24), 4968-4976. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 134:56783 AN 2000:752426 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The addn. of RCH2Cl to [{Rh(?-Pz)(CNBut)2}2] (Pz = pyrazolate, 1) occurs under mild conditions to yield the bis(alkyl)rhodium(III) complexes [{Rh(?-Pz)(?1-CH2R)(CNBut)2}2(?-Cl)]Cl (R = Ph, CH:CH2, CO2Me, COMe). These reactions proceed through two sep. steps, as evidenced by the observation of the intermediate mixed-valence complex [(tBuNC)2RhI(?-Pz)2RhIII(?1-CH2Ph)(Cl)(CNBut)2] resulting from the trans-addn. of PhCH2Cl at a single metal center in 1. Similar Rh(I)-Rh(III) complexes [(cod)Rh(?-Pz)2Rh(?1-CH2R)(Cl)(CNBut)2] (R = Ph (7), CH:CH2, CO2Me) result from the addn. of RCH2Cl to the mixed-ligand complex [(cod)Rh(?-Pz)2Rh(CNBut)2] (6). These exist in benzene and toluene as two interconverting conformers, differentiated by the location of the RCH2 group either between the two metals in the pocket of the complexes (endo conformer) or at the trans position (exo conformer). An intramol. boat-to-boat inversion accounts for this exchange. The thermodn. parameters for 7 were ?H.thermod. = 16.2 kcal mol-1, ?S.thermod. = 4.9 eu, and ?G293.thermod. = 14.9 kcal mol-1. Primary alkyl bromides RCH2Br react with 1 and with 6 to give the Rh(III) complexes [{Rh(?-Pz)(?1-CH2R)(CNBut)2}2(?-Br)]Br (R = Ph, CO2Me) and the mixed-valence complex [(cod)Rh(?-Pz)2Rh(?1-CH2Ph)(Br)(CNBut)2]. However, the secondary alkyl bromide PhCH(Me)Br reacts with 1 and with 6 to give the dirhodium(II) complexes [{Rh(?-Pz)(Br)(CNBut)2}2] and [(cod)(Br)Rh(?-Pz)2Rh(Br)(CNBut)2], resp., along with 2,3-diphenylbutane and traces of styrene and ethylbenzene, suggesting free-radical pathways for these reactions. The thermal decompn. of the bis(alkyl)chloro complexes gives free isobutene and the cyanide complexes [(CNBut)2(?1-CH2R)Rh(?-Pz)2(?-Cl)Rh(?1-CH2R)(CN)(CNBut)] (R = Ph, COMe, CO2Me). Decompn. of the bis(alkyl)bromo derivs.

occurs under sunlight irradn. and anaerobic conditions to give bibenzyl, cis- and trans-stilbene, and toluene. The crystal and mol. structures of [(CNBut)2(?1-CH2Ph)Rh(?-Pz)2(?-Cl)Rh(?1-CH2Ph)(CN)(CNBut)] were detd. by x-ray crystallog.

Answer 53:

Bibliographic Information

Mechanistic investigation of benzene C-H activation at a cationic platinum(II) center: direct observation of a platinum(II) benzene adduct. Johansson, Lars; Tilset, Mats; Labinger, Jay A.; Bercaw, John E. Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, CA, USA. Journal of the American Chemical Society (2000), 122(44), 10846-10855. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 134:42243 AN 2000:742575 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The platinum(II) Me cation [(N-N)Pt(CH3)(solv)]+BF4- (N-N = ArN:C(Me)C(Me):NAr, Ar = 2,6-(CH3)2C6H3, solv = H2O (2a) or TFE = CF3CH2OH (2b)) is prepd. by treatment of (N-N)Pt(CH3)2 with 1 equiv. of aq. HBF4 in TFE. Reaction of a mixt. of 2a and 2b with benzene in TFE/H2O solns. cleanly affords the platinum(II) Ph cation [(N-N)Pt(C6H5)(solv)]+BF4- (3). Investigations of the kinetics and isotopic labeling expts. indicate that reaction of 2 with benzene proceeds via benzene coordination, reversible oxidative addn. of benzene C-H bonds, reversible formation of a methane C,H-? complex, and final dissocn. of methane. Under conditions where [(N-N)Pt(CH3)(H2O)]+BF4- (2a) is the major starting complex, rate-detg. benzene coordination to 2b is implicated by the obsd. kinetic rate law (inverse first order in [H2O] and first order in [C6H6] to 3.8 M) and the small kinetic deuterium isotope effect for C6H6 vs C6D6 (kH/kD = 1.06 ? 0.05 at 25?). When deuterated benzenes C6D6 and 1,3,5-C6H3D3 are used, almost full statistical scrambling of deuterium from one benzene into methane is achieved, indicating that the energetic barriers for dissocg. benzene and methane are considerably higher than interconversions of intermediate hydrocarbon complexes and [(N-N)Pt(C6H5)(CH3)H]+. Protonation of (N-N)Pt(CH3)(C6H5) with HBF4 in TFE, which provides an independent route into the manifold of postulated intermediates, gives a mixt. of 3 + CH4 (82%) and 2 + C6H6 (18%). Protonation of (N-N)Pt(CH3)(C6H5) with triflic acid in methylene chloride/diethyl ether mixts. at -69? allows direct low-temp. NMR observation of a fluxional ? benzene complex, [(N-N)Pt(CH3)(C,C-?2-C6H6)]+.

Answer 54:

Bibliographic Information

The Methylene-Transfer Reaction: Synthetic and Mechanistic Aspects of a Unique C-C Coupling and C-C Bond Activation Sequence. Cohen, Revital; Van der Boom, Milko E.; Shimon, Linda J. W.; Rozenberg, Haim; Milstein, David. Departments of Organic Chemistry and Chemical Services, The Weizmann Institute of Science, Rehovot, Israel. Journal of the American Chemical Society (2000), 122(32), 7723-7734. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 133:266961 AN 2000:514095 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Oxidative addn. of aryl iodides ArI (Ar = (a) Ph, (b) C6H4CF3-4, (c) C6H3(CF3)2-3,5, (d) C6H4CH3-4, (e) C6H4OCH3-4), to the PCP-type complex Rh(PPh3)[CH2C6HMe2-3,5-(CH2PPh2)2-2,6] (1), yields the complexes Rh(Ar)[CH2C6HMe2-3,5-(CH2PPh2)2-2,6]I (2a-e). Compds. 2a-e undergo intramol. methylene transfer from the bis-chelating ligand to the incoming aryl under mild conditions (room temp.) giving Rh(CH2Ar)[C6HMe2-3,5-(CH2PPh2)2-2,6]I (3a-e). The methylene transfer, which is a unique sequence of sp2-sp3 C-C bond reductive elimination and sp2-sp3 C-C bond activation, was studied kinetically (reaction 2a ? 3a), yielding the activation parameters ?H.thermod. = 17 ? 3 kcal/mol, ?S.thermod. = -23 ? 4 eu. The rate-detg. step of this reaction is the C-C reductive elimination rather than the C-C activation step. X-ray structural anal. of 2a and 3b demonstrates that the Rh atom is located in the center of a square pyramid with the aryl (2a) and the benzyl (3b) trans to the vacant coordination site. Reaction of the complex Rh(CH2C6H4CF3)[C6H3(CH2PPh2)2-2,6]Br (7c) with C nucleophiles (MeLi, PhLi, BzMgCl) leads to a competitive sp2-sp3 and sp3-sp3

C-C coupling, resulting in migration of a methylene or benzylidene into the bis-chelating ring and formation of the corresponding org. products. Sp2-sp3 C-C coupling is kinetically preferred over the sp3-sp3 one, and the more electron-rich the benzyl ligand, the better the migratory aptitude obsd. X-ray structural anal. of two benzyl migration products, complexes Rh(PPh3)[CH(C6H4CF3-4)C6H3(CH2PPh2)2-2,6] (11) and Rh(PPh3)[CHPhC6HMe2-3,5-(CH2PPh2)2-2,6] (16), demonstrates that the Rh atom is located in the center of a square planar arrangement where the PPh3 ligand occupies the position trans to the methyne C of the benzylidene bridge. The methylene and benzylidene migration reaction is an important transformation for the regeneration of the methylene-donating moiety in the methylene-transfer process.

Answer 55:

Bibliographic Information

Catalytic oxidation with a non-heme iron complex that generates a low-spin FeIIIOOH intermediate. Roelfes, Gerard; Lubben, Marcel; Hage, Ronald; Que, Lawrence, Jr.; Feringa, Ben L. Dep. of Org. and Mol. Inorg. Chem., Stratingh, Inst., Univ. of Groningen, Groningen, Neth. Chemistry--A European Journal (2000), 6(12), 2152-2159. Publisher: Wiley-VCH Verlag GmbH, CODEN: CEUJED ISSN: 0947-6539. Journal written in English. CAN 133:321565 AN 2000:481319 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The antitumor drug bleomycin is proposed to act via a low-spin iron(I) hydroperoxide intermediate called "activated bleomycin". To gain more insight into the mechanistic aspects of catalytic oxidn. by these intermediates, we have studied the reactivity of [(N4Py)Fe(CH3CN)](ClO4)2 (1) (N4Py = N,N-bis(2-pyridylmethyl)-N-[bis(2-pyridyl)methyl]amine) with excess H2O2. Under these conditions, a transient purple species is generated, [(N4Py)Fe(O2H)]2+ (2), which has spectroscopic features and reactivity strongly reminiscent of activated bleomycin. The catalytic oxidn. of alkanes such as cyclohexane, cyclooctane and adamantane by 1 with H2O2 gave the corresponding alcs. and ketones in up to 31% yield. It was concluded from the O2 sensitivity of the oxidn. reactions, the formation of brominated products in the presence of methylene bromide and the non-stereospecificity of the oxidn. of cis- or trans-dimethylcyclohexane, that long-lived alkyl radicals were formed during the oxidns. Oxidn. of alkenes did not afford the corresponding epoxides in good yields but resulted instead in allylic oxidn. products in the case of cyclohexene and cleavage of the double bond in the case of styrene. Addn. of hydroxyl radical traps, such as benzene and acetone, led to only partial quenching of the reactivity. The kinetic isotope effects for cyclohexanol formation, ranging from 1.5 in acetonitrile to 2.7 in acetone with slow addn. of H2O2, suggested the involvement of a more selective oxidizing species in addn. to hydroxyl radicals. Monitoring the UV/Vis absorption of 2 during the catalytic reaction showed that 2 was the precursor for the active species. On the basis of these results, it is proposed that 2 reacts through homolysis of the O-O bond to afford two reactive radical species: [(N4Py)FeIVO]2+ and .bul.OH. The comparable reactivity of 1 and Fe-bleomycin raises the possibility that they react through similar mechanistic pathways.

Answer 56:

Bibliographic Information

Thermal Stability, Decomposition Paths, and Ph/Ph Exchange Reactions of [(Ph3P)2Pd(Ph)X] (X = I, Br, Cl, F, and HF2). Grushin, Vladimir V. Experimental Station, Central Research and Development, E. I. DuPont de Nemours and Co. Inc., Wilmington, DE, USA. Organometallics (2000), 19(10), 1888-1900. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 132:347713 AN 2000:236500 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Complexes of the type [(Ph3P)2Pd(Ph)X], where X = I (1), Br (2), Cl (3), F (4), and HF2 (5), possess different thermal stability and reactivity toward the Pd-Ph/P-Ph exchange reactions. While 1 decompd. (16 h) in toluene at 110? to [Ph4P]I, Pd metal, and Ph3P, complexes 2 and 3 exhibited no sign of decompn. under these conditions. Kinetic studies of the aryl-aryl exchange reactions of [(Ph3P)2Pd(C6D5)X] in benzene-d6 demonstrated that the rate of exchange decreases in the order 1 > 2 > 3, the obsd. rate const. ratio,

kI:kBr:kCl, in benzene at 75? being ca. 100:4:1 for 1-d5, 2-d5, and 3-d5. The exchange was facilitated by a decrease in the concn. of the complex, polar media, and a Lewis acid, e.g., Et2O?BF3. Unlike [Bu4N]PF6, which speeded up the exchange reaction of 2-d5, [Bu4N]Br inhibited it due to the formation of anionic four-coordinate [(Ph3P)Pd(C6D5)Br2]-. The latter and its iodo analog were generated in dichloromethane and benzene upon addn. of [Bu4N]X or PPNCl to [(Ph3P)2Pd2(Ph)2(?-X)2] (X = I, Br, or Cl) and characterized in soln. by 1H and 31P NMR spectral data. The mechanism of the aryl-aryl exchange reactions of [(Ph3P)2Pd(C6D5)X] in noncoordinating solvents of low polarity may not require Pd-X ionization but rather involves phosphine dissocn., the ease of which decreases in the order X = I > Br > Cl, as suggested by crystallog. data. Two mechanisms govern the thermal reactions of [(Ph3P)2Pd(Ph)F], 4. One of them is similar to the aryl-aryl exchange and decompn. path for 1-3, involving a tight ion pair intermediate, [Ph4P][(Ph3P)PdF], within which two processes were shown to occur. At 75?, the C-P oxidative addn. restores the original neutral complex 4. At 90?, reversible fluoride transfer from Pd to the phosphonium cation resulted in the formation of covalent [Ph4PF] and [(Ph3P)Pd], which was trapped by PhI to produce [(Ph3P)2Pd2(Ph)2(?-I)2]. The other decompn. path of 4 leads to the formation of [(Ph3P)3Pd], Pd, Ph2, Ph3PF2, and Ph2P-PPh2 as main products.

Unlike the aryl-aryl exchange, this decompn. reaction is not inhibited by free phosphine. The formation of biphenyl was shown to occur due to PdPh/PPh coupling on the metal center. Mechanisms accounting for the formation of these products are proposed and discussed. The facile (4 h at 75?) thermal decompn. of [(Ph3P)2Pd(Ph)(FHF)] (5) in benzene resulted in the clean formation of PhH, Ph3PF2, Pd metal, and [(Ph3P)3Pd].

Answer 57:

Bibliographic Information

Transition Metal Polyhydride Complexes. 11. Mechanistic Studies of the Cis to Trans Isomerization of the Iridium(III) Dihydride Ir(H)2(CO)L (L = C6H3(CH2P(H)2)2). Li, Shuhua; Hall, Michael B. Department of Chemistry, Texas A&M University, College Station, TX, USA. Organometallics (1999), 18(26), 5682-5687. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 132:122740 AN 1999:758170 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

D. functional theory (B3LYP) was used to study the mechanism of the cis-trans isomerization in Ir(H)2(CO)L [L = C6H3(CH2P(H)2)2], a model for Ir(H)2(CO)L' [L' = C6H3(CH2P(i-Pr)2)2]. This complex is initially formed as the cis isomer by bubbling H2 through a benzene soln. of Ir(CO)L' at room temp. mol. structure. Over period of 18 h at 90?, the cis isomer quant. converts to the trans isomer (Organometallics 1997, 16, 3786). Five possible mechanisms were examd. in detail: (i) CO dissocn. and reassocn.; (ii) CO migratory insertion into the Ir-H bond and subsequent elimination; (iii) Ph-H reductive elimination to an arene intermediate and subsequent oxidative addn.; (iv) phosphine dissocn., complex rearrangement, and phosphine reassocn.; and (v) nondissociative trigonal twist. The preferred mechanism involves two consecutive trigonal twists in which the complex passes through a distorted octahedral intermediate.

Answer 58:

Bibliographic Information

Models for the initial stages of oxidative addition. Synthesis, characterization, and mechanistic investigation of ?1-I2 organometallic "pincer" complexes of platinum. X-ray crystal structures of [PtI(C6H3[CH2NMe2]]2-2,6)(?1-I2)] and exo-meso-[Pt(?1-I3)(?1-I2)(C6H3[CH2N(t-Bu)Me]]2-2,6)]. Gossage, Robert A.; Ryabov, Alexander D.; Spek, Anthony L.; Stufkens, Derk J.; van Beek, Johannus A. M.; van Eldik, Rudi; van Koten, Gerard. Department of Metal-Mediated Synthesis Debye Institute and Laboratory of Crystal Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Utrecht, Neth. Journal of the American Chemical Society (1999), 121(11), 2488-2497. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 130:296803 AN 1999:163600 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reaction of I_2 with Pt pincer complexes [PtI(NCN'')] (NCN'' = [C6H3(CH2NRR')2-2,6]-; R = R' = Me or Et; or R = Me, R' = t-Bu) is reported. All three complexes contain an end-on (?1) I2 unit, and these compds. represent the only known isolable organometallic species which contain I2 in this bonding motif. These compds. can be envisioned as representing the initial stages of oxidative addn. of dihalides to d8 transition metal complexes. [PtI{C6H3(CH2NMe2)2-2,6}(?1-I2)] (1) and exo-meso-[PtI3{C6H3(CH2NMe[t-Bu])2-2,6}(?1-I2)] (3b) were structurally characterized by single-crystal x-ray diffraction methods. Mechanistic and spectroscopic (IR, Raman, NMR, UV/visible) studies indicated that complex 1 is formed via a 1,2-shift of the dihalide from the primary product [Pt(?1-I3){C6H3(CH2NMe2)2-2,6}]. The role of the metal-bound halide anion as the point of initial attack of I2 is described. The results of these studies are discussed in terms of the basic mechanism of oxidative addn. and its implications for catalysis.

Answer 59:

Bibliographic Information

Isomerization and oxidation of cyclohexadiene mediated by (DMPE)2Ru(NH2)(H): Evidence for an ionic mechanism. Fulton, J. Robin; Bouwkamp, Marco; Bergman, Robert G. Department of Chemistry, University of California, Berkeley, CA, USA. Book of Abstracts, 217th ACS National Meeting, Anaheim, Calif., March 21-25 (1999), INOR-294. Publisher: American Chemical Society, Washington, D. C CODEN: 67GHA6 Conference; Meeting Abstract written in English. AN 1999:92111 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Trans-(DMPE)2Ru(NH2)(H) has recently been prepd. in our lab. This complex catalyzes the isomerization of 1,3- and 1,4-cyclohexadiene. In addn., it formally oxidizes cyclohexadiene to benzene. [Equation Omitted]. Mechanistic studies of this reaction will be presented.

Answer 60:

Bibliographic Information

Isolation and Characterization of Neutral Platinum Silylene Complexes of the Type (R3P)2Pt:SiMes2 (Mes = 2,4,6-Trimethylphenyl). Feldman, Jay D.; Mitchell, Gregory P.; Nolte, Joern-Oliver; Tilley, T. Don. Department of Chemistry, University of California at Berkeley, Berkeley, CA, USA. Journal of the American Chemical Society (1998), 120(43), 11184-11185. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 130:9949 AN 1998:659132 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Photolysis of Mes2Si(SiMe3)2 (Mes = mesityl) and Pt(PCy3)2 in hexanes afforded silylene complex (Cy3P)2Pt:SiMes2 (1) in 54% yield. Benzene-d6 solns. of (iPr3P)2Pt:SiMes2 (2) were also formed, but the complex decompd. to Pt(PPri3)3 and unidentified Si-contg. products when solvent was removed. The structure of 1 was detd. by x-ray crystallog.; the Pt:Si bond distance is 2.210(2) .ANG., which is about 6% shorter than typical Pt-Si single bonds. The reactivity of 1 was studied. Addn. of ROH (R = H, Me, Et) to 1 resulted in clean formation of Pt(PCy3)2 and Mes2Si(OR)H via insertion of the silylene group into the O-H bond. Hydrogenation of 1 in benzene forms trans-(Cy3P)2Pt(H)(SiHMes2) (3). At ambient temp. this hydride decomps. to trans-(Cy3P)2PtH2 (without formation of Mes2SiH2). In refluxing benzene-d6, 3 is irreversibly hydrogenated to trans-(Cy3P)2PtH2 and Mes2SiH2. Complex 3 is fluxional in soln. as obsd. by 31P NMR spectroscopy. Oxidative addn. of Mes2SiH2 to Pt(PCy3)2 exclusively gives cis-(Cy3P)2Pt(H)(SiHSiMes2) (4), which isomerizes to 3 at 90?. The PtH and SiH hydrogens of 4 undergo rapid exchange; possible mechanisms are discussed.

Answer 61:

Bibliographic Information

Activation of CH bonds of cyclohexane and aromatic hydrocarbons with bis(picoline)dichloropalladium(II) in nonpolar solvents. Vedernikov, A. N.; Nasybullina, A. Sh.; Solomonov, B. N. Kazan State Univ., Kazan, Russia. Russian Journal of General Chemistry (Translation of Zhurnal Obshchei Khimii) (1998), 68(2), 277-279. Publisher: MAIK Nauka/Interperiodica Publishing, CODEN: RJGCEK ISSN: 1070-3632. Journal written in English. CAN 129:275534 AN 1998:622618 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

(pic)2PdCl2 (pic = ?- or ?-picoline) were prepd. and studied in reactions with cyclohexane, C6H6, PhMe and o-xylene. At 120?, these hydrocarbons are converted to the corresponding monochloro derivs. (chlorocyclohexane, PhCl, and isomeric chlorotoluene and -xylene), and the Pd complex is reduced to form metallic Pd, picoline, and picolinium chloride. The initial rates of these reactions were estd. The most active are PhMe and o-xylene, C6H6 has the lowest activity, and cyclohexane has intermediate activity. Addn. of I2 to the reaction mixt. revealed no organopalladium compds. The reaction mechanism was studied. Activation of the hydrocarbons by oxidative addn. to the Pd complex via C-H bonds was proposed.

Answer 62:

Bibliographic Information

Stereochemical Investigations of the Mechanism of C-H Bond Activation. Diastereomeric and Isotopic Scrambling in (Hydrido)alkyliridium Complexes. Mobley, T. Andrew; Schade, Christian; Bergman, Robert G. Department of Chemistry, University of California, Berkeley, CA, USA. Organometallics (1998), 17(16), 3574-3587. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 129:189468 AN 1998:485815 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Diastereomeric (RS),(SR)-((2,2-dimethylcyclopropyl)(Cp*)(PMe3)IrH) (2a) and (RR),(SS)-((2,2-dimethylcyclopropyl)(Cp*)(PMe3)IrH) (2b) and their ?-deuterated analogs (2a-?d1, 2b-?d1) were synthesized in racemic form and sepd. by low-temp. (-80?) column chromatog. Thermolysis (140?) of diastereomerically pure 2a or 2b in C6D6 results in its interconversion to the other diastereomer. Thermolysis of the D-labeled analogs 2a-?d1 and 2b-?d1 results addnl. in scrambling of D from the ?-position of the dimethylcyclopropyl ring to the metal hydride position. Diastereomer interconversion and isotopic scrambling occur at similar rates, which are faster than the rate obsd. for the reductive elimination of dimethylcyclopropane and subsequent oxidative addn. of C6D6. Quant. anal. of these rate data is reported. The similarity of these rates is discussed in terms of a common intermediate mechanism involving a metal alkane (or ?-alkane) complex. This mechanism was used as a basis for comparison of the rearrangement processes in the current Ir system and the previously reported analogous Rh system. The crystal and mol. structures of ((1-methylcyclopropyl)methyl)(Cp*)(PMe3)IrH and (RS),(SR)-((2,2-dimethylcyclopropyl)(Cp*)(PMe3)IrBr) were detd. by x-ray crystallog.

Answer 63:

Bibliographic Information

Intramolecular Ligand Hydroxylation: Mechanistic Studies on the Reaction of a Copper(I) Schiff Base Complex with Dioxygen. Ryan, Sara; Adams, Harry; Fenton, David E.; Becker, Michael; Schindler, Siegfried. Department of Chemistry, University of Sheffield, Sheffield, UK. Inorganic Chemistry (1998), 37(9), 2134-2140. Publisher: American Chemical Society, CODEN: INOCAJ ISSN: 0020-1669. Journal written in English. CAN 128:225102 AN 1998:240035 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The dinuclear copper(I) complex of 1,3-bis[N-(2-pyridylethyl)formimidoyl]benzene, [Cu2(H-BPB-H)(CH3CN)2](BF4)2, as well as the 5-nitro deriv., [Cu2(NO2-BPB-H)(CH3CN)2](BF4)2, react with dioxygen to form phenolate-bridged complexes as products. In a detailed kinetic study activation parameters of ?H.thermod. = 47 ? 9 kJ/mol, ?S.thermod. = -53 ? 11 J/(mol K), and ?V.thermod. = -9.5 ? 0.5 cm3/mol for the reaction of [Cu2(H-BPB-H)(CH3CN)2](BF4)2 with dioxygen were obtained which account, together with further kinetic findings, for the occurrence of an intermediate peroxo complex that cannot be obsd. spectroscopically. The crystal structures of the products of the reaction were detd. Crystal data: complex [Cu2(H-BPB-O)OH(H2O)](BF4)2, formula C22H24B2Cu2F8N4O3, monoclinic space group P21/c, Z = 4, a 10.122(2), b 28.711(6), c 9.283(2) .ANG., ? 100.78(3)?; complex [Cu2(NO2-BPB-O)OH(H2O)3](BF4)2, formula C22H27B2Cu2F8N5O7, triclinic space group, P.hivin.1, Z = 2, a 10.144(2), b 10.7612(2), and c 16.000(4) .ANG., ? = 106.15(2), ? = 96.13(2) and ? = 114.810(10)?.

Answer 64:

Bibliographic Information

Alkylboranes in the Suzuki-Miyaura Coupling: Stereochemical and Mechanistic Studies. Matos, Karl; Soderquist, John A. Department of Chemistry, University of Puerto Rico, Rio Piedras, P. R. Journal of Organic Chemistry (1998), 63(3), 461-470. Publisher: American Chemical Society, CODEN: JOCEAH ISSN: 0022-3263. Journal written in English. CAN 128:61544 AN 1998:48188 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Both erythro and threo isomers of B-(3,3-dimethyl-1,2-dideuterio-1-butyl)-9-BBN (6) were prepd. from 3,3-dimethyl-1-butyne through a hydroboration-deuterolysis-hydroboration sequence employing 1st 9-BBN-H and then 9-BBN-D, or in reverse order, resp. Employing the Whitesides protocol, the stereochem. of B ? Pd alkyl group transfer in the Suzuki-Miyaura coupling of 6 to PhBr occurs with complete retention of configuration with respect to C. For the coupling process, the Lewis acidity of the B plays an important role with B-alkyl-9-BBN (10) forming [HO(R)-9-BBN]- (12) with the added base, in marked contrast to their B-alkyl-9-oxa-10-borabicyclo[3.3.2]decane counterparts (ROBBD, 11) which do not. This behavior parallels their coupling rates with the exclusive reaction of 10 over 11 in competitive expts. Five possible roles were demonstrated for the added base in the coupling: (1) the formation of 12, (2) the hydrolysis of Ph(Ph3P)2PdBr (14) to provide monomeric Ph(Ph3P)2PdOH (15), (3) the complexation of HOBR2 byproducts which can compete with 10 for base, (4) accelerated coupling rates for 11, and (5) catalyst regeneration. Kinetic studies reveal that the couplings are zero-order in the borane but for 10 exhibit a 1st-order dependence on [PhBr] (i.e., oxidative addn.), while for 11 exhibit a 1st-order dependence on [OH-] (i.e., Pd(II)X hydrolysis). These data are interpreted in terms of attack of 14 by 12 to form a hydroxo ?2-bridged intermediate 8a [PhL2Pd ? (OH)BBR(9-BBN)]. This provides the precursor to transmetalation through a four-centered transition state 9. Because the analogous hydroxyborate complex is absent for 11, 14 is hydrolyzed by OH- forming 15 in a slower process, with this ultimately reacting with 11 to form a related intermediate 8b [PhL2Pd(OH) ? BR(OBBD)] which also collapses to products through 9.

Answer 65:

Bibliographic Information

Synthesis and Reactivity of Labile MeCN Adducts of Diruthenium Bis(?-methylene) Species, Cp2Ru2(?-CH2)2(CO)n(MeCN)2-n (n = 1, 2): Reaction with H Sources, H-X (X = SiR3, SnR3, H), and C-C Coupling with Alkynes and Diazoalkanes. Akita, Munetaka; Hua, Ruimao; Nakanishi, Sadahiro; Tanaka, Masako; Moro-oka, Yoshihiko. Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Yokohama, Japan. Organometallics (1997), 16(25), 5572-5584. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 128:22995 AN 1997:733026 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Irradn. of the diruthenium bis(?-methylene) complex Cp2Ru2(?-CH2)2(CO)2 (1), in acetonitrile gives the mono- and bis(acetonitrile) species Cp2Ru2(?-CH2)2(CO)(MeCN) (2) and Cp2Ru2(?-CH2)2(MeCN)2 (3) in a successive manner. The mono-MeCN species 2 has been characterized spectroscopically and crystallog., but the bis-MeCN species 3 is too unstable to be fully characterized. Reaction of 2 with hydrosilanes and hydrostannanes results in oxidative addn. of the H-Si and H-Sn bond to give hydrido-?-methylene complexes, Cp2Ru2(?-CH2)2(H)(mR3)(CO) (m = Si (7), Sn (9)). In the case of the reactions with dihydrosilane, phenylsilane, and triphenyltin, one of the two methylene bridges is eliminated as methane (and benzene from phenylsilane) to give ?-methylene-?-silylene complexes, Cp2Ru2(?-CH2)(?-SiR2)(H)(SiR3)(CO) (8), and a tristannyl-?-methylene complex, Cp2Ru2(?-CH2)(?-H)(SnPh3)3(CO) (10). Treatment of 2 with alkynes (R1C?CR2) and diphenyldiazomethane produces the metalacyclic products Cp2Ru2[?-?3-C(R1)C(R2):CH2](?-CH2)(CO) (12), and the vinylidene complex Cp2Ru2(?-C:CPh2)(?-?3-CPh2) (14), resp., via C-C coupling. In contrast to 2, corresponding reactions of the bis-MeCN species 3 are sluggish and only the simple MeCN replacement reaction proceeds in a selective manner.

Answer 66:

Bibliographic Information

A Combined Gas-Phase, Solution-Phase, and Computational Study of C-H Activation by Cationic Iridium(III) Complexes.
Hinderling, Christian; Feichtinger, Derek; Plattner, Dietmar A.; Chen, Peter. Laboratorium fuer Organische Chemie, Eidgenoessischen Technischen Hochschule, Zurich, Switz. Journal of the American Chemical Society (1997), 119(44), 10793-10804. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 127:319057 AN 1997:667351 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A combination of electrospray ionization MS/MS techniques, isotopic labeling expts. in the gas-phase and soln., and ab initio calcns. (d.-functional theory with B3LYP functional and LANL2DZ basis set) was used to study the C-H activation reactions of [Cp*Ir(PMe3)Me]+ and [CpIr(PMe3)Me]+. The reaction in the gas phase proceeds through a Cp or [Cp*Ir(?2-CH2PMe2)]+ intermediate. Quant. collision-induced dissocn. (CID) threshold measurements were used along with general models for ion-mol. reactions to construct potential energy diagrams which rationalize the gas-phase results. The comparison between the two complexes, and between the reactions in the gas phase and in soln., suggests that the reaction through the intermediacy of a metallaphosphacyclopropane could be favored over the conventional (and simpler) oxidative addn./reductive elimination mechanism when the Ir(III) complex is rendered more electron deficient. The crystal and mol. structures of [CpIr(PMe3)(Me)I] were detd. by x-ray crystallog. (reported in supplementary material).

Answer 67:

Bibliographic Information

C-O Bond Homolysis in a Tungsten Alkoxide: The Mechanism of Alcohol Deoxygenation by WCl2(PMe3)4 and WH2Cl2(PMe3)4. Crevier, Thomas J.; Mayer, James M. Department of Chemistry, University of Washington, Seattle, WA, USA. Journal of the American Chemical Society (1997), 119(36), 8485-8491. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 127:234019 AN 1997:565058 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Reactions of alcs. with WCl2(PMe3)4 (1) or WH2Cl2(PMe3)4 (2) yield W(O)Cl2(PMe3)3 (3), PMe3, and hydrocarbons. Cyclopropanemethanol is deoxygenated to give 1-butene and a trace of trans-2-butene as the org. products; benzyl alc. yields toluene and bibenzyl. These products indicate the intermediacy of org. radicals. Benzyl radicals in the reaction of 1 with PhCH2OH can be trapped by added 2 or by 9,10-dihydroanthracene (DHA), leading to increased yields of toluene vs bibenzyl. With WD2Cl2(PMe3)4 (2-d2) or DHA-d12, PhCH2D is formed. The reaction of methanol with 1 proceeds similarly in the presence of DHA, forming 3 and

methane. Kinetic studies on the reaction of 1 with benzyl alc. indicate that the reaction proceeds via alkoxide intermediates. A mechanism involving homolysis of the C-O bond in an alkoxide intermediate is suggested by these results. The thermodn. of this unusual transformation are discussed.

Answer 68:

Bibliographic Information

New catalyst system based on platinum(II) complexes and tetrachloromethane for activation of alkane and arene C-H bonds. Vedernikov, A. N.; Zazynin, A. G.; Borisoglebskii, S. B.; Solomonov, B. N. Kazan. Gos. Univ., Kazan, Russia. Zhurnal Obshchei Khimii (1996), 66(12), 1977-1980. Publisher: Nauka, CODEN: ZOKHA4 ISSN: 0044-460X. Journal written in Russian. CAN 126:277088 AN 1997:225081 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The Pt(II) complex cis-PtCl2(PPh3)2 catalyzed the chlorination of RH (cyclohexane, n-hexane, toluene) with CCl4: for cyclohexane reactant, chlorocyclohexane was formed in 700% yield based on catalyst; toluene was approx. and order of magnitude less reactive, and produced benzyl chloride; n-hexane afforded 2- and 3-chlorohexane; and benzene was unreactive. Catalytic activity decreased in the series cis-Ph2Pt(PPh3)2 > cis-PtCl2(PPh3)2 > cis-PtCl2(MeCN)2 symbatically with decrease in electron d. on Pt, consistent with an oxidative addn. mechanism. The kinetics and mechanism were discussed.

Answer 69:

Bibliographic Information

Direct observation of a dissociative mechanism for C-H activation by a cationic iridium(III) complex. Hinderling, Christian; Plattner, Dietmar A.; Chen, Peter. Lab. Organische Chemie, Eidgenoessische Techn. Hochschule Univ., Zurich, Switz. Angewandte Chemie, International Edition in English (1997), 36(3), 243-244. Publisher: VCH, CODEN: ACIEAY ISSN: 0570-0833. Journal written in English. CAN 126:238461 AN 1997:141905 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A mechanistic study of C-H activation in pentane, cyclohexane and benzene by [CpIr(PMe3)Me]+ by electrospray tandem mass spectrometry yields the unexpected result that neither the oxidative addn.-elimination nor the concerted ?-bond metathesis mechanism is operative. An elimination-addn. mechanism through IrIII intermediates is obsd. and confirmed by isotopic labeling. [CpIr(?2-Me2PCH2)]+ is formed from [CpIr(PMe3)Me]+ and is more reactive than the latter, presumably because of the combination of better steric access to the metal center and relief of strain.

Answer 70:

Bibliographic Information

Recent developments in the surface and catalytic chemistry of supported organoactinides. Luo, Xiao-Liang. Los Alamos National Laboratory, USA. Chemtracts: Organic Chemistry (1996), 9(6), 340-342. Publisher: Data Trace Chemistry Publishers, CODEN: CMOCEI ISSN: 0895-4445. Journal; Miscellaneous written in English. AN 1997:15762 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The purpose of this review is to highlight some recent developments at Northwestern University in the catalytic chem. of organoactinide complexes supported on dehydroxylated ?-alumina (DA). The organothorium catalyst precursors are adsorbed from pentane solns. onto DA under rigorously anhyd. and anaerobic conditions. The adsorption process involves transfer of hydrocarbyl anions from the organothorium complexes to Lewis acidic Al3+ sites on the surface of DA, resulting in cation-like, coordinatively unsatd. surface species that are extremely active catalysts for a no. of highly demanding catalytic transformations such as arene hydrogenation, hydrogenation fo sterically hindered olefins, and alkane activation. The relative activities for benzene hydrogenation at 90?C and under 190 psi of H2 follows the order (?5-c5Me5)Th(CH2Ph)3/DA < Th(CH2(3,5-Me2)c6H3)4/DA < Th(?3-allyl)4 /DA, with a turnover frequency of .apprx.25,000 h-1 per active site obtained with Th(?3-allyl)4.DA. The relative rates of Th(?3-allyl)4/DA-catalyzed hydrogenation of various substituted arenes follow the order benzene > toluene >> p-xylene >> naphthalene. Th(?3-allyl)4/DA also catalyzes C-H/D2 exchange for a variety of linear and cyclic alkanes (Th:substrate ? 1:1,000) at 90?C and under 50 psi of D2 (D2:substrate ? 100:1), with a turnover frequency of .apprx.1,300 h-1 per active site obtained for cyclohexane substrate. Active site characterizations using D2O poisoning, hydrogenolysis, and CH3Cl dosing indicate that ?8 ? 1% of the surface Th sites are of catalytic significance. The ESR and x-ray photoelectron spectroscopic studies provide no evidence for surface Th oxidn. states lower than +4. The proposed mechanisms for the aforementioned process invoke electrophilic four-center heterolytic ?-bond activation processes at single Th(IV) sits. The coupled two-electron oxidative addn./reductive elimination sequence, which is ubiquitous in organometallic chem.

and homogeneous catalysis utilizing middle-late transition metals, is considered to be energetically unfeasible. A plausible mechanistic scenario for the Th(?3-allyl)4/DA-catalyzed arene hydrogenation is summarized in Figure 1. Steps 1 and 2 resemble the well-known processes of olefin insertion into Th-H bonds. The resulting coordinatively unsatd. insertion product is stabilized by polyhapto pentadienyl ligation. The hydrogenation step (step 3) yields a butadiene complex that undergoes rapid insertion (step 4) to give an ?3-allyl complex. Subsequent hydrogenolysis of the ?3-allyl complex (steps 5-7) yields the cycloalkane and regenerates the thorium hydride species. A possible mechanistic sequence for the Th(?3-allyl)4/DA-catalyzed C-H activation and isomerization of alkanes is shown in Figure 2. The alkane C-H/D2 exchange process involves Th-C bond formation and HD elimination (step E) via a four-center heterolytic ?-bond metathesis pathway followed by deuterolysis (step F). The cycloalkane skeletal isomerization occurs via a ?-hydride elimination (step G) and readdn. of the Th-H to the opposite face of the olefin.

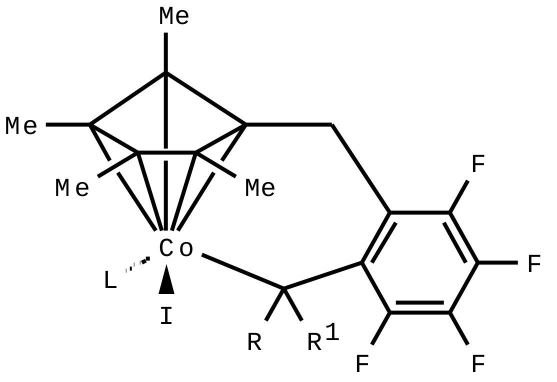
Answer 71:

Bibliographic Information

Perfluorobenzyl Complexes of Cobalt and Rhodium. Unusual Coupling between Pentafluorophenyl and Pentamethylcyclopentadienyl Rings. Hughes, Russell P.; Lindner, Danielle C.; Rheingold, Arnold L.; Yap, Glenn P. A. Burke Chemistry Laboratory, Dartmouth College, Hannover, NH, USA. Organometallics (1996), 15(26), 5678-5686. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 126:47350 AN 1996:721749 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Oxidative addn. of perfluorobenzyl iodide to [M(?5-C5R5)(CO)2] (M = Co, Rh; R = H, Me) in benzene affords the perfluorobenzyl complexes [M(?5-C5R5)(CF2C6F5)I(CO)] (M = Co, R = H (1a), Me (2a); M = Rh, R = Me (2b)). Further reaction of 1a or 2a with PMe3 in benzene results in a substitution reaction to give complexes [Co(?5-C5R5)(CF2C6F5)I(PMe3)] (R = H (3a), Me (4a)). While the reaction of (pentamethylcyclopentadienyl)cobalt complex 2a with PMe3 in benzene gives 4a, the analogous reaction in THF results in alkyl C-H activation and aryl C-F activation, with coupling of the pentamethylcyclopentadienyl ligand and the perfluorobenzyl ligand, to give cobalt complex I (R, R1 = F, L = PMe3). Similarly, the reaction of 2a with PMe2Ph in THF affords the analogous ring-coupled complex I (R, R1 = F, L = PMe2Ph), while reaction of the cyclopentadienyl analog 1a with PMe2Ph affords the simple substitution product 5a. In contrast to the reactions of the (pentamethylcyclopentadienyl)cobalt complexes, reaction of the rhodium analog 2b with PMe3 or PMe2Ph result in a simple substitution to give [Rh(?5-C5Me5)(CF2C6F5)I(L)] (L = PMe3 (5a) PMe2Ph (5b)). Attempts to purify complexes I result in facile hydrolysis of the CF2 group to give acyl complexes I (RR1 = O, L = same). A mechanism is proposed for this coupling reaction, and an analog of a proposed cationic intermediate has been isolated and shown to react with iodide to afford I (RR1 = O), via I (R, R1 = F). Heating of 2a results in a different coupling reaction to afford the org. cyclopentadiene. The solid state structures of 3a, 5b, and I (RR1 = O, L = PMe2Ph) were detd. by x-ray crystallog.



I

Answer 72:

Bibliographic Information

Mechanistic and synthetic aspects of a novel route to poly-p-xylylene (PPX) via nickel complex catalyzed electropolymerization of 1,4-bis(chloromethyl)benzene. Amatore, Christian; Gaubert, Florence; Jutand, Anny; Utley, James H. P. Departement de Chimie, Ecole Normale Superieure, Paris, Fr. Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry (1996), (11), 2447-2452. Publisher: Royal Society of Chemistry, CODEN: JCPKBH ISSN: 0300-9580. Journal written in English. CAN 126:8747 AN 1996:719090 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The electrochem. polymn. of 1,4-bis(chloromethyl)benzene to poly-p-xylylene (PPX) in the presence of catalytic amts. of NiCl2L (L = dppe or dppp) is reported. Cyclic voltammetric examn. of this reaction, and the analogous conversion of benzyl chloride to bibenzyl, is combined with the construction of reactant/product vs. charge profiles to develop a detailed mechanistic description. There is compelling evidence that, in contrast with the established cathodic formation of PPX from 1,4-bis(halomethyl)benzene via electrogenerated quinodimethane, the Ni complex catalyzed route involves oxidative addn. of the halide deriv. to NiL2.

Answer 73:

Bibliographic Information

Control of Ligand Substitution and Addition Reactions of (Arene)Cr(CO)3 Complexes by Attachment of a Self-Closing Redox Switch. Yeung, Lee K.; Kim, Jung Eun; Chung, Young K.; Rieger, P. H.; Sweigart, D. A. Departments of Chemistry, Brown University, Providence, DE, USA. Organometallics (1996), 15(18), 3891-3897. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 125:222059 AN 1996:488878 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The ferrocenyl group attached to the benzene ring in (C6H5Fc)Cr(CO)3 (3) functions as a reversible redox switch by providing a mechanism for the Cr center to be oxidatively activated to ligand substitution and addn. reactions. Because initial oxidn. of 3 occurs at the ferrocenyl group, the potentials required for activation are far lower than would otherwise be the case, and this allows for controlled reactions without the unproductive decompn. that often accompanies oxidn. of (arene)Cr(CO)3 complexes. Although the Cr in 3+ is predominantly an 18-electron center, it is sufficiently activated to undergo very rapid CO substitution by P(OEt)3 to afford (C6H5Fc)Cr(CO)2P(OEt)3+ (4+). Internal electron transfer from Cr to Fe accompanies this CO substitution, with the result that the

ferrocenium group in 3+ reverts to ferrocenyl in 4+, thus closing the redox switch. Upon oxidn. of 4+ to 42+, the switch reopens and the Cr center is again activated, this time being attacked by P(OEt)3 to give the purple addn. complex, (C6H5Fc)Cr(CO)2[P(OEt)3]22+ (52+), which is readily isolated. The formation of 52+ from 42+ is also accompanied by internal electron transfer from Cr to Fe and automatic switch closing to afford a product with 18-electron centers. The degree of activation of 3 upon oxidn. of the ferrocenyl switch is directly related to the difference in oxidn. potentials of the Cr and Fe centers. Probably the attachment of a remote redox switch may be a useful general methodol. for the quant. control of the reactivity of a metal center.

Answer 74:

Bibliographic Information

Control of ligand substitution and addition reactions of (Arene)Cr(CO)3by attachment of a self-closing redox switch.
Yeung, L. K.; Kim, J. E.; Chung, Y. K.; Sweigart, D. A. Departments Chemistry, Brown University, Providence, RI, USA. Book of Abstracts, 212th ACS National Meeting, Orlando, FL, August 25-29 (1996), INOR-063. Publisher: American Chemical Society, Washington, D. C CODEN: 63BFAF Conference; Meeting Abstract written in English. AN 1996:414220 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The ferrocenyl group attached to the benzene ring in (C6H5Fc)Cr(CO)3 (1) functions as a reversible redox switch by providing a mechanism for the chromium center to be oxidatively activated to ligand substitution and addn. reactions. Oxidn. of 1 occurs at the ferrocenyl group rather than at the chromium center, and this allows for controlled reactions rather than unproductive decompn. that usually accompanies oxidn. of (arene)Cr(CO)3 complexes. Although the chromium in 1+ is an 18-electron center, rapid CO substitution by P(OEt)3 occurs to afford (C6H5Fc)Cr(CO)2P(OEt)3+ (2+). Internal electron transfer from Cr to Fe accompanies this CO substitution, with the result that the ferrocenium group in 1+ reverts to ferrocenyl in 2+, thus closing the redox switch. Upon oxidn. of 2+ to 22+, the switch reopens and the chromium center is again activated, this time being attacked by P(OEt)3 to give the purple addn. complex, (C6H5Fc)Cr(CO)2[P(OEt)3]22+ (32+), which is readily isolated. The formation of 32+ from 22+ is also accompanied by internal electron transfer from Cr to Fe and automatic switch closing to afford a product with 18-electron centers.

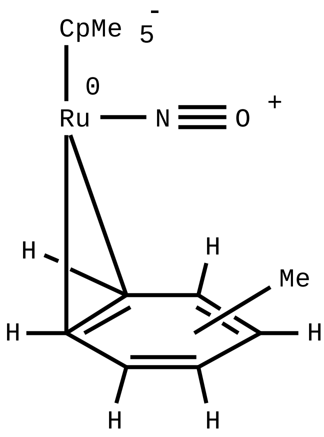
Answer 75:

Bibliographic Information

Synthesis, x-ray Structure Determination, and Reactions of (Pentamethylcyclopentadienyl)(nitrosyl)ruthenium ?2-Arene Complexes. Tagge, Christopher D.; Bergman, Robert G. Department of Chemistry, University of California, Berkeley, CA, USA. Journal of the American Chemical Society (1996), 118(29), 6908-6915. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 125:222087 AN 1996:394097 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The thermally induced reductive elimination of biphenyl from Cp*Ru(NO)Ph2 (1) was restudied. Careful monitoring of the reaction in arom. solvents by 1H NMR spectroscopy revealed intermediate Cp*Ru(NO)(?2-arene) complexes (4a, arene = benzene; 4b, arene = toluene). 4 Were independently prepd. from Cp*Ru(NO)(Me)(OTf) (5) and LiHBEt3 in benzene with loss of CH4 and LiOTf. At 25? added naphthalene displaced the bound arene to generate Cp*Ru(NO)(?2-naphthalene) (6). The crystal structure of 6 was detd.; it crystallizes in triclinic space group P.hivin.1, with a 8.6333(16), b 9.8642(10), c 11.2055(13) .ANG., ? 80.551(13)?, and Z = 2. The ligand substitution and oxidative addn. reactions of 6 with several org. substrates were studied. A kinetic study showed that the reactions of 6 with phosphines, triphenylsilane, and di-Me disulfide require initial naphthalene dissocn. The oxidative addn. of diaryl disulfides also occurs, but the mechanism is much more complicated. Probably the reaction of 6 with diaryl disulfide (aryl = Ph, p-tolyl) is catalyzed by a small concn. of a secondary product. The crystal and mol. structures of Cp*Ru(NO)(SCMe3)2 also were detd. by x-ray crystallog.



I

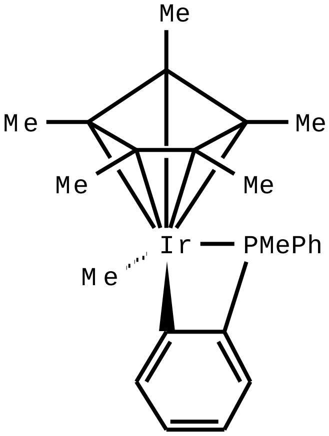
Answer 76:

Bibliographic Information

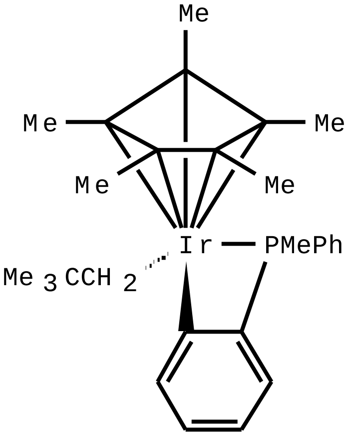
Electron-transfer catalysis in the activation of arene C-H bonds by iridium complexes and the importance of steric factors in determining the nature of the activation products. Diversi, Pietro; Ferrarini, Andrea; Ingrosso, Giovanni; Lucherini, Antonio; Uccello-Barretta, Gloria; Pinzino, Calogero; De Biani Fabrizi, Fabrizia; Laschi, Franco; Zanello, Piero. Dipartimento Chimica, Chimica Industriale, Universita Pisa, Pisa, Italy. Gazzetta Chimica Italiana (1996), 126(6), 391-399. Publisher: Societa Chimica Italiana, CODEN: GCITA9 ISSN: 0016-5603. Journal written in English. CAN 125:114822 AN 1996:339953 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The outcome of the activation reactions of arene C-H bonds with the complexes [IrMe2Cp*L] (Cp*=?5-C5Me5; L=PPh3, 1a; PMePh2, 1b; PMe2Ph, 1c; PMe3, 1d) in the presence of catalytic amts. of [FeCp2]+ is strongly dependent on the nature of the phosphine. While 1a gives a mixt. of intra- and inter-mol. reaction products, 1b and 1c give only the corresponding Me Ph derivs. [IrMePhCp*L] 3b and 3c. The intramol. reaction product I is obtained by treatment of 1b with [FeCp2]+ in the absence of benzene, as a 1:1 mixt. of the two diastereomers, whose configurations, together with that of the related (RR:SS)-II obtained by a different route, have been established by 1H NMR techniques. I, if reacted with benzene in the presence of the ferrocenium cation, produced quant. the Me Ph deriv. 3b. The oxidatively induced activation of benzene-d6 proceeds with different rates depending on the phosphine: krel=1 (1a), 2 (1b) 2.5 (1c), 7.5 (1d). 1D is able to activate C-H bonds of biphenyl and naphthalene. Electrochem. techniques and ESR spectroscopy have been used for a mechanistic investigation of these reactions.



I



II

Answer 77:

Bibliographic Information

Photochemistry of Dihydrido(hydrotris(3,5-dimethylpyrazolyl)borato)(Z-cyclooctene)iridium. Synthetic Intermediates and Mechanism of the Photochemical Formation of Hydridophenyl(hydrotris(3,5-dimethylpyrazolyl)borato)(trimethyl phosphite)iridium. Ferrari, Arlen; Polo, Eleonora; Ruegger, Heinz; Sostero, Silvana; Venanzi, Luigi M. Dipartimento di Chimica, Universita di Ferrara, Ferrara, Italy. Inorganic Chemistry (1996), 35(6), 1602-8. Publisher: American Chemical Society, CODEN: INOCAJ ISSN: 0020-1669. Journal written in English. CAN 124:189092 AN 1996:121386 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The photolysis of a benzene soln. of [TpMe2IrH2(COE)], 1, (TpMe2 = hydrotris(3,5-dimethylpyrazolyl)borate, COE = Z-cyclooctene), in the presence of P(OMe)3, gives the stable novel complex [TpMe2IrH(C6H5)(P(OMe)3)], 3a. The photochem. prepn. of [TpMe2IrH2(P(OMe)3)], from 1 and P(OMe)3 in di-Et ether and that of [TpMe2IrH2(CH2:CHCOOtBu)], from 1 in tert-Bu acrylate are also reported. The above reactions and several expts. using C6D6 and P(OCD3)3 show that, in all cases, the primary photoproduct is the 16-electron, five-coordinate iridium(III) intermediate {TpMe2IrH2}, 6a, produced by loss of COE from 1. The above expts. also allow the postulation of a mechanistic pathway for the formation of 3a which involves the oxidative addn. of an arom. C-H bond by 6a. Furthermore, the photochem. reaction of 1 in the presence of P(OCD3)3 shows that, under the reaction conditions used, oxidative addn. of C-H bonds of P(OMe)3 and of coordinated TpMe2-ligands, presumably, to the intermediates 6a and {TpMe2IrH(C6H5)}, also occurs. Thus, coordinatively unsatd. iridium(III) species readily activate C-H bonds.

Answer 78:

Bibliographic Information

Synthesis of ?-ketocycloalkanecarboxylic acid esters by regiospecific alkoxy carbonylation of ?,?-ketocycloolefins catalyzed by palladium. Cavinato, G.; Toniolo, L. Department of Inorganic Chemistry, University of Padua, Via F. Marzolo, 4, Padua, Italy. Journal of Molecular Catalysis A: Chemical (1996), 104(3), 221-7. Publisher: Elsevier, CODEN: JMCCF2 ISSN: 1381-1169. Journal written in English. CAN 124:231877 AN 1996:30339 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

PdCl2(PPh3)2, in combination with HCl, is highly active in the alkoxycarbonylation of ?,?-ketocycloolefins to 3-oxocycloalkanecarboxylic acid esters. The reaction is regiospecific. The catalytic system is stabilized by addn. of PPh3, which depresses the activity but prevents decompn. to inactive palladium metal. Typical reaction conditions were: Pd/P/cyclohexenone/HCl = 1/2-4/200-600/50-100; [Pd] = 0.1-1?10-2 mol l-1; PCO = 100 atm; temp. 100?C; solvent dioxane, THF, or benzene. With 2-cyclohexen-1-one the effect of the following variables on the yield was examd.: temp., pressure of carbon monoxide, concn. of cyclohexenone, ethanol, catalyst, Pd/P ratio, cyclohexenone/HCl ratio, reaction time, and solvent. As expected the yield increases with increasing reaction time, pressure of carbon monoxide, concn. of catalyst at const. Pd/P ratio, and temp. The yield passes through a max. when increasing the concn. of HCl and EtOH, after which the yield decreases because the catalyst decomps. to palladium metal. The yield is almost insensitive to the polarity of solvents such as dioxane, THF, or benzene, but it rather depends on the bulkiness of the alkanol as the reaction rate decreases in the order: MeOH>EtOH>n-PrOH>n-BuOH>s-PrOH. The proposed reaction mechanism proceeds through the following steps: the starting PdII precursor is reduced to a Pd0 complex which gives oxidative addn. of HCl with formation of a Pd-hydride species; cyclohexenone inserts into a Pd-H bond giving a ?-ketocyclohexyl-Pd intermediate; this inserts CO with formation of the corresponding carbonyl deriv.; alcoholysis of this intermediate yields the final product with regeneration of the hydride. The reaction is regiospecific because of the keto group which directs the anti-Markownikoff addn. of Pd-H to the conjugated C:C double bond.

Answer 79:

Bibliographic Information

Substituent Effects on Reductive Elimination from Disubstituted Aryl Hydride Complexes: Mechanistic and Thermodynamic Considerations. Selmeczy, Anthony D.; Jones, William D.; Osman, Robert; Perutz, Robin. Departments of Chemistry, University of Rochester, Rochester, NY, USA. Organometallics (1995), 14(12), 5677-85. Publisher: American Chemical Society, CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 124:56270 AN 1995:931651 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

(C5Me5)Rh(PMe3)(3,5-C6H3R2)H for R = CMe3, CHMe2, SiMe3, Me, and CF3 (1c-g) were prepd. both by irradn. of (C5Me5)Rh(PMe3)(C2H4) in neat arene and by thermolysis of (C5Me5)Rh(PMe3)(Ph)H (1a) in neat arene. Quenching the hydride species with CHBr3 gave the corresponding bromide complexes (C5Me5)Rh(PMe3)(3,5-C6H3R2)Br (2c-g). Rates of reductive elimination of arene for disubstituted aryl hydride complexes were measured at various temps. and activation parameters ?H.thermod. and ?S.thermod. obtained and compared with those of 1a and (C5Me5)Rh(PMe3)(tolyl)H (1b). ?H.thermod. values range from +35 to +18 kcal/mol, and ?S.thermod. values range from +16.4 to -19 cal/mol K. Laser flash photolysis expts. using (C5Me5)Rh(PMe3)(C2H4) in neat toluene at various temps. allowed the detn. of activation parameters ?H.thermod. and ?S.thermod. for intramol. C-H bond oxidative addn. of the ?2-arene complex (C5Me5)Rh(PMe3)(tolyl) 3b. Equil. measurements allowed detn. of ?G? values for several of the disubstituted aryl hydride complexes vs. the parent Ph hydride complex. A kinetic isotope effect of kH/kD = 1.0 ? 0.1 was measured for the reaction of (C5Me5)Rh(PMe3)(C2H4) with a 1:1 mixt. of 5-deuterio-1,3-di-tert-butylbenzene and 1,3-di-tert-butylbenzene. The equil. isotope effect for the same reaction Keq = 2.27(1) favors the aryl hydride and free deuterated arene.

Answer 80:

Bibliographic Information

Oxidative Addition of Aryl Bromide after Dissociation of Phosphine from a Two-Coordinate Palladium(0) Complex, Bis(tri-o-tolylphosphine)Palladium(0). Hartwig, John F.; Paul, Frederic. Department of Chemistry, Yale University, New Haven, CT, USA. Journal of the American Chemical Society (1995), 117(19), 5373-4. Publisher: American Chemical Society, CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 123:56252 AN 1995:553852 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The 14-electron Pd(0) complex [(o-tol)3P]2Pd (1) undergoes oxidative addn. reactions with aryl bromides that occur by a dissociative mechanism. The products of aryl bromide addn. are dimeric with only one phosphine bound to each palladium. In contrast to typical oxidative addns. to Pt(0), Pd(0), and Ni(0) phosphine compds. that occur to intermediates with two or three phosphine ligands, the addn. to 1 occurs after phosphine dissocn. and generation of a monophosphine intermediate. Clean first order kinetics were obsd. when monitoring the disappearance of 1. Inverse first order rate behavior in phosphine demonstrated that the reaction is dissociative. Reaction rates in benzene, toluene, and xylene were essentially identical, suggesting that solvent coordination does not stabilize the unsatd. intermediate. Rather, displacement of a phosphine by coordinated aryl bromide before irreversible oxidative addn., or coordination of a ligand C-H bond appears to stabilize the monophosphine complex. This mechanism is unusual, but falls in accord with those for the opposite reaction, reductive elimination from Pd(II). Many of these elimination reactions occur after phosphine dissocn. and, therefore, lead to initial products that contain only one phosphine ligand. This initial product from reductive elimination is analogous to the intermediate generated from 1 that undergoes oxidative addn.

Answer 81:

Bibliographic Information

Ligand Electronic Effects in Asymmetric Catalysis: Enhanced Enantioselectivity in the Asymmetric Hydrocyanation of Vinylarenes. Casalnuovo, Albert L.; RajanBabu, T. V.; Ayers, Timothy A.; Warren, Timothy H. E328 Experimental Station, Central Research and Development, E. I. Du Pont de Nemours and Co., Wilmington, DE, USA. Journal of the American Chemical Society (1994), 116(22), 9869-82. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 122:9236 AN 1995:130606 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The enantioselectivity of the nickel-catalyzed, asym. hydrocyanation of vinylarenes using glucose-derived, chiral phosphinite ligands, L, increases dramatically when the ligands contain electron-withdrawing P-aryl substituents. The substrate and solvent also strongly influence the enantioselectivity, with the highest ee's [85-91% for 6-methoxy-2-vinylnaphthalene (MVN)] obtained for the hydrocyanation of electron-rich vinylarenes in a nonpolar solvent such as hexane. Mechanistic studies suggest the catalytic cycle consists of an initial HCN oxidative addn. or vinylarene coordination to NiL, followed by insertion to form an (?3-benzyl)nickel cyanide complex, and irreversible reductive elimination of the nitrile. A kinetic anal. of the NiLa(COD) [La, P-aryl = 3,5-(CF3)2C6H3] catalyzed hydrocyanation of MVN indicates that as the HCN concn. is increased the catalyst resting state shifts from NiLa(COD) to a complex contg. both MVN and HCN, presumably the (?3-benzyl)nickel cyanide intermediate NiLa(?3-CH3CHC10H6OCH3)CN. A 31P NMR anal. of the intermediate NiLa(MVN) shows little ground state differentiation of the MVN enantiofaces and suggests that the enantioselectivity is detd. later in the mechanism. Deuterium labeling studies suggest that electron-withdrawing P-aryl substituents increase the rate of reductive elimination of the product nitrile from the (?3-benzyl)nickel cyanide intermediate and, on this basis, a rationale for the ligand electronic effect is proposed.

Answer 82:

Bibliographic Information

Study of the Mechanism of Photochemical Carbonylation of Benzene Catalyzed by Rh(PMe3)2(CO)Cl. Rosini, Glen P.; Boese, William T.; Goldman, Alan S. Department of Chemistry, Rutgers The State University, Piscataway, NJ, USA. Journal of the American Chemical Society (1994), 116(21), 9498-505. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 122:9408 AN 1995:43382 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Although near-UV irradn. of Rh(PMe3)2(CO)Cl (1) has been shown to lead to efficient carbon-hydrogen bond activation, the title reaction is promoted with much greater efficiency by shorter wavelength (? < ca. 320 nm) irradn.: for example, the carbonylation quantum yield at 314 nm is found to be 1.5 ? 10-3 vs 2.0 ? 10-5 at 366 nm. A comprehensive mechanistic study reveals that the shorter wavelength irradn. is required for two sep. steps in the catalytic cycle. Photoextrusion of CO, which occurs upon near-UV irradn. and leads to efficient C-H bond activation, is not a major step toward carbonylation under the reaction conditions of the present study nor, apparently, is any other dissociative photoreaction. It is proposed that the first reaction step is the oxidative addn. of a benzene C-H bond to an intact photoexcited state of 1. Independently, Field and co-workers have generated and characterized the resulting six-coordinate Ph hydrido complexes, Rh(PMe3)2(Ph)(CO)HCl (2) under low-temp. conditions. Kinetic studies of the catalytic reaction indicate the involvement of a photoactive intermediate, the decay rate of which is in good agreement with the activation parameters detd. by Field et al. for the low-temp. decay of the Ph hydrido complexes, 2. Short wavelength light is required for the efficient photoreaction of 2, possibly because longer wavelength light is not significantly absorbed, particularly in competition with 1. The carbonylation efficiency increases with CO pressure; this is attributable to the reaction of CO with the unsatd. benzoyl complex, Rh(PMe3)2(COPh)HCl, which results from CO insertion into the Rh-Ph bond of 2. Reversible loss of benzoyl chloride from the CO addn. product, Rh(PMe3)2(COPh)(CO)HCl, is shown to lead to the formation of C6H5CDO and C6D5CHO when the reaction is conducted in C6H6/C6D6 mixts.

Answer 83:

Bibliographic Information

Further evidence for multiple pathways in soluble methane-monooxygenase-catalyzed oxidations from the measurement of deuterium kinetic isotope effects. Wilkins, Patricia C.; Dalton, Howard; Samuel, Christopher J.; Green, Jeffrey. Dep. Biological Sciences, University of Warwick, Coventry, UK. European Journal of Biochemistry (1994), 226(2), 555-60. Publisher: Springer, CODEN: EJBCAI ISSN: 0014-2956. Journal written in English. CAN 121:295845 AN 1994:695845 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The data from the deuterium isotope expts. in this study show that the primary kinetic isotope effect for methane oxidn. catalyzed by sol. methane monooxygenase from Methylococcus capsulatus (Bath) is very small, <2. In contrast, the primary kinetic isotope effect for -CH3 group oxidn. in toluene is large, >7. A mechanistic pathway in which a substrate radical is formed from hydrogen atom abstraction by a ferryl species is believed to operate for CH4, the toluene -CH3 group and similar alkanes. Direct oxygen atom addn., rather than H atom abstraction, is indicated for arom. ring oxidns. in benzene and toluene and for styrene oxide formation from styrene. Thus, more than one mechanistic pathway appears to operate in sol. methane-monooxygenase-catalyzed reactions and, in some cases, the pathway chosen may be dictated by the substrate. In the sol. methane-monooxygenase-catalyzed oxidn. of toluene the rates of: (a) substrate dissocn. from the enzyme-substrate complex, (b) product formation and (c) product release (benzyl alc. and p-cresol) from the enzyme-product complex are comparable in magnitude. Therefore all three of these steps are partially rate-detg. in the sol. methane monooxygenase catalytic cycle for toluene oxidn.

Answer 84:

Bibliographic Information

Synthesis, Structure, and C-H Bond Activation Chemistry of (?6-arene)Ru(H)2(SiMe3)2 Complexes. Djurovich, Peter I.; Carroll, Patrick J.; Berry, Donald H. Department of Chemistry, University of Pennsylvania, Philadelphia, PA, USA. Organometallics (1994), 13(7), 2551-3. CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 121:109212 AN 1994:509212 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The (?6-arene)Ru(H)2(SiMe3)2 (arene = C6Me6 (1a), p-cymene (1b), C6H6 (1c)) complexes have been prepd. and characterized. The complexes activate both arom. and aliph. C-H bonds and catalyze H/D exchange in alkylsilanes upon thermolysis in benzene-d6. A mechanism based on oxidative-addn./reductive-elimination steps which utilizes a Ru(II)-Ru(IV) cycle is proposed to account for the C-H bond activation and H/D exchange reactions. It is further proposed that H/D exchange into sites adjacent to silicon in alkylsilanes is due to the intermediacy of an?2-silene complex generated by ?-hydrogen elimination from the silyl group.

Answer 85:

Bibliographic Information

Kinetics of hydroformylation of 1-decene using homogeneous HRh(CO)(PPh3)3 catalyst: a molecular level approach.
Divekar, S.S.; Deshpande, R.M.; Chaudhari, R.V. Chem. Eng. Div., Nat. Chem. Lab., Pune, India. Catalysis Letters (1993), 21(1-2), 191-200. CODEN: CALEER ISSN: 1011-372X. Journal written in English. CAN 120:297807 AN 1994:297807 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The kinetics of hydroformylation of 1-decene using homogeneous HRh(CO)(PPh3)3 catalyst has been reported in the temp. range of 50-70?C. The effect of catalyst, PH2, PCO, and 1-decene concn. on the rate of hydroformylation has been studied. Based on the anal. of initial rate data, a rate equation has been proposed and kinetic parameters evaluated. The activation energy was found to be 11.76 kcal/mol. A mol. level approach to kinetic modeling has also been illustrated. The rate equation derived assuming oxidative addn. of H2 as a rate detg. step, has been found to represent the data satisfactorily. The rate parameters for the mechanistic model have been evaluated for the data at 60?C.

Answer 86:

Bibliographic Information

Supported organoactinide complexes as heterogeneous catalysts. A kinetic and mechanistic study of facile arene hydrogenation. Eisen, Moris S.; Marks, Tobin J. Dep. Chem., Northwestern Univ., Evanston, IL, USA. Journal of the American Chemical Society (1992), 114(26), 10358-68. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 117:250833 AN 1992:650833 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

This contribution reports a kinetic and mechanistic study of arene hydrogenation by the supported organoactinide complexes Cp'Th(benzyl)3/DA (1/DA), Th(1,3,5-CH2C6H3Me2)4/DA (2/DA), and Th(?3-allyl)4/DA (3/DA) where Cp' = ?5-Me5C5, 1,3,5-CH2C6H3Me2 = mesityl, and DA = dehydroxylated ?-alumina. In slurry reactions (90?, PH2 = 180 psi), the activity for benzene hydrogenation follows the order 1/DA < 2/DA < 3/DA with an Nt value for 3/DA of .apprx.25000 h-1 active site-1. This approaches or exceeds most conventional platinum metal catalysts in efficacy for benzene redn. Benzene hydrogenation by 3/DA at 90?, PH2 = 180 psi, follows the rate law Nt = ?[benzene]0[PH2]1 with Nt(H2)/Nt(D2) = 3.5 ? 0.3 and Ea = 16.7 ? 0.3 kcal mol-1. Partially hydrogenated products cannot be detected at partial conversions, and there is no D2 incorporated in the unconverted benzene. D2 is not delivered to a single benzene face, but rather a 1:3 mixt. of all-cis and cis,cis,trans,cis,trans isotopomers is formed. Active site characterizations using D2O poisoning, hydrogenolysis, and CH3Cl dosing indicate that ?8 ? 1% of the Th surface sites are responsible for the bulk of the benzene hydrogenation. EPR and XPS studies provide no evidence for surface Th oxidn. states less than +4. As a function of arene, the relative rates of Th(?3-C3H5)4/DA-catalyzed hydrogenation are benzene > toluene > p-xylene > naphthalene, with the regiochem. of p-xylene redn. similar to that for benzene. Expts. with 1:1 benzene-p-xylene mixts. reveal that benzene is preferentially hydrogenated with almost complete exclusion of p-xylene (.apprx.97:3), inferring that the benzene binding const. to the active sites is .apprx.6.7 times that of p-xylene. It is possible to propose a mechanism for arene hydrogenation which involves single Th(IV) sites, includes inoperativity of oxidative addn./reductive elimination sequences, and passes among established metal-ligand structures via precedented pathways.

Answer 87:

Bibliographic Information

Reductive dechlorination of aryl chlorides catalyzed by palladium complexes containing basic, chelating phosphines. Ben-David, Yehoshua; Gozin, Michael; Portnoy, Moshe; Milstein, David. Dep. Org. Chem., Weizmann Inst. Sci., Rehovot, Israel. Journal of Molecular Catalysis (1992), 73(2), 173-80. CODEN: JMCADS ISSN: 0304-5102. Journal written in English. CAN 117:150615 AN 1992:550615 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Aryl chlorides undergo efficient, homogeneously catalyzed reductive dechlorination to the corresponding arenes using Pd(dippp)2 as catalyst [dippp = 1,3-bis(diisopropylphosphino)propane], which may be generated in situ from Pd(OAc)2 and two equiv. of dippp. Two reducing systems are described: (a) NaOH in MeOH;(b) sodium formate in alc. or DMF. Base-sensitive functional groups (CHO, CN) do not survive the conditions of system (a), but remain unaffected during dechlorination with sodium formate. Various functional groups are tolerated, and high yields are obtained. The reaction rate is retarded by electron-donating substituents, indicating a rate-detg. oxidative addn. step. Reaction of the model complex (dippp)Pd(Ph)Cl with sodium formate in the presence of dippp leads to the formation of Pd(dippp)2 and benzene. Dippp homologs are also effective ligands in the catalytic reaction, the reactivity order being dippp > dippb > dippe. Triisopopylphosphine is only marginally effective. A mechanistic interpretation of these observations is given.

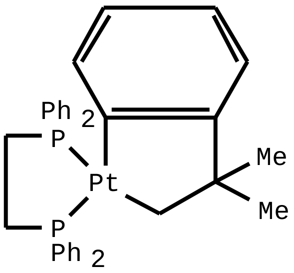
Answer 88:

Bibliographic Information

Mechanistic studies of the thermolytic and photolytic rearrangement of [bis(diphenylphosphino)ethane]bis(neophyl)platinum(II). Ankianiec, Bernardeta C.; Hardy, David T.; Thomson, S. Katherine; Watkins, W. Niall; Young, G. Brent. Inorg. Chem. Lab., Imp. Coll. Sci. Technol. Med., London, UK. Organometallics (1992), 11(7), 2591-8. CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 117:48853 AN 1992:448853 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Comparative mechanistic studies are presented of the thermolytic and photolytic behavior of the bis(neophyl)platinum(II) deriv. Pt(CH2CMe2Ph)2(dppe) [neophyl = 2-methyl-2-phenylpropyl; dppe = 1,2-bis(diphenylphosphino)ethane]. Thermolytic rearrangement is less facile than for monodentate P-donor analogs and affords the platinaindan I by intramol. arom. C-H activation and H-transfer to eliminated tert-butylbenzene. The kinetic isotope effect on metallacyclization (kobsH/kobsD = 2.40) and the neg. activation entropy (?S.thermod.obs = -13 (?4) J?K-1?mol-1) suggest a pathway in which scission of one Pt-P is mechanistically significant but C-H addn. to Pt has the most energetic transition state. Photolytic rearrangement in toluene-d8 proceeds by two major paths, both of which involve primary Pt-C homolysis. The resultant neophyl radical may then provide a destination for migrating hydrogen in a cyclometalation of the residual 17-electron organoplatinum species, leading to I. Alternatively, H-abstraction by the neophyl fragment within the solvent cage produces a benzyl radical, which recombines with the metal moiety to give Pt(CH2Ph)(CH2CMe2Ph)(dppe). This benzylplatinum complex is also photolabile, giving ultimately platinaindan via benzyl radical expulsion. This indirect solvent metalation is not evident during photolysis in toluene-d8 and in benzene.



I

Answer 89:

Bibliographic Information

Electron transfer reactions in organic chemistry. XX. Fate of tris(4-bromophenyl)ammoniumyl hexachloroantimonate during catalysis of the Diels-Alder dimerization of 1,3-cyclohexadiene. Eberson, Lennart; Olofsson, Berit. Chem. Cent., Univ. Lund, Lund, Swed. Acta Chemica Scandinavica (1991), 45(3), 316-26. CODEN: ACHSE7 ISSN: 0904-213X. Journal written in English. CAN 115:7863 AN 1991:407863 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The Diels-Alder (DA) dimerization of 1,3-cyclohexadiene (CHD) by the radical cation salt, tris(4-bromophenyl)ammoniumyl hexachloroantimonate (TBPA+.bul. SbCl6-), has been studied by kinetic methods and product identification. The main goal was to elucidate the pathways by which TBPA+.bul. is consumed. These can be summarized as follows. In the absence of any added base, DA dimers are formed in high yield and the radical cation is consumed in an essentially quant. oxidative addn. reaction between CHD+.bul. and a chloride ion source, most likely hexachloroantimonate ion. In the presence of a hindered pyrimidine base, DA dimerization is almost blocked and CHD+.bul. is deprotonated by the base ultimately to give benzene (up to 40% yield) and oligomers of CHD. Thus in both cases the role of TBPA+.bul. is to abstr. an electron from CHD, the radical cation of which is presumably the product-forming species. The mechanism is complex, but it could be shown that DA dimerization is second-order in [CHD] under the hypothetical conditions that [TBPA+.bul.]/[TBPA] is const. It is assumed (and supported by Marcus-type calcns.) that the redn. of the dimer radical cation, (CHD)2+.bul., occurs via reaction with TBPA, thus making the mechanism of rather conventional catalytic type. TBPA is formed to an extent of >50% in the very early part of the run. The measured rate const., k(CHD)obs, is then proportional to [TBPA+.bul.]0/[TBPA]? . The disappearance of the radical cation via the oxidative addn. process was second order in [TBPA+.bul.], indicative of the so-called complexation mechanism for radical cation/nucleophile reactions. The authors warn of over-pressure is the thermal dimerization of CHD.

Answer 90:

Bibliographic Information

Inhibition of dimeric dihydrodiol dehydrogenases of rabbit and pig lens by ascorbic acid. Hara, Akira; Shinoda, Michio; Kanazu, Takushi; Nakayama, Toshihiro; Deyashiki, Yoshihiro; Sawada, Hideo. Dep. Biochem., Gifu Pharm. Univ., Gifu, Japan. Biochemical Journal (1991), 275(1), 121-6. CODEN: BIJOAK ISSN: 0306-3275. Journal written in English. CAN 114:224348 AN 1991:224348 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The dehydrogenase activity of dimeric dihydrodiol dehydrogenases (DD) purified from pig and rabbit lenses was inhibited by either

L-ascorbic acid or its epimer, isoascorbic acid, at pH 7.5. Isoascorbate [IC50 (concn. giving 50% inhibition) = 0.043 mM for the pig enzyme; IC50 = 0.13 mM for the rabbit enzyme] was a more potent inhibitor than ascorbate (IC50 values 0.45 and 0.90 mM, resp.), but 1 mM-dehydroascorbate gave less than 30% inhibition. Glucose, glucuronate, gulono-?-lactone, glutathione and dithiothreitol did not inhibit the enzyme activity. The inhibition by isoascorbate and ascorbate was instantaneous and reversible, and their inhibitory potency was decreased by addn. of ascorbate oxidase. In the reverse reaction, isoascorbate and ascorbate gave low IC50 values of 0.013 and 0.10 mM, resp., for the pig enzyme and 0.025 and 0.25 mM for the rabbit enzyme. The inhibition patterns by the two compds. were competitive with respect to dihydrodiols of naphthalene and benzene and uncompetitive with respect to NADI, but those in the reverse reaction were uncompetitive with respect to both carbonyl substrate and NADPH. The steady-state kinetic measurements in the forward and reverse reactions by the pig enzyme were consistent with an ordered Bi Bi mechanism, in which NADP binds to the enzyme first and NADPH leaves last. The results indicate that ascorbate and its epimer directly bind to an enzyme:NADP binary complex as dead-end inhibitors. Thus ascorbate may be an important modulator of DD in the lens.

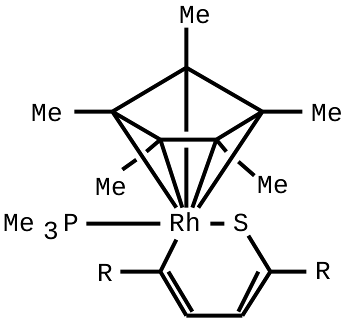
Answer 91:

Bibliographic Information

Insertion of rhodium into the carbon-sulfur bond of thiophene. Mechanism of a model for the hydrodesulfurization reaction. Jones, William D.; Dong, Lingzhen. Dep. Chem., Univ. Rochester, Rochester, NY, USA. Journal of the American Chemical Society (1991), 113(2), 559-64. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 114:43136 AN 1991:43136 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reaction of (C5Me5)Rh(PMe3)(Ph)H with thiophene leads to the elimination of benzene and oxidative addn. of the thiophene C-S bond across the Rh(I) center, giving rhodathiacyclohexadiene I (R = H). Similar reactions occur with 2-methylthiophene, 3-methylthiophene, 2,5-dimethylthiophene, benzothiophene, and dibenzothiophene. Selectivity studies performed with these complexes are consistent with the coordination of S to Rh prior to C-S bond cleavage. Reversible reductive elimination of thiophene occurs at .apprx.80?. The diene portion of the C-S insertion ligand undergoes a Diels-Alder reaction with di-Me acetylenedicarboxylate to give di-Me phthalate as a major product. The dimethylthiophene complex I (R = Me) was structurally characterized by x-ray diffraction.



I

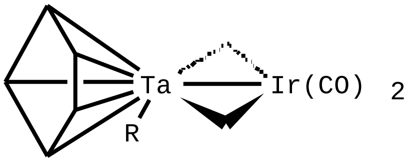
Answer 92:

Bibliographic Information

Synthesis and reactivity of Cp2Ta(CH2)2Ir(CO)2: an early-late heterobimetallic complex that catalytically hydrogenates, isomerizes and hydrosilates alkenes. Hostetler, Michael J.; Bergman, Robert G. Dep. Chem., Univ. California, Berkeley, CA, USA. Journal of the American Chemical Society (1990), 112(23), 8621-3. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 113:231666 AN 1990:631666 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Reaction of (?5-C5H5)2Ta(CH2)Me with dicarbonyl(?5-indenyl)iridium gave the title complex (I, R = ?5-C5H5) in 88% yield. I (R = ?5-indenyl) was similarly prepd. and was subjected to x-ray anal. I (R = ?5-C5H5) catalyzed the hydrogenation of C2H4 and the isomerization of higher olefins in benzene. In THF overall rates were higher, both ethylene and 1-alkenes were hydrogenated, and disubstituted alkenes underwent only isomerization. I (R = ?5-C5H5) was also a hydrosilation catalyst. In this reaction a variety of silanes were used, but in contrast to the hydrogenation process ethylene was the only olefin hydrosilated in either benzene or THF. Kinetic and isotope-labeling studies provided evidence that the mechanism of the hydrogenation reaction involves oxidative addn. of H2 to the Ir center, followed by reductive elimination of a methylene bridge to open a site for alkene coordination. Hydrosilation is also initiated by oxidative addn. at Ir, but in this case the vacant coordination site is generated by dissocn. of a CO ligand.



I

Answer 93:

Bibliographic Information

Facile arene carbon-hydrogen bond activation by tantalum silyl complexes. Berry, Donald H.; Jiang, Qian. Dep. Chem., Univ. Pennsylvania, Philadelphia, PA, USA. Journal of the American Chemical Society (1989), 111(20), 8049-51. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 111:153991 AN 1989:553991 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

In the presence of 0.7 to 2.0 equiv of di(tert-butyl)silane, the 18 e-, Ta(III) alkyl complex Cp2Ta(CH3)(PMe3) (I, Cp = ?-cyclopentadienyl) reacts with benzene solvent under photolytic (350 nm) or thermal (100?) conditions to form methane and Cp2Ta(C6H5)(PMe3) (II) in virtually quant. yield (91% isolated). However, in the absence of H2Si(CMe3)2, I only slowly decomps. in benzene under these reaction conditions (ca. 50% in 24 h) to a complex mixt. of products contg. less than 1% of II. Reactions employing D2Si(CMe3)2 produce CH3D and (D)(H)Si(CMe3)2, consistent with the intermediacy of an unsatd. silyl complex, Cp2TaSi(D)(CMe3)2 which activates benzene, producing the aryl and regenerating the silane. Photolysis of I with neat H2Si(CMe3)2 at 10? forms methane and Cp2Ta(PMe3)(Si(CMe3)2H) (III) in 92% isolated yield. Compd. III activates benzene under extremely mild conditions, forming II and H2Si(CMe3)2 at 25? in the dark. Benzene C-H bond activation by III is inhibited by added PMe3, consistent with a mechanism involving formation of a 16 e- intermediate by ligand dissocn. followed by oxidative addn. of the C-H bond. Benzene C-H activation by Ta complexes of smaller silyl ligands is also obsd.; an equil. mixt. contg. ca 10% of the Ph product II is established from a benzene soln. of Cp2Ta(PMe3)(SiMe3) after several h at 100?. In this instance the silyl complex is thermodynamically favored over II.

Answer 94:

Bibliographic Information

Electrosynthesis of symmetrical ketones from organic halides and carbon dioxide catalyzed by 2,2'-bipyridine-nickel complexes. Garnier, L.; Rollin, Y.; Perichon, J. Catal. Synth. Org., Lab. Electrochim., Thiais, Fr. Journal of Organometallic Chemistry (1989), 367(3), 347-58. CODEN: JORCAI ISSN: 0022-328X. Journal written in English. CAN 111:86026 AN 1989:486026 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The electrochem. redn. of a Ni-2,2'-bipyridine complex, in the presence of CO2 in N-methylpyrrolidone or DMF as solvent gives the corresponding Ni(0) complex assocd. with 2 mols. of CO. The oxidative addn. of an alkyl halide to this complex, followed by an internal CO shift and reductive elimination, leads to the formation of a sym. ketone in high yield along with Ni(II), whereas aryl or vinyl halides mainly give acyl derivs. The Ni(0) species is electrochem. regenerated, thus giving rise to an efficient catalytic process. A possible mechanism of these reactions is discussed.

Answer 95:

Bibliographic Information

Selective hydrogen-deuterium exchange in alkylsilanes catalyzed by osmium phosphine complexes: the first evidence for ?-hydrogen elimination from a metal silyl. Berry, Donald H.; Procopio, Leo J. Dep. Chem., Univ. Pennsylvania, Philadelphia, PA, USA. Journal of the American Chemical Society (1989), 111(11), 4099-100. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 110:231712 AN 1989:231712 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Catalytic H/D exchange is obsd. between alkyl silanes and benzene-d6 in the presence of Os(PMe3)4(SiMe2R)(H) (I; R = Me, Et) at 90?. For example, (CH3)3SiH is converted to (CD3)3SiD with concomitant formation of C6D5H. Deuterium is also incorporated into the coordinated phosphine and silyl ligands. The failure of (CH3)4Si to undergo deuteration under these reaction conditions suggests that an Si-H bond is necessary for alkylsilane C-H exchange. The selective deuteration of (CH3)2(CH2CH3)SiH to form (CD3)2(CD2CH3)SiD indicates that only sites adjacent to silicon are labeled. Consistent with these facts, the following mechanism is proposed: following phosphine dissocn. from I, deuterium is incorporated into the cycle via addn. of C6D6 to the 16 e- intermediate (PMe3)3Os(H)(SiMe3), yielding (PMe3)3Os(H)(D)(SiMe3)(C6D5), which eliminates C6D5H, producing (PMe3)3Os(D)(SiMe3). ?-Hydrogen elimination from the silyl leads to the osmium silene (or silametallacycle) complex (PMe3)3Os(D)(H)(?2-SiMe2CH2). Reverse hydride migration then scrambles hydrogen and deuterium between the osmium hydride and the C-H positions adjacent to silicon. Subsequent silane reductive elimination and oxidative addn. steps exchange free and coordinated silanes.

Answer 96:

Bibliographic Information

Oxidation of malonic acid derivatives by manganese(III) acetate. Aromatic malonylation reaction. Scope and limitations. Citterio, Attilio; Santi, Roberto; Fiorani, Tiziana; Strologo, Sauro. Dip. Chim. Politec., Milan, Italy. Journal of Organic Chemistry (1989), 54(11), 2703-12. CODEN: JOCEAH ISSN: 0022-3263. Journal written in English. CAN 110:230916 AN 1989:230916 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The oxidn. of malonic acid derivs. RCH(COOR1)COOR2 (R1, R2 = H, Me, Et; R = H, Me, Et, Bu, CHMe2, C6H5, 4-MeOC6H4) by anhyd. or dihydrate manganese(III) acetate was studied in acetic acid in the presence of arom. substrates at 20-80?, generally with stoichiometric amts. of reagents. Electron-rich aroms. [ionization potential (IP) > 7.5 eV] underwent nuclear acetoxylation or quinone formation, the process being exclusive with anthracene and competitive with nuclear malonylation for 1- and 2-methoxynaphthalene. With other less electron-rich substrates (IP > 8.5 eV) only the products coming from the oxidn. of the malonic acid derivs. (aryl malonates, tartronates, etc., or dimerization and disproportionation products) were obsd. The selectivity and the yield of arom. substitution by the malonyl group was found to be affected by the electron d. of the arom. ring, the steric inhibition of substituents in the Mn(III) oxidn. of the malonic acid deriv., the oxidizability of malonyl radical by Mn(III), the base (acetate ions or water) eventually present in the medium, and the further easy oxidn. of the primary aryl malonate product, when unsubstituted dialkyl malonates or malonic acid were used. A mechanism is suggested in which inner-sphere electron transfer from Mn(III)-malonate complex affords Mn(II) malonyl radicals that are partitioned between oxidn., dimerization (or disproportionations), and reversible addn. to the aroms.

Answer 97:

Bibliographic Information

Kinetics and mechanism of C-H activation following photoexcitation of (?5-C5H5)Ir(CO)2 in hydrocarbon solutions. Marx, D. E.; Lees, A. J. Univ. Cent., State Univ. New York, Binghamton, NY, USA. Editor(s): Yersin, Hartmut; Vogler, Arnd. Photochem. Photophys. Coord. Compd., [Proc. Int. Symp.], 7th (1987), 239-42. Publisher: Springer, Berlin, Fed. Rep. Ger CODEN: 56HCAC Conference written in English. CAN 110:213051 AN 1989:213051 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Kinetics and UV and transient UV studies, and the nondependence of the quantum yield on CO concn. indicate that the mechanism of oxidative addn. of the title compd. (I) to C6H6 involves the attack of (?5-C5H5)Ir(CO)2* on C6H6 to give (?3-C5H5)Ir(CO)2(C6H6), which then rapidly gives (?5-C5H5)Ir(CO)HPh. The photoreaction of I with PhMe, heptane, pentane, cyclohexane, or isooctane was discussed.

Answer 98:

Bibliographic Information

Synthesis of a highly reactive (benzyne)ruthenium complex. Carbon-carbon, carbon-hydrogen, nitrogen-hydrogen and oxygen-hydrogen activation reactions. Hartwig, John F.; Andersen, Richard A.; Bergman, Robert G. Dep. Chem., Univ. California, Berkeley, CA, USA. Journal of the American Chemical Society (1989), 111(7), 2717-19. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 110:154549 AN 1989:154549 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The new benzyne complex (Me3P)4Ru(?2-C6H4) (I) was the product of thermolysis of either Ru(Ph)2(PMe3)4 or Ru(Ph)(Me)(PMe3)4. Kinetic evidence showed that this thermolysis proceeds by a mechanism which involves initial dissocn. of a phosphine ligand, probably followed by oxidative addn. of a Ph C-H bond to the metal center, as is typical for low valent electron rich compds. However, much of the reactivity of I is similar to that seen earlier in electrophilic, rather than electron-rich, benzyne complexes, and some is completely unprecedented. For example, complex I reacts with the C-H bonds of hydrocarbons to undergo ring exchange processes, and it reacts with OH and NH bonds to form monomeric hydroxide and amide complexes. Reaction of the benzyne complex with benzaldehyde yields simple M-C insertion products, while reaction with acetophenone yields an oxygen-bound enolate complex. The reaction of I with acetone is most unusual, cleaving the C-C bond of the org. substrate to yield methane, along with the same oxygen-bound enolate complex formed in the reaction with acetophenone. The crystal structure of I was detd.

Answer 99:

Bibliographic Information

Comparative reactivities of hydrocarbon carbon-hydrogen bonds with a transition-metal complex. Jones, William D.; Feher, Frank J. Dep. Chem., Univ. Rochester, Rochester, NY, USA. Accounts of Chemical Research (1989), 22(3), 91-100. CODEN: ACHRE4 ISSN: 0001-4842. Journal written in English. CAN 110:115099 AN 1989:115099 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Mechanistic studies with a series of homogeneous rhodium organometallic complexes, i.e., (C5Me5)Rh(PMe3)(R)H, are summarized that provide for the first time a comparative evaluation of the relative equil. consts. and rates of reaction for both alkane and arene hydrocarbon activation.

Answer 100:

Bibliographic Information

Thermodynamics of homogeneous hydrogenation. Part III. Oxidative addition of hydrogen to rhodium(I) complexes: correlation of dihydride structure to the thermodynamics of the catalyzed homogeneous hydrogenation of cyclohexene.
Khan, M. M. Taqui; Rao, E. Rama; Siddiqui, M. R. H.; Khan, Badar Taqui; Begum, Safia; Ali, S. Mustafa; Reddy, Jaypal. Cent. Salt Mar. Chem. Res. Inst., Bhavnagar, India. Journal of Molecular Catalysis (1988), 45(1), 35-50. CODEN: JMCADS ISSN: 0304-5102. Journal written in English. CAN 110:74585 AN 1989:74585 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The oxidative addn. of H2 to the Rh(I) chelates RhCl(PPh3)3 (I), [RhCl(diphos)]2 (II) and RhCl(NP2) [III; NP2 = HN(CH2CH2PPh2)2] proceeds at 30? and 1 atm of mol. H in EtOH-benzene with the formation of exclusively cis-dihydride products elucidated by their proton and 31P {1H} NMR spectra in situ. The homogeneous hydrogenation of cyclohexene catalyzed by complexes I-III was investigated in the temp. range 10-40% at 0.6-1 atm of H partial pressure. Thermodn. parameters for the formation of the dihydrido complexes of I-III and the monoolefin complexes of Rh(I) were computed. The activation parameters corresponding to the rate const. for the homogeneous hydrogenation of cyclohexene were also calcd. The enthalpy of formation of the dihydrido complexes ?H0 is more favorable (exothermic) for those hydrido species where there are minimal changes in the configuration of the dihydrido complex in oxidative addn. reaction. The enthalpies ?H0 increase in the order III < II .mchlt. I, in accord with the configurational changes obsd. in NMR. Complex I has an unfavorably large pos. ?H.thermod. of reaction. The highest catalytic activity of I is thus entirely due to entropy effect where the ?S.thermod. is about 50 e.u. more pos. than complexes II and III.

Answer 101:

Bibliographic Information

Gas-phase chemistry of transition metal-imido and -nitrene ion complexes. Oxidative addition of nitrogen-hydrogen bonds in ammonia and transfer of NH from a metal center to an alkene. Buckner, Steven W.; Gord, James R.; Freiser, Ben S. Dep. Chem., Purdue Univ., West Lafayette, IN, USA. Journal of the American Chemical Society (1988), 110(20), 6606-12. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 109:141530 AN 1988:541530 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The gas-phase chem. of bare transition metal-nitrene and -imido ion complexes (MNH+) is examd. Group 3, 4, and 5 at. metal ions react with NH3 at thermal energies to generate MNH+ via dehydrogenation. A reaction mechanism is proposed involving initial oxidative addn. to an N-H bond, in analogy to mechanisms proposed for reactions of gaseous at. metal ions with hydrocarbons. Cr+ reacts with NH3 via slow condensation to form CrNH3+, as do all group 6-11 at. metal ions investigated. However, excited-state Cr+ reacts with NH3 via bond-insertion reactions to form CrNH2+ and CrNH+. An unidentified metastable electronic state of Cr+, produced by direct laser desorption of chromium foil, reacts with much higher efficiency than does kinetically excited Cr+. FeO+ reacts with NH3 to generate FeNH+ with loss of H2O. Thermochem. studies of VNH+ and FeNH+ involving ion-mol. reactions are used to est. D?(V+-NH) and D?(Fe+-NH); the latter value agrees with photodissocn. ests. The high bond strength for VNH+ indicates multiple bonding, analogous to that in the isoelectronic VO+; the weaker bond strength for FeNH+ indicates a single bond, analogous to that in the isoelectronic FeO+. Proton transfer expts. are used to det. the proton affinity and ?Hf of VN and D?(V-N). VNH+ is unreactive with ethene and benzene, but FeNH+ transfers NH to ethene and benzene through metathesis and homologation reactions. A cyclic metalloaminobutane intermediate is consistent with the products of the FeNH+/ethene reaction.

Answer 102:

Bibliographic Information

Synthesis of an (?3-allyl)(hydrido)iridium complex and its reactions with arenes and alkanes. Sequential intermolecular carbon-hydrogen oxidative addition and hydride-to-alkene migratory insertion reactions. McGhee, William D.; Bergman, Robert G. Dep. Chem., Univ. California, Berkeley, CA, USA. Journal of the American Chemical Society (1988), 110(13), 4246-62. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 109:37972 AN 1988:437972 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The iridium allyl hydride complex (?5-C5Me5)(?3-C3H5)(H)Ir (I) has been prepd. from [(?5-C5Me5)IrCl2]2, and its reaction with arenes and alkanes has been investigated. The hydride reacts with C-H bonds in benzene and cyclopropane in the presence of phosphines L, leading to the Ph and cyclopropyl complexes (?5-C5Me5)(L)Ir(n-propyl)(R) (R = Ph, cyclopropyl). Irradn. of I in the presence of PMe3 takes a different course, giving the previously uncharacterized (?5-C5Me5)Ir(PMe3)2. Thermal reaction of I in alkane solvents such as butane and isobutane, which are capable of ?-elimination, leads to isomeric (?5-C5Me5)(?3-C3H4Me)(H)Ir (C3H4Me = methallyl), formed by replacement of the allyl group in I by a substituted allyl ligand formed by overall dehydrogenation of the alkane. Thermolysis of I in the presence of arenes such as propylbenzene and cumene leads to more complicated products resulting from intermol. C-H activation followed by cyclometalation to give iridium complex II. The structure of cyclometalated dimer II has been detd. by x-ray diffraction. Mechanistic studies, including kinetics, isotope tracer expts., and intra- vs. intermol. isotope effect detns., implicate the coordinatively unsatd. species (?5-C5Me5)(?2-propene)Ir as the initially formed intermediate in the thermal reactions of (?5-C5Me5)(?3-C3H5)(Cl)Ir with alkanes and arenes. Significant differences exist between the behavior of this intermediate and that of the closely related phosphine-substituted complex (?5-C5Me5)(PMe3)Ir studied earlier; possible reasons for these differences are discussed.

Answer 103:

Bibliographic Information

Photochemistry of dicarbonyl(?5-cyclopentadienyl)iridium in hydrocarbon solutions: kinetics and mechanism of carbon-hydrogen bond activation. Marx, David E.; Lees, Alistair J. Univ. Cent. Binghamton, State Univ. New York, Binghamton, NY, USA. Inorganic Chemistry (1988), 27(7), 1121-2. CODEN: INOCAJ ISSN: 0020-1669. Journal written in English. CAN 108:150701 AN 1988:150701 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The photochem. of (?5-C5H5)Ir(CO)2 in hydrocarbon solns. has been investigated. Steady-state photolysis and transient absorption measurements illustrate that photoexcited (?5-C5H5)Ir(CO)2 undergoes rapid (kapp ? 4.4 ?0.9 ? 106 M-1 s-1; kapp = kobs/[C6H6]) intermol. C-H bond activation of benzene at 293 K to form (?5-C5H5)Ir(CO)(H)(C6H5) and CO products. Perfluorobenzene has been established as an inert solvent for this photochem. system. Quantum yields obtained for benzene C-H bond activation depend on the concn. of benzene in perfluorobenzene (? = 3 ?0.3 ? 10-2 in neat benzene) indicating that this reaction incorporates a bimol. process in which the assocn. of benzene with the metal complex is the rate detg. step. Quantum yields measured in several other hydrocarbon solns. illustrate that substrate ?-interaction and steric factors influence the efficiency of C-H bond activation. A mechanism involving a ring hapticity change (?5? ?3) is proposed and it is supported by the observation that the concn. of dissolved CO has no discernible effect on the reaction.

Answer 104:

Bibliographic Information

Reactivity and mechanism in the formation of (?-hydrocarbyl)diplatinum(IV) complexes by oxidative addition of ?,?'-dibromoxylenes to dimethylplatinum(II) complexes. Scott, John D.; Crespo, Margarita; Anderson, Craig M.; Puddephatt, Richard J. Dep. Chem., Univ. West. Ontario, London, ON, Can. Organometallics (1987), 6(8), 1772-7. CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 107:78053 AN 1987:478053 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Formation of binuclear complexes with ?-hydrocarbyl ligands by double oxidative addn. of ?,?'-dibromoxylene (ortho and para isomers), and I(CH2)nI (n = 3-6) to binuclear platinum complexes was studied. In bridged 2,2'-bipyrimidine (bipym) systems, [Me2Pt(?-bipym)PtMe2(CH2C6H4CH2Br-4)Br] underwent rapid intramol. oxidative addn. to give [Me2BrPt(?-bipym)(?-4-CH2C6H4CH2)PtBrMe2], but the analogous complexes [Me2Pt(?-bipym)PtMe2(2-CH2C6H4CH2Br)Br] and [Me2Pt(?-bipym)PtMe2{(CH2)nI}I] were long-lived and rearranged slowly to tetranuclear complexes. Reasons for these differences are suggested based on conformational or ring strain effects. Binuclear complexes with ?-hydrocarbyl groups were formed more easily from [Pt2Me4(?-pyen)] [pyen = bis(2-pyridyl)ethylenediimine] as a result of the flexibility of the ?-pyen ligand, but I(CH2)nI failed to give ?-polymethylene derivs. Kinetic studies of several of these reactions indicated that the para isomer of C6H4(CH2Br)2 is more reactive than the ortho isomer and that a Pt center can activate a remote C-Br bond by a neighboring group effect. The apparent intermol. oxidative addns. of binuclear complexes to give tetranuclear complexes follow first-order kinetics and probably involve an intramol. reaction followed by rapid dimerization. The intramol. reaction would involve dissocn. of platinum(IV) from the diimine ligand.

Answer 105:

Bibliographic Information

The catalytic activation and functionalization of carbon-hydrogen bonds. Aldimine formation by the insertion of isonitriles into aromatic carbon-hydrogen bonds. Jones, William D.; Foster, Glenn P.; Putinas, Jeanne M. Dep. Chem., Univ. Rochester, Rochester, NY, USA. Journal of the American Chemical Society (1987), 109(16), 5047-8. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 107:78024 AN 1987:478024 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The complexes Fe(PMe3)2(CNR)3 (R = Me, CMe3, CH2CMe3, Ph, 2,6-xylyl) have been prepd. from the reaction of isocyanides, RNC, with Fe(PMe3)4. Irradn. of the neopentyl or xylyl derivs. in benzene soln. formed the corresponding aldimine, PhCH:NR. In the presence of low concns. of added isonitrile the reaction was catalytic in iron. A mechanism involving photochem. isonitrile labilization, benzene oxidative addn., and isonitrile insertion is proposed.

Answer 106:

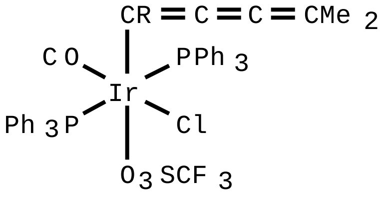
Bibliographic Information

Kinetics, stereochemistry, and mechanism of interaction of Vaska's complex with ethynylvinyl triflates. Formation of novel ?-butatrienyliridium compounds. Stang, Peter J.; Dixit, Vandana; Schiavelli, Melvyn D.; Drees, Paul. Dep. Chem., Univ. Utah, Salt Lake City, UT, USA. Journal of the American Chemical Society (1987), 109(4), 1150-6. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 106:138608 AN 1987:138608 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reaction of Vaska's complex [(Ph3P)2Ir(CO)(Cl)] with Me2C:C(O3SCF3)C?CR (R = H, D, Me, Ph, SiMe3) was investigated. Oxidative addn. readily occurs in benzene or toluene at room temp. to give hexacoordinate Ir(III) butatrienyl complexes I (R = same). Rate studies indicate steric inhibition by bulky substituents on the terminal acetylenic C and give high neg. entropies of activation.

The reaction occurs with complete (or nearly complete) retention of olefin stereochem. A two-step SN2' process with syn approach of the incoming Ir nucleophile is proposed to account for these observations.



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Answer 107:

Bibliographic Information

Isomerization of the hydridoalkylrhodium complexes formed on oxidative addition of rhodium to alkane carbon-hydrogen bonds. Evidence for the intermediacy of ?2-alkane complexes. Periana, Roy A.; Bergman, Robert G. Dep. Chem., Univ. California, Berkeley, CA, USA. Journal of the American Chemical Society (1986), 108(23), 7332-46. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 106:102511 AN 1987:102511 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The products of insertion of the coordinatively unsatd. fragment Cp*RhL (I; Cp* = ?5-pentamethylcyclopentadienyl, L = PMe3 throughout this abstr.) into alkane C-H bonds are generated by irradn. of Cp*(L)RhH2 (II) or thermal decompn. of Cp*(L)Rh(R)H (III; R = CH2CMe3) at <-30? in alkane solvents. The products III (R = alkyl) were synthesized independently, also at low temp., from the corresponding Cp*(L)Rh(R)X (X = halo) by lithiation with Me3CLi followed by protonation. Alternatively, the highly nucleophilic complex Li[Cp*(L)RhH], prepd. by deprotonating II, gives III (R = alkyl) upon treatment with alkyl tosylates. Generating I in mixts. of linear alkanes gave only the products of insertion into primary C-H bonds, even at -100?. The relative rate consts. for I formation correlate directly with the no. of secondary C-H bonds in the alkane, suggesting that insertion occurs initially into all the C-H bonds of the alkane. However, even at very low temps. the secondary-insertion products rearrange quickly and intramolecularly to the primary products, probably via ?2-C-H alkane complexes. These synthetic and 13C-labeled III (R = alkyl) at low temps. Warming these complexes to -80? in an arom. solvent reveals isotope rearrangements which confirm that they interconvert intramolecularly at rates competitive with or in some cases faster than their reductive elimination. E.g., rearrangement of the 13C,2H-labeled III [R = Et, (1-methylcyclopropyl)methyl] showed that the I fragment migrates and inserts most rapidly into the ? positions; reductive elimination is the slowest process which occurs. The kinetic isotope effect for oxidative addn. of I into the C-H bonds of hexane (detd. by competition techniques) is small [(kH/kD) = 1.1 ? 0.1], whereas that for reductive elimination (obtained from directly measured rates) from III (R = Et) is both large and inverse [(kH/kD) = 0.5 ? 0.1]. These results provide further support for the existence of intermediate ?2-C-H alkane complexes.

Answer 108:

Bibliographic Information

Activation of benzene by a tetrakis(trimethylphosphine)osmium(II) system. Mechanism of activation. Desrosiers, Peter J.; Shinomoto, Ronald S.; Flood, Thomas C. Dep. Chem., Univ. South. California, Los Angeles, CA, USA. Journal of the American Chemical Society (1986), 108(25), 7964-70. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 106:50423 AN 1987:50423 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The intermol. activation of the C-H bond in C6H6 is examd. by the thermolysis of cis-L4OsHR [I; L = PMe3; R = Me (II), CH2CMe3

(III), CH2SiMe3 (IV)]. Thermolysis of III at 70? in C6H6 results in activation of C (acyl)-H bonds to give I (R = Ph) quant. via initial reversible L dissocn. to form an unsatd. intermediate L3OsHCH2CMe3 (V), which is configurationally stable during its lifetime and which rapidly and reversibly activates the C-H bonds of its own neopentyl ligand. Unsatd. intermediate V reacts with C6H5 by oxidative addn. of the C (acyl)-H bond to form the Os (IV) intermediate, L3OsH2(CH2CMe3)Ph, which then undergoes reductive elimination of Me4C. The activation step has a kinetic D isotope effect of 3.32 ? 0.30. The thermolysis of IV in C6H6 proceeds by the same mechanism of initial dissocn. of L followed by oxidative addn. of C6H6, reductive elimination of SiMe4, and reuptake of L. The unsatd. intermediate in this case, L3OsHCH2SiMe3 also rapidly and reversibly activates the C(?)-H bond of its own CH2SiMe3 ligand. The rates of Me3P dissocn. for II, III, and IV establish a strong steric effect, by the alkyl group, on the ease of this dissocn.

Answer 109:

Bibliographic Information

Activation of carbon-hydrogen bonds by rhenium. Catalytic intermolecular hydrogen-deuterium exchange with (?6-C6H6)Re(PPh3)2H. Jones, William D.; Fan, Mingxin. Dep. Chem., Univ. Rochester, Rochester, NY, USA. Organometallics (1986), 5(5), 1057-9. CODEN: ORGND7 ISSN: 0276-7333. Journal written in English. CAN 104:186584 AN 1986:186584 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

(?6-C6H6)Re(PPh3)2H undergoes slow photochem. loss of phosphine. The intermediate formed catalyzed H/D exchange between C6D6 and other arenes in soln., as well as with the meta and para H atoms of the coordinated phosphine ligand. Labeling studies indicate that the simplest oxidative addn.-reductive elimination mechanism is not operating in these exchanges.

Answer 110:

Bibliographic Information

A new aromatic metalation reaction involving rhodium and iridium; the unusual reactivity of iodobenzene. Gomez, Manuel; Yarrow, Paul I. W.; Robinson, David J.; Maitlis, Peter M. Dep. Chem., Univ. Sheffield, Sheffield, UK. Journal of Organometallic Chemistry (1985), 279(1-2), 115-30. CODEN: JORCAI ISSN: 0022-328X. Journal written in English. CAN 102:220999 AN 1985:220999 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Benzenes PhR (R = H, F, Cl, Br, iodo, CO2Me, OMe, NO2, CF3, cyano, NH2, Ac) reacted with Cp*IrMe2L (Cp* = pentamethylcyclopentadienyl; L = Me2SO) to give CH4 and Cp*IrMeR1L (I; R1 = C6H4R-3, C6H4R-4, C6H4NH2-3; R ? NH2). Longer reaction times and higher temps. gave Cp*IrR12L (R1 = C6H4R-3, C6H4R-4; R = H, Cl, Br, iodo). The reactivity of PhR to Cp*IrMe2L decreased as R = iodo > NO2 > CF3 > cyano > CO2Me > Br > H > OMe > Cl > F > NH2; the pseudo-first order and second order rate consts. were detd. The mechanism involved L dissocn., oxidative addn. of H-C6H4R, and reductive elimination of CH4. The analogous Rh complex Cp*RhMe2L reacted similarly but much more slowly with PhR (R = H, iodo, nitro, CF3). I (R1 = C6H4R; R = Cl, Br, iodo, NO2) reacted with IrCl62- with coupling, to give MeC6H4R as the predominant product. Similarly, Cp*IrPh2L and IrCl62- gave biphenyl.

Answer 111:

Bibliographic Information

Mechanism of the reaction of gas-phase iron ions with neutral olefins. Peake, D. A.; Gross, M. L.; Ridge, D. P. Chem. Dep., Univ. Nebraska, Lincoln, NE, USA. Journal of the American Chemical Society (1984), 106(16), 4307-16. CODEN:

JACSAT ISSN: 0002-7863. Journal written in English. CAN 101:72913 AN 1984:472913 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The structures of FeCnH2n+ species formed by reaction of Fe(CO)+ with olefins (n = 2-14) and cycloalkanes (n = 3-6) in a high-pressure source were examd. by mass spectrometric techniques. Ethylene, propene, and isobutene retained their structures in complexes with Fe+, but all of the other olefins rearranged to a structure with 2 or more ligands. These rearrangements were consistent with addn. of an allylic C-C bond to the metal ion followed by abstraction of a ?-H atom from the resulting alkyl ligand to form a hydrido ?-allyl intermediate. Transfer of the H atom to the allylic fragment produced a bis(olefin) complex. This mechanism dominated unless the required ?-H were absent. The generality of the allylic insertion mechanism was tested by examg. a series of FeC8H16+ ions formed from isomeric octenes and methylheptenes.

Answer 112:

Bibliographic Information

The mechanism and thermodynamics of alkane and arene carbon-hydrogen bond activation in (C5Me5)Rh(PMe3)(R)H.
Jones, William D.; Feher, Frank J. Dep. Chem., Univ. Rochester, Rochester, NY, USA. Journal of the American Chemical Society (1984), 106(6), 1650-63. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 100:121341 AN 1984:121341 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

(C5Me5)Rh(PMe3)(R)X (R = Me, Ph, p-tolyl, 3,4-C6H3Me2, 3,5-C6H3Me2, 2,5-C6H3Me2, 1-cyclopentenyl; X = Br) react with the hydride donors Li+ [HB(CHMeEt)3]- or Na+ [H2Al(OCH2CH2OMe)2]- to produce (C5Me5)Rh(PMe3)(R)H. The complexes with R = alkyl or R = vinyl are unstable, undergoing rapid reductive elimination at 25?, but can be obsd. by 1H NMR below -20?. (C5Me5)Rh(PMe3)(Me)H undergoes first-order reductive elimination with k = (6.38 ? 0.10) ? 10-5 s-1 at -17?. In contrast, (C5Me5)Rh(PMe3)(Ph)H undergoes a more complicated first-order process in C6D6, producing C6H6 and (C5Me5)Rh(PMe3)(C6D5)D with the overall activation parameters ?H.thermod. = 30.5 ? 0.8 kcal/mol and ?S.thermod. = 14.9 ? 2.5 entropy units. The alkyl and aryl hydride complexes can also be generated by photochem. extrusion of H2 from (C5Me5)Rh(PMe3)H2 in the presence of alkane or arene solvent. In a competition expt., a 5.4:1 selectivity for benzene over cyclopentane was exhibited at -35?. Irradn. in PhMe at -45? produced products in which activation of all possible C-H bonds of PhMe was obsd.: 57% meta, 36% para, 7% ortho, and <1% benzyl. Thermodynamically controlled competition between activation of benzene and PhMe, m-xylene, o-xylene, or p-xylene showed preferences for benzene of 2.7, 12.1, 7.6, and 58.6. The aryl complexes (C5Me5)Rh(PMe3)(aryl)H were in rapid equil. with their ?2-arene derivs. at temps. above -15?. Mechanistic studies revealed a [1,2]-shift pathway around the ring with ?H.thermod. = 16.3 ? 0.2 kcal/mol and ?S.thermod. = 6.3 ? 0.8 entropy units for the deriv. with R = 2,5-C6H3Me2. Generation of the coordinatively unsatd. species (C5Me5)Rh(PMe3) in the presence of p-C6H4(CMe3)2 permitted the direct observation of an ?2-arene complex at -15?. The kinetics of C-H bond activation in this system are interpreted in terms of two distinct rate-detg. reactions, arene coordination vs. alkane oxidative addn. The Rh-Ph bond is .apprx.13 kcal/mol stronger than the Rh-Me bond.

Answer 113:

Bibliographic Information

Organic chemistry of subvalent transition metal complexes. Part 7. Desulfurization of dibenzothiophene by nickel(0) complexes: evidence for electron transfer in oxidative additions. Eisch, John J.; Hallenbeck, Lawrence E.; Han, Kyoung Im. Dep. Chem., State Univ. New York, Binghamton, NY, USA. Journal of Organic Chemistry (1983), 48(18), 2963-8. CODEN: JOCEAH ISSN: 0022-3263. Journal written in English. CAN 99:104575 AN 1983:504575 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Two equiv. of (2,2'-bipyridyl)(1,5-cyclooctadiene)nickel(0) (I) cleave dibenzothiophene (II) in homogeneous media to form Ni-substituted biphenyl derivs. and NiS. The cleavage proceeds more readily in THF than in benzene, and excess amine (either bipyridyl or pyridine) retards the reaction. Neither biphenylene nor 2-phenylbenzenethiol were detectable transients in the desulfurization process. The possible fleeting formation of a biphenylene was ruled out by a study of the desulfurized products obtained from the 2,8-di-Me and the 3,7-di-Me derivs. of dibenzothiophene. A possible role of a Ni hydride in some of the C-S bond cleavage is suspected from the obsd. effects of either acid or LiAlH4 used in the workup of the reaction mixt. The reaction is not catalytic in Ni when an excess of LiAlH4 is used which indicates that Ni(0) is not regenerated from NiS under these conditions. The obsd. cleavage of .apprx.50% of the II by 2 equiv of I is ascribed to the gradual formation of (C10H8N2)2Ni, which is ineffectual in cleaving II. Finally, the relative reactivity of the dibenzothiophenes (II > 2,8-dimethyldibenzothiophene .mchgt. 3,7-dimethyldibenzothiophene), the relative effectiveness of amine donors or solvents, and the obsd. H abstraction from the solvent indicate an electron-transfer mode of action by the nickel(0) desulfurizing agent.

Answer 114:

Bibliographic Information

Carbon-hydrogen activation in completely saturated hydrocarbons: direct observation of M + R-H ？ M(R)(H). Janowicz, Andrew H.; Bergman, Robert G. Dep. Chem., Univ. California, Berkeley, CA, USA. Journal of the American Chemical Society (1982), 104(1), 352-4. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 96:35524 AN 1982:35524 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The first example of intermol. oxidative addn. of a transition metal complex in homogeneous soln. to single C-H bonds in satd. hydrocarbons, leading to hydridometal alkyl complexes at room temp. is reported. (Me5C5)IrH2(PMe3) (Me5C5 = ？5-pentamethylcyclopentadienyl), prepd. in a straightforward way from the known dimer [(Me5C5)IrCl2]2, loses H2 on irradn. This presumably leads to the coordinatively unsatd. transient intermediate (？5-Me5C5)(PMe3)Ir. In benzene, the metal center in this species inserts into a benzene C-H bond, which is a precedented process. However, in cyclohexane the unsatd. intermediate also reacts directly with solvent, leading to (Me5C5)IrHR(PMe3) (I, R = cyclohexyl) in 90% yield at 74% conversion. In neopentane, C-H oxidative addn. also occurs, leading to the corresponding hydridoalkyl complex I (R = CH2CMe3) 83% conversion. Selectivity and crossover expts. were carried out which indicate strongly that concerted insertion, rather than a free radical or other intermol. process, is the most likely mechanism for these reactions. Treatment with mild oxidizing or electrophilic reagents causes reductive elimination of the hydrocarbon, and reaction with bromoform converts I to the corresponding bromoalkyl complexes.

Answer 115:

Bibliographic Information

Oxidative addition of allyl acetate to palladium(0) complexes. Yamamoto, Takakazu; Saito, Osamu; Yamamoto, Akio. Res. Lab. Resour. Utilization, Tokyo Inst. Technol., Yokohama, Japan. Journal of the American Chemical Society (1981), 103(18), 5600-2. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 95:149466 AN 1981:549466 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Reaction of Pd(PCy3)2 (Cy = cyclohexyl) and CH2:CHCH2OAc at room temp. affords Pd(？3-C3H5)(OAc)PCy3 (I) and [Cy3PCH:CHMe]+ [OAc]- (II). In reactions with amines and PCy3, the ？3-allyl ligand of I is transferred to the nucleophiles to give allylated amines and II, resp. This supports a mechanism usually proposed for Pd-catalyzed allylation reactions. Pd(PCy3)2 and

Pd(PPh3)4 catalyze a clean pair-wise 1,3-shift of CH2:CHCD2OAc (III) to give a mixt. of III and CD2:CHCH2OAc.

Answer 116:

Bibliographic Information

Reactions of organic halides and cyanides with bis(tricyclohexylphosphine)nickel(0). Morvillo, A.; Turco, A. Univ. Padova, Padua, Italy. Journal of Organometallic Chemistry (1981), 208(1), 103-13. CODEN: JORCAI ISSN: 0022-328X. Journal written in English. CAN 95:81184 AN 1981:481184 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reactions of the complex bis(tricyclohexylphosphine)nickel(O) (Ni(PCy3)2) with org. halides and cyanides RX (R = Me, X = I, CN; R = Et, X = Br, I, CN; R = Pr X = Br, CN; R = Ph, X = Cl, CN), all involving fission of the R-X bond, were studied in toluene at various temps. Oxidative addn. of the bromides produces the stable complexes [NiIBr(PCy3)2]2 and NiII(H)(Br)(PCy3)2. MeI affords phosphonium salts of a Ni(II) complex. The org. products of these reactions involve alkanes, alkenes, benzene, and reductive coupling products RR. Except for the Me and Ph derivs. the distribution of org. products is rather insensitive to the functional group X. The reactions are discussed in terms of mol. and radical mechanisms. The reactivity of Ni(PCy3)2 is compared with that of Ni(PEt3)3 and Ni(PMe3)4.

Answer 117:

Bibliographic Information

Intramolecular rearrangements of sulfines coordinated to platinum. A unique equilibrium between oxidative-addition stereoisomers cis-(E)- and cis-(Z)-bis(triphenylphosphine)(methylthio)(arylsulfine)platinum(II) and the two stereoisomers of the reductive coupling product bis(triphenylphosphine)[aryl(methylthio)sulfine]platinum(0). Crystal and molecular structure of bis(triphenylphosphine)(9-sulfinylfluorene)platinum(0)-0.5-benzene. Gosselink, Johan W.; Van Koten, Gerard. Anorg. Chem. Lab., Univ. Amsterdam, Amsterdam, Neth. Inorganic Chemistry (1981), 20(3), 877-84. CODEN: INOCAJ ISSN: 0020-1669. Journal written in English. CAN 94:113585 AN 1981:113585 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

An x-ray single-crystal study revealed the mol. structure of [Pt(PPh3)2L].0.5C6H6 (L = 9-sulfinylflourene): monoclinic space group C2/c with a 12.951(4), b 17.958(5), c 37.088(3) .ANG., ? 98.48(2)?, V = 8531.8 .ANG.3, and Z = 8. The crystal structure was solved by std. Patterson and Fourier techniques. Anisotropic blocked full-matrix least-squares refinement with 5884 obsd. diffractometer data converged to RF = 0.038 (RwF = 0.041). L is coordinated via ?2-CS to the Pt(PPh3)2 unit. By comparison with the planar free sulfines, the C:S bond is lengthened and the C12H8 and SO groups bend out of plane. In CDCl3 the coordination compds. [Pt(PPh3)2[(E)-(MeS)RCSO]] and [Pt(PPh3)2[(Z)-(MeS)RCSO]] (R = Ph, p-MeC6H4; ?2-CS coordinated sulfine stereoisomers) were both converted into an equil. mixt. of the oxidative-addn. stereoisomers cis-(E)- and cis-(Z)-[PtII(MeS)(PPh3)2(RCSO)] (in which the Pt(PPh3)2 unit is inserted into the C-S side bond) and 1 coordination stereoisomer, [Pt(PPh3)2[(E)-(MeS)RCSO]]. Individually, the cis-E and cis-Z stereoisomers were likewise converted into the same equil. mixt. upon dissoln. in CDCl3, which further illustrates the existence of a unique equil. between oxidative addn. and reductive coupling products. Only traces of the sp. stereoisomer [Pt0(PPh3)2[(Z)-(MeS)RCSO]] were found in the equil. mixt., indicating that ?2-CS coordinated sulfines which contain a C-S side bond syn, as opposed to anti (with resp. to the SO group), are more reactive toward oxidative addn. to Pt0. A mechanism is proposed for the intramol. oxidative-addn. process, i.e., gliding movements along S-C:S frames via stereoisomeric intermediates [Pt(PPh3)2[(E)-MeSC(R)SO]] and [Pt(PPh3)2[(Z)-MeSC(R)SO]], in which the sulfines are ?3-SCS coordinated.

Answer 118:

Bibliographic Information

Electrochemistry of nickel complexes. Part 2. Reduction of triphenylphosphinenickel(II) complexes in tetrahydrofuran; reactions of zerovalent nickel with halobenzenes. Troupel, Michel; Rollin, Yolande; Sibille, Soline; Fauvarque, Jean Francois; Perichon, Jacques. Lab. Electrochim. Org., Univ. Paris Val de Marne, Creteil, Fr. Journal of Chemical Research, Synopses (1980), (1), 24-5. CODEN: JRPSDC ISSN: 0308-2342. Journal written in English/French. CAN 93:70528 AN 1980:470528 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

NiX2(PPh3)2 (X = Br, iodo) underwent electrochem. redn. in a medium consisting of LiClO4 or Bu4NClO4 and excess PPh3 in THF to give Ni(I) and Ni(0) complexes. In the presence of excess PPh3 and a small amt. of Ni(II) halide, Ni(ClO4)2 underwent quant. electrochem. redn. to Ni(0) by a catalytic process in which X- was regenerated by redn. of Ni(I) to Ni(0). The Ni(0) complexes underwent oxidative addn. reactions with PhX (I; X = iodo, Br, Cl) in the presence of excess PPh3 to give PhNiX(PPh3)2 (II). The kinetics of the addn. reactions were studied by amperometry. II underwent electrochem. redn. at -2.2 V and oxidn. at +0.2 V. The redn. regenerates Ni(0). Thus, electrochem. redn. of I in excess can be obsd. in the presence of a catalytic amt. of Ni complex.

Answer 119:

Bibliographic Information

Mechanism of oxidative addition of allylic halides to iridium(I) complexes. Pearson, Ralph G.; Poulos, Arthur T. Chem. Lab., Northwestern Univ., Evanston, IL, USA. Inorganica Chimica Acta (1979), 34(1), 67-76. CODEN: ICHAA3 ISSN: 0020-1693. Journal written in English. CAN 91:90772 AN 1979:490772 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A detailed study has been made of the oxidative addn. reaction of allylic halides to IrCl(CO)(PMe2Ph)2 in benzene and in methanol. In benzene the reaction probably occurs by way of a ?-allyl intermediate. This reacts with anion to give a product with a ?-allyl group bonded to the metal cis to the added anion. Both crotyl and ?-methylallyl chlorides give the same products since they form the same ?-allyl. In methanol the ?-allyl is not an intermediate since crotyl chloride and ?-methylallyl chloride give different ?-allyl products with the metal atom bonding predominantly to the carbon atom bearing the chloride. The anion which add in methanol can be one added to the soln. and it bonds trans to the ?-allyl group. A modified SN2 mechanism with double-bond participation is proposed for both solvents.

Answer 120:

Bibliographic Information

Kinetics and mechanism of oxidative olefin arylation by palladium(II). Yatsimirskii, A. K.; Ryabov, A. D.; Berezin, I. V. Dep. Chem., Moscow State Univ., Moscow, USSR. Journal of Molecular Catalysis (1979), 5(6), 399-414. CODEN: JMCADS ISSN: 0304-5102. Journal written in English. CAN 91:73950 AN 1979:473950 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The kinetics of the oxidative arylation of substituted styrenes by ArX (benzene, naphthalene, and PhHgOAc) in the presence of Pd(OAc)2 were detd. in AcOH-AcONa. Rate expressions incorporating Na2Pd2(OAc)6 or Pd3(OAc)6 are given. The data indicate that the reaction proceeds through two simultaneous paths, one zero- and the other is 1st-order in olefin, each involving fast, reversible ?-arene complex formation. For the olefin-dependent path, a ?-arene-?-olefin Pd complex is the reactive intermediate. The rate of the olefin-independent path is .apprx.104 times the rate of the corresponding reaction between ArX and Pd(II), leading to biaryl formation in the absence of olefin. The results suggest that in the case of biaryl formation ArX is attacked by an electrophilic substitution mechanism, while olefin arylation proceeds through the more rapid, reversible formation of Ar-Pd-X species. The latter route may be formally considered to be an oxidative addn. mechanism.

Answer 121:

Bibliographic Information

Kinetics of the oxidative addition reaction of iodine to (dimethyldithiocarbamato)bis(2,4,6-trimethylphenyl isocyanide)rhodium(I). Kuwae, Ryosho; Tanaka, Toshio; Kawakami, Katsuhiko. Fac. Eng., Osaka Univ., Suita, Japan. Bulletin of the Chemical Society of Japan (1979), 52(2), 437-40. CODEN: BCSJA8 ISSN: 0009-2673. Journal written in English. CAN 90:157658 AN 1979:157658 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reaction of Rh(dtc)L2 (dtc = S2CNMe2, L = 2,4,6-Me3C6H2NC) with an equimolar amt. of iodine yields a trans adduct, RhI2(dtc)L2. The rate of this reaction was measured in benzene, employing a stopped-flow technique under pseudo-1st-order conditions with excess iodine. The results indicates that the reaction proceeds via a charge transfer complex Rh(dtc)L2?I2, which is rearranged in 2 consecutive 0-order reactions with respect to the I2 concn.; the rearrangement of Rh(dtc)L2?I2 to a cis adduct followed by isomerization to the trans adduct. This mechanism is supported form kinetic data for the reaction of Rh(acac)L2 (acac = MeCoCHCOMe) with I2. Also, RhI(I3)(dtc)L2 and RhI(I3)(acac)L2 were obtained by reactions of Rh(dtc)L2 and Rh(acac)L2 with excess iodine, resp.

Answer 122:

Bibliographic Information

Kinetics of the oxidative addition of hydrogen to chloro(acrylonitrile)bis(triphenylphosphine)rhodium(I) in benzene. Ohtani, Yoshimi; Yamagishi, Akihiko; Fujimoto, Masatoshi. Fac. Sci., Hokkaido Univ., Sapporo, Japan. Bulletin of the Chemical Society of Japan (1978), 51(9), 2562-5. CODEN: BCSJA8 ISSN: 0009-2673. Journal written in English. CAN 89:186589 AN 1978:586589 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The reaction between chloro(acrylonitrile)bis(triphenylphosphine)rhodium(I) and H was studied by the stopped-flow method under an anaerobic condition. A soln. of RhCl(CH2CHCN)(PPh3)2 (I) was mixed with a benzene soln. contg. H under the condition of [Rh] < [H2]0 < [CH2CHCN]. A fast decrease in the absorbance was followed by a slow increase in the absorbance, until finally the absorbance returned to the initial value. The faster reaction is the oxidative addn. of H to I; I + H2 .dblarw. RhClH2(CH2CHCN)(PPh3)2. The slower reaction is the process in which H is consumed in the course of the hydrogenation of acrylonitrile and I is reproduced. The forward and reverse consts. are ?7.8 ? 103 mol-1 dm3 s-1 and ?53 s-1, resp.

Answer 123:

Bibliographic Information

Deuterium-hydrogen exchange in the presence of bis(cyclopentadienyl)vanadium. Grigoryan, E. A.; D'yachkovskii, F. S.; Zhuk, S. Ya.; Vyshinskaya, L. I. Inst. Khim. Fiz., Chernogolovka, USSR. Kinetika i Kataliz (1978), 19(4), 1063-5. CODEN: KNKTA4 ISSN: 0453-8811. Journal written in Russian. CAN 89:179178 AN 1978:579178 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

H-D exchange between CH4 and D2 or C2D4 in benzene occurred at 70?/0.3-40 atm in the presence of the title complex. The solvent was also deuterated. A mechanism involving oxidative addn. of CH4 to the V complex was proposed.

Answer 124:

Bibliographic Information

A kinetic and mechanistic study of the formation of sulfinato iridium(III) complexes by oxidative addition reactions.
Kubota, M.; Curtis, C. J.; Chappell, T. G. Dep. Chem., Harvey Mudd Coll., Claremont, CA, USA. Inorganica Chimica Acta (1978), 27(2), 261-3. CODEN: ICHAA3 ISSN: 0020-1693. Journal written in English. CAN 89:12729 AN 1978:412729 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The kinetics of oxidative addn. of sulfonyl chloride (RSO2Cl) to trans-Ir(CO)XL2 is given by the 2nd order rate law: rate = k2[Ir(CO)XL2][RSO2Cl]. The rates increase with increasing basicity of ligands L and X in the order Cl < Br < I and P(OPh)3 < PPh3 < P(p-MeC6H4 < Pr. The activation parameters for the reaction of Ir(CO)Cl(PPh3)2 with PhSO2Cl in benzene are ?H* = 16 kcal/mol and ?S* = -14 cal/deg mol. This reaction is not inhibited by radical scavengers galvinoxyl or duroquinone and not promoted by benzoyl peroxide. The mechanistic implications of these results are discussed.

Answer 125:

Bibliographic Information

Kinetic study of the hydrogenation of cyclohexene catalyzed by tris(triphenylphosphine)chlororhodium. Rousseau, C.; Evrard, M.; Petit, F. Lab. Chim. Org. Appl., ENSCL, Villeneuve d'Ascq, Fr. Journal of Molecular Catalysis (1978), 3(5), 309-24. CODEN: JMCADS ISSN: 0304-5102. Journal written in French. CAN 88:189644 AN 1978:189644 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A new scheme is proposed to explain the homogeneous hydrogenation of cyclohexene in benzene using Rh(PPh3)3Cl as catalyst, where Rh(PPh3)2H2Cl is the main active species. Two paths explain the formation of the dihydrido complex: (1) oxidative addn. of mol. H to Rh(PPh3)2Cl; (2) the dissociative reaction of Rh(PPh3)3H2Cl. The contribution of each Rh species was detd. and a rate expression detd.

Answer 126:

Bibliographic Information

Oxidative addition of benzyl halides to bis(triphenylphosphine)ethylenenickel. Bartsch, E.; Dinjus, E.; Fischer, R.; Uhlig, E. Sekt. Chem., Friedrich-Schiller-Univ., Jena, Ger. Dem. Rep. Zeitschrift fuer Anorganische und Allgemeine Chemie (1977), 433 5-12. CODEN: ZAACAB ISSN: 0044-2313. Journal written in German. CAN 88:7029 AN 1978:7029 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The oxdative addn. of PhCH2X to (Ph3P)2Ni(C2H4) gave (Ph3P)2Ni(CH2Ph)X (X = Cl, Br). This oxidative addn. involved both SN2 displacement and one electron mechanisms. In benzene, an equil. between (Ph3P)2Ni(?-CH2Ph)Cl and the blue-violet

(Ph3P)Ni(?-CH2Ph)Cl existed.

Answer 127:

Bibliographic Information

The kinetics and mechanism of the homogeneous hydrogenation of 1-hexene catalyzed by hydridotetrahydroboratotris(triphenylphosphine)ruthenium(II). Holah, D. G.; Hughes, A. N.; Hui, B. C.; Kan, C. T. Dep. Chem., Lakehead Univ., Thunder Bay, ON, Can. Journal of Catalysis (1977), 48(1-3), 340-4. CODEN: JCTLA5 ISSN: 0021-9517. Journal written in English. CAN 87:133512 AN 1977:533512 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The kinetics of the hydrogenation of 1-hexene in benzene at 20? at atm. pressure and catalyzed by RuH(BH4)(PPh3)3, indicates that the reaction proceeds by the unsatd. route, i.e., dissocn. of the catalyst, formation of an alkyl complex, and then oxidative addn. of H in a rate-detg. step.

Answer 128:

Bibliographic Information

Kinetic study of oxidative addition and replacement reactions of chlorotris(triphenylphosphine)rhodium(I) in benzene. Ohtani, Yoshimi; Fujimoto, Masatoshi; Yamagishi, Akihiko. Fac. Sci., Hokkaido Univ., Sapporo, Japan. Bulletin of the Chemical Society of Japan (1977), 50(6), 1453-9. CODEN: BCSJA8 ISSN: 0009-2673. Journal written in English. CAN 87:74072 AN 1977:474072 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Chlorotris(triphenylphosphine)rhodium(I) exists in C6H6 as RhCl(PPh3)3, a dimeric species [RhCl(PPh3)2]2, and a reaction intermediate RhCl(PPh3)2. The rates of oxidative addn. and replacement reactions were examd. in C6H6. For the oxidative addn. reaction, RhCl(PPh3)3, RhCl(PPh3)2, or [RhCl(PPh3)2]2 + X1 .dblharw. products (X1 = H2, O2, C2H4, CHCl=CCl2, CH3I), the reaction intermediate RhCl(PPh3)2 is most reactive, the degree of its reactivity depending largely on the reactants (X1). A significant enhancement of the rate was obsd. for the ligand substitution reaction, RhClX1(PPh3)m + X2 .dblharw. RhClX2(PPh3)n + X1(m,n = 3 or 2), where X1 = H2 and X2 = oelfin and vice versa. The results are discussed in relation to the mechanism of hydrogenation.

Answer 129:

Bibliographic Information

Stereochemistry of oxidative addition of benzyl-?-d chloride to tetrakis(triphenylphosphine)palladium(0). Direct evidence for configurational inversion at carbon via a nonradical mechanism. Wong, P. K.; Lau, K. S. Y.; Stille, J. K. Dep. Chem., Univ. Iowa, Iowa City, IA, USA. Journal of the American Chemical Society (1974), 96(18), 5956-7. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 81:119805 AN 1974:519805 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The oxidative addn. of S-(+)-PhCHDCl to Pd(PPh3)4 (I) to give PhCHDPd(PPh3)2Cl (II) proceeded with inversion of configuration at the benzylic C. The stereochem. was established by carbonylation of II with retention of configuration at C to give PhCHDCOPd(PPh3)2Cl, which was then degraded chem. to the known R-(+)-PhCHD-CH2OH. The formation of Me3CN(O.bul.)CH2Ph in the oxidativeaddn. of PhCH2Cl to I in the presence of Me3CNO was attributed to the radical decompn. (thermal or spin-trap induced) of the oxidative addn. adduct on the basis that the same nitroxide radical was obsd. in the ESR spectrum of a benzene soln. contg.PhCH2Pd(PPh3)2Cl and Me3CNO.

Answer 130:

Bibliographic Information

Kinetics and mechanism of the oxidative addition of methyl iodide to tetrakis- and tis(triphenylphosphine)platinum(O). Pearson, Ralph G.; Rajaram, Jayaraman. Chem. Lab., Northwest. Univ., Evanston, IL, USA. Inorganic Chemistry (1974), 13(1), 246-7. CODEN: INOCAJ ISSN: 0020-1669. Journal written in English. CAN 80:149273 AN 1974:149273 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The kinetics of MeI reactions with Pt(PPh3)3 (I) and Pt(PPh3)4 were detd. at 25? in benzene, cyclohexane, and dichloromethane solns. The results with I are consistent with a mechanism in which I partially dissocs. to Pt(PPh)2 + PPh3 and both I and Pt(PPh3)2 react with MeI to form PtIMe(PPh3)2. The solvent effect indicates a polar transition state for the reaction. MeI also reacted with Pt(PMe2Ph)4, producing PtI2Me2(PMe2Ph)2.

Answer 131:

Bibliographic Information

Arylation of olefin with iodobenzene catalyzed by palladium. Mori, Kunio; Mizoroki, Tsutomu; Ozaki, Atsumu. Res. Lab. Resour. Util., Tokyo Inst. Technol., Tokyo, Japan. Bulletin of the Chemical Society of Japan (1973), 46(5), 1505-8. CODEN: BCSJA8 ISSN: 0009-2673. Journal written in English. CAN 79:31601 AN 1973:431601 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Arylation of propylene, ethylene, styrene, and Me acrylate with PhI was catalyzed by metallic Pd in MeOH to give methylstyrene, styrene, trans-stilbene, and Me cinnamate, resp. Their yields and selectivities increased significantly by the addn. of excess AcOK as an acceptor of HI formed. The course of catalytic reaction was discussed in terms of the oxidative addn. of PhI to a Pd complex of low oxidn. state.

Answer 132:

Bibliographic Information

Kinetic study of the oxidative addition of substituted benzenethiols to trans-halocarbonylbis(triphenylphosphine)iridium(I). Gaylor, J. R.; Senoff, C. V. Dep. Chem., Univ. Guelph, Guelph, ON, Can. Canadian Journal of Chemistry (1972), 50(12), 1868-73. CODEN: CJCHAG ISSN: 0008-4042. Journal written in English. CAN 77:79954 AN 1972:479954 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The kinetics of the oxidative addn. of a series of para-substituted benzenethiols, HSC6H4Y, where Y = 4-NO2, 4-Br, 4-Cl, 4-F, 4-H, 4-CH3, or 4-CH3O towards the complexes, trans-IrX(CO)(Ph3P)2 where X = Cl, Br, or I have been studied in benzene at 15-45?. These

reactions follow simple 2nd order kinetics, rate = k2[IrX(CO)(Ph3P)2][HSC6H4Y]. The 2 principal factors which influence the rates of these reactions are the mesomeric and inductive effects of the para-substituent and the nature of the ligand, X, coordinated to Ir. The rate of reaction increases as the substituent becomes more electron-withdrawing and as X varies from Cl to Br to I. The kinetic data together with spectroscopic data (ir and NMR) suggest that oxidative addn. proceeds via a 3-centered activated complex to give the cis-product.

Answer 133:

Bibliographic Information

Chromyl chloride oxidations. VI. Nature of the activated complex in the electrophilic addition to styrenes. Freeman, Fillmore; Yamachika, Nira J. Dep. Chem., California State Coll., Long Beach, CA, USA. Journal of the American Chemical Society (1972), 94(4), 1214-19. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 76:98679 AN 1972:98679 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

The kinetics of the rapid chromyl chloride addn. to (oxidn. of) styrene and substituted styrenes, to give the 1:1 chromyl chloride-styrene adducts, were measured using a spectrophotometric stopped flow system. The rates of addn. are increased by electron releasing groups on the benzene ring. A-Methylstyrene is more reactive than cis-? methylstyrene. Is-?-Methylstyrene is oxidized at a slower rate than the corresponding trans isomer while cis-stilbene reacts almost twice as fast as trans-stilbene. ,1-Diphenylethene is almost twice as reactive as ?-methylstyrene and .apprx.13 times as reactive as styrene. The kinetic data suggest an unsym. charged benzylic type carbonium ion like activated complex in the rate-detg. step for the chromyl chloride addn. to styrenes. The relative rates of oxidn. of styrene in CS2, CCl4, CHCl3, and CH2Cl2 are 1.0:1.1:1.7:5.3. A negligible secondary D kinetic isotope effect of 0.98 is obsd. in the oxidn. of ?-deuteriostyrene, and an inverse secondary D kinetic isotope effect (kH/kD = 0.88) is obtained in the oxidn. of ?,?-dideuteriostyrene. Large neg. entropies of activation (?S.++. = -23.8 to -42.4 entropy units) and low enthalpies of activation (?H.++. = 2.0-9.0 kcal/mole) are characteristic of the oxidns. The kinetic data, including the previously obsd. ?+ of -1.99, suggest a rate-detg. step involving a partially pos. charged benzylic C atom in a cyclic epoxide like 3-membered ring activated complex or in a partly bridged resonance-stabilized 5-membered ring-activated complex. Comparisons of product yields from the chromyl chloride, chromyl acetate, and chromic acid oxidns. of unsatd. hydrocarbons suggest that chromyl chromyl chloride is the preferred oxidant for a 1-step high-yield conversion of 2,2-disubstituted alkenes to aldehydes and ketones. A comparison of the postulated activated complexes for the oxidn. of C-C double bonds by chromic acid, chromyl acetate, and chromyl chloride is also presented.

Answer 134:

Bibliographic Information

Alkyl group isomerization in the oxidative addition of acyl chlorides to iridium(I) complexes. Bennett, M. A.; Charles, R. Res. Sch. Chem., Aust. Natl. Univ., Canberra, Australia. Journal of the American Chemical Society (1972), 94(2), 666-7. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 76:71764 AN 1972:71764 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Oxidative addn. of acyl chlorides, RCOCl, to the planar Ir(I) complex IrCl(PPh3)3 gives octahedral alkyliridium(III) complexes IrCl2(R)(CO)(PPh3)2. Use of acyl halides which are branched at the ?-C atom, e.g., Me2CHCOCl gives complexes contg. the normal alkyl, e.g. IrCl2(Pr)(CO)(PPh3)2. The reaction proceeds via the secondary alkyl deriv. which rapidly isomerizes to the n-alkyl via a hydrido-olefin intermediate. The previously reported octahedrally coordinated, dimeric, chlorine-bridged isopropyliridium(III) complex {IrCl2[CHMe2](CO)}2, obtained by adding Me2CHCOCl to the cycloocteneiridium(I) complex [IrCl(CO)(C8H14)2]2, undergoes isomerization in refluxing benzene to give an equil. mixt. of isopropyl and Pr complexes in approx. equal amts. Steric factors may

favor the n-alkyls vs. the sec-alkyls in the case of the alkyliridium(III)-phosphine complexes.

Answer 135:

Bibliographic Information

Allylic and homoallylic oxidation of cyclohexene by palladium(II) salts. Solvolytic behavior of possible organopalladium intermediates. Wolfe, Saul; Campbell, P. G. C. Dep. Chem., Queen's Univ., Kingston, ON, Can. Journal of the American Chemical Society (1971), 93(6), 1499-501. CODEN: JACSAT ISSN: 0002-7863. Journal written in English. CAN 74:124523 AN 1971:124523 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

A ?-allylic Pd complex is formed during the allylic oxidn. of cyclohexene by PdCl2-Hg(OAc)2. A dimeric ?-allylic Pd chloride complex is solvolyzed in HOAc in the presence of Hg(OAc)2 to give cyclohex-2-en-1-yl acetate (I). A dimeric ?-allylic Pd acetate complex (II) is not an intermediate in the allylic oxidn. with Pd(OAc)2; benzene is obtained in addn. to I in the HOAc solvolysis of II in the presence of HNO2.

Answer 136:

Bibliographic Information

Impurity effects in the fouling of heat transfer surfaces by organic coolants. Bancroft, A. R.; Charlesworth, D. H.; Duerksen, J. H. At. Energy Can. Ltd., Chalk River, At. Energy Can. Ltd., Chalk River (1965), AECL-1913 56 pp. Journal written in English. CAN 63:86338 AN 1965:486338 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Data compiled on the studies of the fouling characteristics of an org. coolant system suggested that fouling films were deposited by 2 mechanisms: (1) org. type fouling in which films were formed by chem. bonding of the org. portion of particulate matter in the coolant to the heat transfer surface; (2) mass-transfer fouling which involved Fe transport through an Fe-Cl-org. complex. The complex was formed by extracting Fe from the system walls and was partially decompd. at higher temps., thus depositing Fe on hot surfaces as ?-Fe or Fe3O4. Terphenyls alone did not contribute significantly to fouling. Nor did irradiation or oxidn. of terphenyls and addn. of water to coolants have a major effect on fouling. Cl impurities were by far the strongest promoter of fouling. Tests indicated that for a coolant with Cl contents ranging from <1 to 190 mg./kg., the fouling rates were from 1 to almost 200 ?/cm.2 hr. For the same Cl contents, the effects of CHCl:CCl2 were almost 20 times higher than those of chlorinated biphenyl and terphenyl, C6H5Cl, and FeCl3. Fouling film deposition rates with stainless steel systems were lower by factors of 5-10 than for similar tests with mild steel. For converting deposition rate to thermal resistance, the factor 140 degree-cm.4/g.-w. was recommended for low fouling rate systems. Experience in loop systems demonstrated that impurity levels could be controlled to maintain an acceptably low fouling rate, 0.2-0.3 ?/cm.2 hr. for power reactor operation. Cl impurities were effectively removed by Pd-on-Al2O3 catalyst, by Mg metal, and by removal of a small volatile portion of the coolant.

Answer 137:

Bibliographic Information

Homolytic aromatic substitution. XVII. Phenylation of tritiobenzene. Shih, Chang; Hey, D. H.; Williams, Gareth H. Queen Mary Coll., London, Journal of the Chemical Society (1959), 1871-3. CODEN: JCSOA9 ISSN: 0368-1769. Journal language unavailable. CAN 54:28509 AN 1960:28509 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

cf. C.A. 53, 10082a. Phenylation of tritiated benzene (Ia) with B2O2 (I) was shown not to involve a kinetic isotope effect. The substitution stage of this reaction was therefore considered to proceed by slow formation of an addn. complex between the Ph radical and the substrate, followed by loss of a H atom, probably as a result of interaction of the complex with another radical or other oxidizing agent in a fast, kinetically insignificant, stage. Ia was prepd. by the exchange reaction of C6H6 with tritiated aq. H2SO4. C6H6 (24 ml.) shaken 4 days at room temp. with 10 ml. tritiated 83% H2SO4, the C6H6 sepd. from the acid, washed, dried, and twice distd. gave product, b. 79.5?, n20D 1.5008. It was dild. with inactive C6H6. At tracer level of activity the mole fraction of Ia was of the order of 10-6, so that the concn. of doubly tritiated mols. was quite negligible. In two expts., 6 g. I was allowed to decomp. in 20 ml. and 12 ml. Ia, resp. for 24 hrs. at 80?. In expt. 3, 30 g. I was allowed to decomp. in 20 ml. Ia under the same conditions. The residual Ia was collected by distn. and redistd. once and analyzed for tritium activity by gas counting. The % conversion of Ia was 11, 18, and 55 in the 3 expts. Ia was introduced into a gas counter at known pressure together with the basic filling gas, which was butane (II). Ia formed 10-30% of the gas mixt. Before each detn. the counter tube was heated in a stream of warm air, pumped out continuously, then filled with pure II, flushed, and filled for the detn. of the activity of Ia. The following results were obtained (expt. no., sp. activity in counts/min./ml. original C6H6, sp. activity in counts/min./ml. residual C6H6 given): 1, 499, 496; 2, 499, 505; 3, 1298, 1271. It was concluded that the contribution of energy assocd. with the partial cleavage of the C-H or C-T bond could make, at the most, only a small contribution to the activation energy for the substitution reaction, and the mechanism was one of slow formation of an addn.

complex between the Ph radical and substrate, followed by loss of a H atom.

Answer 138:

Bibliographic Information

Swamping catalyst effect. II. Nuclear halogenation of aromatic aldehydes and ketones. Pearson, D. E.; Pope, H. W.; Hargrove, W. W.; Stamper, W. E. Vanderbilt Univ., Nashville, TN, Journal of Organic Chemistry (1958), 23 1412-19. CODEN: JOCEAH ISSN: 0022-3263. Journal language unavailable. CAN 53:39724 AN 1959:39724 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

cf. C.A. 51, 275d. Sufficient AlCl3 to complex with aromatic carbonyl compds. completely was found to deactivate the aliphatic side chain toward substitution and to permit nuclear substitution. In this manner, good yields of 3-bromo- (I), 3-bromo-4-methyl- (II), 3,4-dibromo- (III), 3-bromo-4-tert-butyl- (IV), 3-bromo-4-ethyl- (V), and 3,5-dibromo-4-methylacetophenones (VI) and of 3-BrC6H4CHO (VII), 3-bromo-4-tolualdehyde (VIII), 3-bromopropiophenone (IX), and 3,3'-dibromobenzophenone (X) were obtained. Good yields of chloroaldehydes and ketones, including tetrachloroacetophenones, and fair yields of iodoketones were also obtained by this method using the reagents Cl and iodine monochloride, resp. No other catalyst was found to function in the same manner as AlCl3 or AlBr3. General procedure is shown by prepn. of I. Acetophenone (Xa) (40.4 g.) was added during 10-15 min. in a slow stream to 110 g. AlCl3 in a 3 necked round bottomed flask (considerable heat evolved), and the material stirred to prevent charring; toward the end of the addn. the mass became molten and was easily stirred. In cases where the mass was higher melting than that of AlCl3-acetophenone, the AlCl3 was heated before the addn. of the ketone, and a min. temp. maintained to keep the complex molten. A molten mixt. was essential to the success of all halogenation reactions. Br(64.4 g.) added during 20 min. to the molten mass, after 1 hr. the mass solidified, the complex dropped portionwise into ice and 100 ml. concd. HCl, the oil extd. with Et2O, the Et2O washed with H2O and NaHCO3 soln., dried, and distd. gave 47 g. I, b0.5 75-6?, n25D 1.5740, m. 7-8?; oxime, m. 100-1?. When the mixt. was maintained at 80-5? during addn. of the Br rather than at room temp. the yield of I was 73.5% rather than 71%. The temp. of the reaction was not critical. Three runs were made under the same conditions to test the effect of mole ratio of catalyst as follows (run no., AlCl3, Xa, Br2, time in min., and % yield given): 1, 3, 1, 1, 69, 60;

2, 2.5, 1, 1.2, 65, 59; 3, 1.2, 1, 1, 180, 63. On the basis of these expts., the mole ratio AlCl3 2.5, ketone 1.0, and Br2 1.1 was used for most other expts. unless otherwise stated. The general procedure for prepg. 3-chloroacetophenone (XI) was similar to the above except that an inlet tube was used for the passage of Cl. The complex was made in the same way as above and 19.5 ml. Cl collected in a trap, the gas bubbled through H2SO4 into the complex during 5 hrs., stirred 1 hr. longer, and the mixt. handled as above giving 5.2 g. Xa and 38.8 g. XI, b0.5 61-3?, n25D 1.5480; oxime, m. 87.5-8.5?. IX was prepd. in 60% yield as plates, m. 40-1? (hexane);

semicarbazone, m. 181.5-2.0?. II was obtained in 56% yield, plates, m. 42-3? (ligroine); oxime, m. 94-5?. III was prepd. from p-bromoacetophenone, but the rate of bromination was slower than that for Xa. The complex in contact with Br was left 24 hrs. at room temp. (a higher temp. may have improved the yield) to yield 55% needles, m. 89-90? (hexane); oxime, m. 116-17?. Hypobromite oxidation of III gave 3,4-dibromobenzoic acid, m. 235-6?, and rearrangement of the oxime gave 3,4-dibromoacetanilide, m. 126.5-7.5?. IV was prepd. in 42% yield as an oil, b1 112-13?, d2625 1.325, n25D 1.5589-1.5595, which was not chem. pure. Oximation of IV apparently gave an oxime of good quality, m. 94.5-5.5?. Hydrolysis of the oxime with aq. HCl gave pure IV, b0.1 92?, n25D 1.5582. The Beckmann rearrangement of the oxime in concd. H2SO4 gave an impure anilide with the odor of polyisobutylene. The rearrangement in polyphosphoric acid 10 min. at 120? gave predominantly 3-bromo-4-tert-butylacetanilide, m. 141-2?. V was obtained in 59% yield, b2 105-6?, n25D 1.5668; 2,4-dinitrophenylhydrazone, m. 193-4?; oxime, m. 70-1?. The prepn. of VII was more difficult, more heat was evolved in forming the complex, the complex was more difficult to stir, and was less stable. BzH was added within 7 min. and the Br in 13 min. and the mixt. stirred an addnl. 4 hrs.;

care was taken to minimize the contact of VII with air during purification. The yield was 52%, b0.5 68?, n25D 1.5920; oxime, m. 72-3?. VIII was obtained in 44% yield, b0.5 79-86?, m. 48-9? (hexane). Oxidation of VII gave 72% 3-bromo-4-toluic acid, m. 205-6?. In the attempted di-bromination of Xa the mole ratio was Xa 1 Br 2.1, AlCl3 3.1. The reaction temp. was kept at 80-5? during addn. of Br and from 0.27 mole Xa was obtained 57.6 g. crude oil which yielded 0.07 mole I and a mixt. of dibromoacetophenones from which was isolated 4.6 g. 2,5-dibromoacetophenone (XII), m. 40-1?. Oxidation of XII gave 2,5-dibromobenzoic acid, m. 156-7?. Attempts to dibrominate Xa at room temp. led to complexes which could not be stirred and subsequently to mixts. of I and XII and some lachrymatory material assumed to be phenacyl bromide. In the attempted monobromination of 3-methylacetophenone a mixt. of brominated ketones was obtained, b2 94-117?, n25D 1.5632-1.5731, which could not be sepd. In the prepn. of VI the ratio of reagents was ketone 1, Br 2.3, and AlCl3 3. The crude VI distd. at 109-140?/0.5 mm., m. 102.5-3.5? (hexane), in 57% yield. VI by hypobromite oxidation gave 3,5-dibromo-4-toluic acid, m. 239.5-40.5?. X was obtained from 0.05 mole benzophenone, 0.11 mole AlCl3, and 0.11 mole Br. The Br added dropwise during 0.5-2 hrs., the temp. maintained at 25?, at the completion of the Br addn. the mixt. warmed to 70? and held there 1 or 2 hrs., the mixt. poured into ice and H2O, an equal vol. of concd. HCl added, the mixt. refluxed 1 hr., cooled, the solids removed, and crystd. gave 5-6 g. crude product and recrystn. gave X, plates, m. 138-40?. Attempts to prep. 3-bromobenzophenone in good yield were unsuccessful. Bromination at higher temps. resulted in resinous materials. The above prepn. of X is superior to any other method of direct bromination. The above results suggest that the orientation of the 2nd Br atom entering Xa was not well controlled.

The presence of a 4-Me group was sufficient to alter a mixed orientation to one where the 2nd Br atom entered meta to the ketone group. Although the yield of X was low it is the best yield recorded for direct bromination. The difficulty was the sepn. of other brominated ketones. BzH-AlCl3 complex maintained at 75-85? while treated with Cl during 120 min., the mixt. kept 3 hrs. at 80?, and decompd. as usual gave 43% conversion and 59% yield 3-chlorobenzaldehyde, b15 93-6?; phenylhydrazone, m. 133-5?; semicarbazone, m. 227-8?. The 3-chlorobenzoic acid obtained by oxidation m. 155-6?. In the dichlorination of Xa the ratio of reagents was AlCl3 2, Cl 2.3, and ketone 1. The complex maintained 12 hrs. at 50? during the addn. of Cl and decompd. in the usual manner gave on fractionation 43% 2,5-dichloroacetophenone (XIII), b2 71-2.5?, n25D 1.5595; oxime, m. 127-30?, rearranged to 2,5-dichloroacetanilide, m. 133-3.5?. Apparently XIII was the only dichloro, deriv. obtained although some crude mono- and trichlorinated compds. were isolated. In the dichlorination of 4-methylacetophenone the ratio of reagents was ketone 1, AlCl3 2.5, and Cl 2; the mixt. was heated 4 hrs. at 55? with addn. of Cl, a slurry of ice and HCl added all at once, the complex decompd. after standing in contact with H2O overnight (this reverse addn. for decompn. was used whenever it was too difficult to remove the complex from the flask), and the crude product stripped from the tar to give 7.2 g. 3-chloro-4-methylacetophenone, m. 45-6? (pentane), 8.3 g. 3,5-dichloro-4-methylacetophenone, b3 108-11?, m. 66-7? (oxidized to the acid, m. 191-2?) (oxime, m. 153.5-4.0?, rearranged to 3,5-dichloro-4-acetotoluidide, m. 220-1?), and traces of hexachlorobenzene, m. 230?. The remainder of the product was a solid of wide m.p. range. For trichlorination of Xa the mole ratio was ketone 1, AlCl3 2.5, and Cl 3. The reaction temp. was maintained at 40? during the 9-hr. addn. period, the complex decompd. as above, and distd. giving 11 g. XIII and 29.5 g.

crude 2,3,5-trichloroacetophenone (XIV), b7 132?, n25D 1.5720. Oxidation of XIV with NaOBr gave 2,3,4-trichlorobenzoic acid, m. 162.5-3.0?. XIV oxime, m. 143-5?, was rearranged in polyphosphoric acid to 2,3,5-trichloroacetanilide, m. 173?. 2,3,5,6-Tetrachloroacetophenone (XV.), m. 61.5-2.5?, was sepd. in 22% yield from the 2,3,4,5-isomer (XVI) by its lower b.p., b5 130?, and its difference in crystal form (rhombic plates which were handpicked). XV failed to form an oxime and a 2,4-dinitrophenylhydrazone and also failed to form the corresponding acid by hypobromite oxidation, but it was converted to 2,3,5,6-tetrachlorobenzoic acid by oxidation with C5H5N-H2O-KMnO4, m. 181.5-2.0?. XV was also cleaved to 1,2,4,5-tetrachlorobenzene, m. 139-9.5?, by 50% KOH in aq. alc. XVI b5 at 133?, 5% yield, m. 74-5.5? (pentane). XVI was converted to 2,3,4,5-tetrachlorobenzoic acid, m. 194-4.5? (oxime, m. 172-4?, rearranged to 2,3,4,5-tetrachloroacetanilide, m. 165-6?). During exhaustive chlorination of Xa, the mole ratio was ketone 1, AlCl3 2, and excess Cl; the mixt. was kept 18 hrs. at 50? and the crude product distd. in vacuo to give a liquid fraction, b1 107-11?, consisting chiefly of di- and trichlorinated Xa, and a solid fraction, b1 112-15?, consisting of a mixt. of XV and XVI. The mixt. of the latter 2 compds. was treated with 2,4-dinitrophenylhydrazine in acidic aq.

alc. and the 14 g. 2,4-dinitrophenylhydrazone of XVI sepd., m. 270?, from the unreacted XV. XV was recovered by concn. of the pentane, treatment of the concentrate with C, and recrystn., giving 54% XV. No pentachloroacetophenone was detected. During exhaustive chlorination of p-methylacetophenone the reaction was carried out as above except that the temp. was maintained 5 hrs. at 85? and then 1 hr. at 95?, the flow rate of Cl was increased with rise in temp., at the end of the 6th hr. (the mixt. froze to a solid), and the crude solid obtained from the Et2O ext. stripped from tar giving 78.4 g. crude distillate, which dissolved in hexane and chromatographed on Al2O3 gave hexachlorobenzene and 67% 2,3,5,6-tetrachloro-4-methylacetophenone (XVII), plates, m. 98.5-9.5? (alc.). XVII was converted to 2,3,5,6-tetrachlorotoluene, m. 93.5-4.0?. Thus, 2 chief differences exist between chlorination and bromination in swamping catalyst expts.: Cl must be fed into the system over a longer period to avoid its loss with the effluent gases; the reactivity of Cl is much greater thus giving less product control but also permitting the introduction of up to 4 Cl atoms. From these results it is suggested that the Cl atoms enter in the following sequence: m, ?, m, ? (more) and p (less). Iodine failed to react with Xa in the presence of swamping amts. of AlCl3. Only Xa with a small amt. of polymeric material was recovered. ICl reacted to give mixts. of 3-chloro- and 3-iodoacetophenone (XVIII). The mole ratio was ketone 1, AlCl3 2.5, ICl 1.5. The mixt. was held at room temp. while ICl was added dropwise during 70 min., the mixt. stirred several hrs., left at room temp. overnight, the Et2O ext. washed with NaHSO3, and the residue obtained on distn. fractionated to give 11.5 g. Xa and 22 g. crude 3-chloroacetophenone, b1.5 87-96?, n25D 1.5440-1.5490; short path distn. of the residue gave 12.5 g. XVIII, b1.5 112-20?, n25D 1.6188. Distn. through a Helipak column promoted decompn. of XVIII. Redistn. of 3-chloroacetophenone gave a pure compd., b0.5 61-3?, n25D 1.548; oxime, m. 87.5-8.5?. Slow distn. of XVIII gave a pure compd., b0.5 85-6?, m. 27.5-9.5?, n25D 1.620, d2525 1.754. The formation of these 2 compds. from ICl suggested that ICl was disproportionated by the catalyst to unreactive iodine and Cl. To prove this point the ICl was mixed with equimolar amts. of AlCl3 and this mixt. added portionwise to the ketone-AlCl3 complex. The yields of ketones of comparable purity to the ordinary runs were 32% chloro compd. and 6.5% XVIII. Reducing the molar ratio of AlCl3 reduced the yield of both products. The concn. of a single ketone in a mixt. could be estd. from the refractive index. The Cl deriv. (%) in Xa had the following refractive indices: 100%, 1.5479; 73.1%, 1.5427; 27.6%, 1.5354; 0%, 1.5319. For XVIII in the 3-Cl compd.: 100%, 1.6199; 77.1%, 1.5966; 50.9, 1.5765. For iodination of 4-methylacetophenone the molar ratio was ketone 1, AlCl3 2, and ICl 1.2. The mixt. was kept 0.5 hr. at 80?; the work up of halogenated ketones was the same as usual except a wash with aq. NaHSO3 was done first. The sepn. of the ketones was accomplished by slow distn. in a Vigreux column to give 22 g. crude starting material, 18 g. 3-chloro-4-methylacetophenone (XIX), b1 72-80?, m. 43-4? (hexane) (oxime, m. 94.5-5.5?; 2,4-dinitrophenylhydrazone, m. 245-7.5?), and 41 g. crude 3-iodo-4-methylacetophenone (XX), b1 106?, m. 41.5-2.0?, n25D 1.617 (supercooled liquid); oxime, m. 107-7.5?; 2,4-dinitrophenylhydrazone, m. 270-2? (decompn.). With more precise fractionation greater amts. of XIX and XX could be obtained. In a run carried out at room temp. the yields were 18% recovered ketone, 22% XIX, and 23% XX. Despite the fact that mixts. were obtained, this process is the method of choice for the synthesis of m-iodoketones. I was obtained in 77% yield by using anhyd. AlBr3. Xa (24 g.) added dropwise to 55 ml. 100% H2SO4 held at ice temp., 34 g. Br added, the mixt. allowed to reach room temp. during 6 hrs., decompd. with ice and worked up as usual gave only a small amt. of Xa and some phenacyl bromide. H2SO4 (184 g.) treated with 45.7 g. anhyd. AlCl3 as catalyst with addnl. 100 ml. H2SO4 added to make the system fluid, 40.4 g. Xa added dropwise and 53.7 g. Br added during 1 hr., and left overnight gave 45% phenacyl bromide, b1.5 71-3?. Chlorosulfonic acid gave a completely H2O sol. product BCl3 (142 g.) treated in the cold by dropwise addn. of 90 g. Xa then 20 min. with 120 g. Br gave no evolution of HBr; the mixt. allowed to warm to room temp. during 6 hrs. the products isolated gave Xa, some phenacyl bromide, and about 5 g. I. BF3 similarly used gave a dark polymerized mass from which a few g. of lachrymatory oil could be distd. BzH (51.9 g.) added dropwise to 454 g. SnCl4 and the mixt. treated 3 hrs. with Cl, left 5 hrs., and isolated as usual gave 37 g. BzH and 3 g. residue, which on oxidation gave a quant. yield of BzOH. The mechanism of the reaction is discussed.

Answer 139:

Bibliographic Information

Alkynyl compounds of transition metals. VII. Alkynylpentacyanocomplexes of iron(II). Nast, R.; Urban, R. Univ. Heidelberg, Germany. Z. anorg. u. allgem. Chem. (1957), 289 244-9. Journal language unavailable. CAN 51:51089 AN 1957:51089 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

cf. C.A. 51, 3347a. K4Fe(CN)5C2Ph (I) and K4Fe(CN)5C2Me are formed in 50% and 67% yield, resp., by mixing excess

K2Fe(CN)5NO (II) with KC2Ph and KC2Me, resp., in liquid NH3 at -70?. The stable, yellow, diamagnetic salts decomp. in moist air, and form yellow aq. solns., which require 1 equiv. HCl per mole; further addn. of acid yields HCN and, on boiling, Berlin blue. The alkynes released in the hydrolysis undergo secondary reactions; I gives colorless cryst. org. compds. with cinnamon-like odor. K4Fe(CN)5C2H?NH3 (III) is similarly prepd. (90% yield) at -78?, from II and C2H2, but if the mixt. is warmed to -33? before filtration the ppt. is rapidly oxidized to blue-black K8[(NC)5Fe-C?C-C?C-Fe(CN)5]?2NH3 (IV), which explodes in moist air, on addn. of a drop of H2O, or on heating. IV is also diamagnetic but becomes paramagnetic on standing for several days. The proposed formation mechanism for the mononuclear complexes is: (1) KC2R + NH3 = HC2R + KNH2, (2) K2Fe(CN)5NO + KC2R + KNH2 = K4Fe(CN)5C2R + ON-NH2; (3) ON-NH2 = N2 + H2O (R = Ph, Me, or H).

Answer 140:

Bibliographic Information

Air oxidation of hydrocarbons. III. Mechanism of inhibitor action in benzene and chlorobenzene solutions. Hammond, George S.; Boozer, Charles E.; Hamilton, Chester E.; Sen, Jyotirindra N. Iowa State Coll., Ames, Journal of the American Chemical Society (1955), 77 3238-44. CODEN: JACSAT ISSN: 0002-7863. Journal language unavailable. CAN 50:19973 AN 1956:19973 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

Most of the potent com. antioxidants are either phenols of aromatic amines of the type ArNHR. The labile H have been viewed as the critical part of the structures and the characterization of the inhibition products shows that they are indeed removed during the course of the reactions. However, several lines of evidence indicate that H abstraction is not a discrete 1st step in the inhibition process. The key observations are: (1) there is no kinetic isotopic effect noted if PhNDMe (XXI) and Ph2ND (XXII) are compared with the PhNHMe and Ph2NH; (2) specifically designed compds. such as (PhNH)2, do not prove to be as potent as inhibitors as their close relatives despite the fact that the former apparently should have a good aptitude for the H abstraction reaction; (3) the effects of substituents on the inhibitory efficiency of aromatic amines and phenols can be correlated with the Hammett equation in a manner which suggests that electron removal from the inhibitor is of paramount importance; (4) despite the absence of labile H, PhNMe2 (XXIII) shows distinct, but weak, inhibitory action and p-C6H4(NMe2)2 (XXIV) is a strong inhibitor; and (5) it has been found that XXIV is converted to a complex which may be hydrolyzed to form a W.ovrddot.urster dye. These data are held to be consistent with the view that the 1st step of the inhibition process is the reversible formation of a loose mol. complex between the inhibitor and RO2?. This complex is then destroyed by reaction with a 2nd RO2?radical. 1,2,3,4-Tetrahydronaphthalene washed with concd. H2SO4 until the acid layer showed no color, washed with H2O, dried, and distd. under N gave purified material, b. 204.5-5.0?, nD25 1.5444. 9,10-Dihydrophenazine, m. 305-6? (scaled tube) (from PhCl), gave phenazine, m. 169?. XXI and XXII were prepd. by exchange in acid soln. of the amine with 99.8% D2O; each exchange effected by refluxing the mixt. about 0.5 hr., removing the H2O layer, adding fresh D2O, and carrying out 5 exchanges with 400% excess D2O on 1-g.

samples of the amines; at least 60% of the available H had been replaced by D. XXI and XXII gave oxidation rate curves which were identical with those obtained with PhNHMe and Ph2NH in the inhibition runs with cumene and Tetralin in PhCl at 62.5?. A no. of inhibitors (In) were evaluated in PhCl with Tetralin as the substrate at 62.5? (inhibitor, k3/kIn1/2 ? 104, and the relative efficiency referred to PhOH as the standard are given): PhNHMe, 5.27, 0.67; PhOH, 3.6, 1.00; XVII, 1.07, 3.30; XVIII, 1.07, 3.30; p-MeOC6H4NHMe, 0.80, 4.60; p-MeC6H4NHMe, 2.5, 1.42; p-BrC6H4NHMe, 7.8, 0.45; p-O2NC6H4NHMe, 1970, 0.0018. The inhibition of the oxidation of I in PhCl by various inhibitors at 62.5? and at l atm. O pressure was detd. in the usual manner in the presence of a standard concn. of the inhibitor and the relative efficiency (given) referred to PhOH as the standard calcd. for: III 3.3, IV 1.3, V 1.6, VI 14, VII 1.2, VIII 6.1, IX 1.00, X 3.3, XI 2.4, XII 2.1, XIII 16, XIV 6.7, XV 5.6, XVI 1.7. The oxidation of Tetralin in the presence of VII was studied in a series of 6 solvents at 62.5? (solvent, k3/kIn1/2 ? 104, and dielec. const. given): C6H6 4.8, 2.27; o-C6H4Cl2, 6.0, 10.36; PhCl, 5.27, 5.62; PhNO2, 5.15, 34.82; MeNO2, 1.92, 35.86; CCl4, 0.63, 2.23. XXIV was very susceptible to air oxidation and, therefore, difficult to obtain in a pure state; standard solns. of XXIV changed appreciably in less than 1 day. During the course of the inhibition period in the expts. in MeNO2 the soln. took on the characteristic purple color of the W.ovrddot.urster cation, but the color had disappeared by the end of the inhibition period; this color was also developed by the addn. of H2O to PhCl contg. partially oxidized inhibitor.

Answer 141:

Bibliographic Information

Alkylation and arylation of 1,9-benz-10-anthrone by Grignardization. Oxidative degradation of 4-phenyl-1,9-benz-10-anthrone.

Charrier, G.; Gighi, E. Berichte der Deutschen Chemischen Gesellschaft [Abteilung] B: Abhandlungen (1936), 69B 2211-32. CODEN: BDCBAD ISSN: 0365-9488. Journal language unavailable. CAN 31:3010 AN 1937:3010 CAPLUS (Copyright (C) 2007 ACS on SciFinder (R))

Abstract

cf. Atti soc. progr. sci., 22nd meeting, Bari, 1933, and earlier papers. It had been shown that alkyl- and arylmagnesium halides add to ordinary 1,9-benz-10-anthrone (I) chiefly in the 1,4-position, forming in general a 4-alkyl- or 4-arylbenzanthrone. The products were assigned such a structure because oxidn. with CrO3 gave the corresponding 4-substituted anthraquinone-1-carboxylic acids which, in turn, were converted in every case into 1,4-C6H4(CO)2C6H2(CO2H)2 (II) by HNO3. The 4-phenylbenzanthrone (III) obtained from I with PhMgBr behaves quite differently on oxidn., however. Clar (C. A. 26, 4046) and Nakanishi (C. A. 28, 762.9) assumed that in the Grignard reaction 1,6-addn. takes place with formation of bz-3-derivs., but their belief that the products of CrO3 oxidn. of the latter are 1-C6H4(CO)2C6H3CO2H was erroneous. N.'s prepn. of his supposed bz-3-butylbenzanthrone was repeated; oxidn. with CrO3 gave 4-butylanthraquinone-1-carboxylic acid (IV), which in turn yielded II. Clar now (C. A. 30, 1051.8) agrees that the products of Grignardization of I are undoubtedly 4-derivs.; cf. also Allen and Overbaugh, C. A. 29, 3673.5. The latter by alk. KMnO4 oxidn. of III obtained 4-phenylanthraquinone-1-carboxylic acid (V); if they had been familiar with the work of the authors they would not have overlooked the main product of the oxidn., viz. biphenyl-3,4-dicarboxylic-2(?)-glyoxylic acid (VI), which is formed in about 47% yield with only 8% (as the Na salt) of V. Although the rule that Grignardization of I (and also of its bz-1-Ph deriv.) gives 4-derivs. is quite general, there are some exceptions, as found by the authors with MeMgI and by Allen and Overbaugh (C. A. 29, 5835.2) with tert-BuMgCl. The authors have now succeeded in completely clearing up the mechanism of the oxidative cleavage of III in both alk. and acid soln. With alk. KMnO4 100 parts III gives about 17 parts VI (as the salt C21H11O4Na.3H2O) + 3(CO2H)2 + CO2; with KMnO4 in dil.

H2SO4 VI yields biphenyl-2,3,4-tricarboxylic acid (VII), and both VI and VII on heating with concd. H2SO4 at 150-60? give fluorenone-1,2-dicarboxylic acid (VIII), from which were prepd. the anhydride, the mono- and di-Me esters, and, by partial decarboxylation, the 2-monocarboxylic acid (IX). With PhNHNH2 VII yields 2 products: the simple hydrazone (X) and the anilinoimide phenylhydrazone (XI). Whereas X, as a dicarboxylic acid, is very easily sol. in alkalies and carbonates, XI is wholly insol. V is completely converted into VI by KMnO4 in boiling and concd. alk. soln., and it may therefore be concluded that it is the 1st product of the oxidative cleavage of III. The structure of V, proven by its decarboxylation to C6H4(CO)2C6H3Ph (Allen and Overbaugh) is further confirmed by its redn. with Zn dust in NH4OH to 4-phenylanthracene-1-carboxylic acid (XII) which is decarboxylated to the known 1-phenylanthracene, m. 110-12?. The introduction of Ph into the 4-position of I makes the bz-ring vulnerable to oxidative cleavage by alk. KMnO4. The oxidn. of III with CrO3-AcOH proceeds through a III-CrO3 complex (XIII) to form an acid C22H12O4 (XIV) having 1 more C atom than was originally believed. When III is heated with CrO3-AcOH there first seps. the bright red XIII, which on hydrolysis regenerates III and H2CrO4. The enolic acid XIV is indifferent in the cold to carbonates and NaOH, but heating with NaOH converts it into the salt of the ketocarboxylic acid (XV). The free XV could not be isolated. Long boiling with 20% NaOH opens the xanthone ring at the O atom with formation of 9-(2-hydroxybenzoyl)fluorene-1,9-dicarboxylic acid (XVI). The structure of XV was proven by oxidative degrdn. with alk. KMnO4 to salicylic acid and biphenyl-2,3,2'-tricarboxylic acid (XVII). Dry distn. with Zn dust gives phenanthrene, benzene, a little Ph2 and PhOH, and the same 1,2,3,4-dibenzoxanthone (XVIII) as is obtained by simple decarboxylation of XIV. XVII was further identified by conversion with concd.

H2SO4 at 150-60? into fluorenone-1,5-dicarboxylic acid (XIX) which was decarboxylated with quinoline and Cu to the 1-monocarboxylic acid (XX). XVIII is obtained quant. by heating XIV with quinoline and reduced Cu; on dry distn. with Zn dust it yields chiefly phenanthrene; it is very stable to oxidn. but on long treatment with alk. KMnO4 gives diphenic acid; heating with alkalies in alc. at 180? produces 9-hydroxy-10-(2-hydroxybenzoyl)phenanihrene (XXI), and alkali fusion gives salicylic acid and 9-hydroxyphenanthrene (XXII). 4-Propyl-1,9-benz-10-anthrone, from I and PrMgI, yellow, m. 83-4?; 4-propylanthraquinone-1-carboxylic acid, straw-colored, m. 180-1?, reacts strongly acid and vigorously decomps. alkali carbonates. 4-Butyl-1,9-benz-10-anthrone (12 g. from 20 g. I), yellow, m. 99?. IV, yellowish white, m. 175?. III, obtained in 75% yield, m. 186?. V, light yellow, m. 288-90?. VI, m. 256-7? (decompn.). VII, repeatedly dissolved in ether, treated with benzene and freed from the ether by distn., yields crystals, m. 210-12? (decompn.), having the compn. of an anhydride of VII. VIII, lemon-yellow, m. 330?; di-Me ester, yellow, m. 199?; mono-Me ester, m. around 230? (decompn.), resolidifies 235-40? and m. again 315-20?; anhydride, yellow, m. 315-20?. X, yellow, m. 330?; Me ester, m. 186?. Because of the discrepancies in the literature on IX, the 1-isomer (XX), orange-red, m. 191-2?, was also prepd. from XIX, which is made by the action of

concd. H2SO4 at 150-60? on XVII; Me ester, m. 89?. XI, m. 276? (decompn.). X, light yellow, m. 305-7?, shows a tendency to lose water and form the anhydride, faintly yellowish, m. 315?. XII, yellow, m. 246-7?, shows strong green fluorescence in AcOH. Enolic 1,2,3,4-dibenzoxanthone-o-carboxylic acid (XIV), m. 296-305? (decompn.), does not give the characteristic red color of anthraquinone derivs. with alkalies and Na2S2O4 or Zn dust. Me ester of XV, m. 217?. XIV is not attacked by boiling concd. H2SO4. XVI (6.3 g. from 7 g. XIV boiled 14 h. with 350 g.

of 20% NaOH), m. 210-12? (decompn.), reacts strongly acid and dissolves in cold Na2CO3 with vigorous evolution of CO2; with hot concd. H2SO4 it yields a light yellow condensation product; in alc. it gives a red color with FeCl3. XVII, m. 195-6? (decompn.). XIX, K2Cr2O7-colored crystals, m. 295-9? (decompn.); di-Me ester, faintly yellow, m. 120?. XVIII, m. 207-9?, reacts neutral, dissolves in concd. H2SO4 with yellow color and faint green fluorescence; the color does not change on heating. XXI, dark yellow, m. 152?, gives in alc. with FeCl3 a transient green color, dissolves in cold alkalies with orange-red color changed to yellow by excess of alkali, is insol. in alkali carbonates and is completely pptd. from alk. soln. by CO2. Dil. alkalies or boiling alc. acidified with HCl quant. convert it into XVIII. With concd. H2SO4 it gives a dark red color gradually changing to yellow with faint fluorescence. XXII, m. 153-4?; 10:benzeneazo deriv., red, m. 165?; picrate, m. 190?.

Answer 142:

Bibliographic Information

Reevaluation of the mechanism of the amination of aryl halides catalyzed by BINAP-ligated palladium complexes. Shekhar Shashank; Ryberg Per; Hartwig John F; Mathew Jinu S; Blackmond Donna G; Strieter Eric R; Buchwald Stephen L Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107, USA Journal of the American Chemical Society (2006), 128(11), 3584-91. Journal code: 7503056. ISSN:0002-7863. Journal; Article; (JOURNAL ARTICLE); (RESEARCH SUPPORT, N.I.H., EXTRAMURAL); (RESEARCH SUPPORT, NON-U.S. GOV'T) written in English. PubMed ID 16536531 AN 2006148603 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

Two previous mechanistic studies of the amination of aryl halides catalyzed by palladium complexes of 1,1'-binaphthalene-2,2'-diylbis(diphenylphosphine) (BINAP) are reexamined by the authors of both studies. This current work includes a detailed study of the identity of the BINAP-ligated palladium complexes present in reactions of amines with aryl halides and rate measurements of these catalytic reactions initiated with pure precatalysts and precatalysts generated in situ from [Pd2(dba)3] and BINAP. This work reveals errors in both previous studies, and we describe our current state of understanding of the mechanism of this synthetically important transformation. 31P NMR spectroscopy shows that several palladium(0) species are present in the catalytic system when the catalyst is generated in situ from [Pd2(dba)3] and BINAP, and that at least two of these complexes generate catalytic intermediates. Further, these spectroscopic studies and accompanying kinetic data demonstrate that an apparent positive order in the concentration of amine during reactions of secondary amines is best attributed to catalyst decomposition. Kinetic studies with isolated precatalysts show that the rates of the catalytic reactions are independent of the identity and the concentration of amine, and studies with catalysts generated in situ show that the rates of these reactions are independent of the concentration of amine. Further, reactions catalyzed by [Pd(BINAP)2] with added BINAP are found to be first-order in bromoarene and inverse first-order in ligand, in contrast to previous work indicating zero-order kinetics in both.

These data, as well as a correlation between the decay of bromobenzene in the catalytic reaction and the predicted decay of bromobenzene from rate constants of studies on stoichiometric oxidative addition, are consistent with a catalytic process in which oxidative addition of the bromoarene occurs to [Pd(BINAP)] prior to coordination of amine and in which [Pd(BINAP)2], which generates [Pd(BINAP)] by dissociation of BINAP, lies off the cycle. By this mechanism, the amine and base react with [Pd(BINAP)(Ar)(Br)] to form an arylpalladium amido complex, and reductive elimination from this amido complex forms the arylamine.

Answer 143:

Bibliographic Information

Oxidative addition of phenyl bromide to Pd(BINAP) vs Pd(BINAP)(amine). Evidence for addition to Pd(BINAP). Shekhar Shashank; Ryberg Per; Hartwig John F Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107, USA Organic letters (2006), 8(5), 851-4. Journal code: 100890393. ISSN:1523-7060. Journal; Article; (JOURNAL ARTICLE); (RESEARCH SUPPORT, N.I.H., EXTRAMURAL); (RESEARCH SUPPORT, NON-U.S. GOV'T) written in English. PubMed ID 16494457 AN 2006109507 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

[STRUCTURE: SEE TEXT] The rates of oxidative addition of phenyl bromide to [Pd(BINAP)2] have been measured in the presence and absence of added amine to assess a previous hypothesis that addition to [Pd(BINAP)(amine)] is faster than addition to [Pd(BINAP)]. These data show that addition to the amine complex is not faster than addition to [Pd(BINAP)]. Instead, they are consistent with oxidative addition, even in the presence of amine, to [Pd(BINAP)] as the major pathway. These data underscore the value of studying the stoichiometric reactions of isolated complexes when assessing the mechanism of a catalytic process.

Answer 144:

Bibliographic Information

The F/Ph rearrangement reaction of [(Ph3P)3RhF], the fluoride congener of Wilkinson's catalyst. Macgregor Stuart A; Roe D Christopher; Marshall William J; Bloch Karen M; Bakhmutov Vladimir I; Grushin Vladimir V School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, UK. s.a.macgregor@hw.ac.uk Journal of the American Chemical Society (2005), 127(43), 15304-21. Journal code: 7503056. ISSN:0002-7863. Journal; Article; (JOURNAL ARTICLE) written in English. PubMed ID 16248673 AN 2005599797 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

The fluoride congener of Wilkinson's catalyst, [(Ph(3)P)(3)RhF] (1), has been synthesized and fully characterized. Unlike Wilkinson's catalyst, 1 easily activates the inert C-Cl bond of ArCl (Ar = Ph, p-tolyl) under mild conditions (3 h at 80 degrees C) to produce trans-[(Ph(3)P)(2)Rh(Ph(2)PF)(Cl)] (2) and ArPh as a result of C-Cl, Rh-F, and P-C bond cleavage and C-C, Rh-Cl, and P-F bond formation. In benzene (2-3 h at 80 degrees C), 1 decomposes to a 1:1 mixture of trans-[(Ph(3)P)(2)Rh(Ph(2)PF)(F)] (3) and the cyclometalated complex [(Ph(3)P)(2)Rh(Ph(2)PC(6)H(4))] (4). Both the chloroarene activation and the thermal decomposition reactions have been shown to occur via the facile and reversible F/Ph rearrangement reaction of 1 to cis-[(Ph(3)P)(2)Rh(Ph)(Ph(2)PF)] (5), which has been isolated and fully characterized. Kinetic studies of the F/Ph rearrangement, an intramolecular process not influenced by extra phosphine, have led to the determination of E(a) = 22.7 +/- 1.2 kcal mol(-)(1), DeltaH(++) = 22.0 +/- 1.2 kcal mol(-)(1), and DeltaS(++) = -10.0 +/- 3.7 eu. Theoretical studies of F/Ph exchange with the [(PH(3))(2)(PH(2)Ph)RhF] model system pointed to two possible mechanisms: (i) Ph transfer to Rh followed by F transfer to P (formally oxidative addition followed by reductive elimination, pathway 1) and (ii) F transfer to produce a metallophosphorane with subsequent Ph transfer to Rh (pathway 2). Although pathway 1 cannot be ruled out completely, the metallophosphorane mechanism finds more support from both our own and previously reported observations. Possible involvement of metallophosphorane intermediates in various P-F, P-O, and P-C bond-forming reactions at a metal center is discussed.

Answer 145:

Bibliographic Information

Oxidative addition of methyl iodide to a new type of binuclear platinum(II) complex: a kinetic study. Jamali Sirous; Nabavizadeh S Masoud; Rashidi Mehdi Chemistry Department, Persian Gulf University, Bushehr 75168, Iran

Inorganic chemistry (2005), 44(23), 8594-601. Journal code: 0366543. ISSN:0020-1669. Journal; Article; (JOURNAL ARTICLE) written in English. PubMed ID 16271001 AN 2005592945 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

A new organodiplatinum(II) complex cis,cis-[Me2Pt(mu-NN)(mu-dppm)PtMe2] (1), in which NN = phthalazine and dppm = bis(diphenylphosphino)methane, is synthesized by the reaction of cis,cis-[Me2Pt(mu-SMe2)(mu-dppm)PtMe2] with 1 equiv of NN. Complex 1 has a 5d(pi)(Pt) --> pi(imine) metal-to-ligand charge-transfer band in the visible region, which was used to easily follow the kinetics of its reaction with MeI. Meanwhile, the complex contains a robust bridging dppm ligand that holds the binuclear integrity during the reaction. A double MeI oxidative addition was observed, as shown by spectrophotometry and confirmed by a low-temperature 31P NMR study. The classical S(N)2 mechanism was suggested for both steps, and the involved intermediates were suggested. Consistent with the proposed mechanism, the rates of the reactions at different temperatures were slower in benzene than in acetone and large negative deltaS values were found in each step. However, some abnormalities were observed in the related rate constants and deltaS values, which were demonstrated to be due to the associative involvement of the polar acetone molecules in the reactions. The rates are almost 6 times slower in the second step as compared to the first step because of the electronic effects transmitted through the ligands and the steric effects.

Answer 146:

Bibliographic Information

Mechanism of the mild functionalization of arenes by diboron reagents catalyzed by iridium complexes. Intermediacy and chemistry of bipyridine-ligated iridium trisboryl complexes. Boller Timothy M; Murphy Jaclyn M; Hapke Marko; Ishiyama Tatsuo; Miyaura Norio; Hartwig John F Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107, USA Journal of the American Chemical Society (2005), 127(41), 14263-78. Journal code: 7503056. ISSN:0002-7863. Journal; Article; (JOURNAL ARTICLE); (RESEARCH SUPPORT, NON-U.S. GOV'T) written in English. PubMed ID 16218621 AN 2005543718 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

This paper describes mechanistic studies on the functionalization of arenes with the diboron reagent B(2)pin(2) (bis-pinacolato diborane(4)) catalyzed by the combination of 4,4'-di-tert-butylbipyridine (dtbpy) and olefin-ligated iridium halide or olefin-ligated iridium alkoxide complexes. This work identifies the catalyst resting state as [Ir(dtbpy)(COE)(Bpin)(3)] (COE = cyclooctene, Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl). [Ir(dtbpy)(COE)(Bpin)(3)] was prepared by independent synthesis in high yield from [Ir(COD)(OMe)](2), dtbpy, COE, and HBpin. This complex is formed in low yield from [Ir(COD)(OMe)](2), dtbpy, COE, and B(2)pin(2). Kinetic studies show that this complex reacts with arenes after reversible dissociation of COE. An alternative mechanism in which the arene reacts with the Ir(I) complex [Ir(dtbpy)Bpin] after dissociation of COE and reductive elimination of B(2)pin(2) does not occur to a measurable extent. The reaction of [Ir(dtbpy)(COE)(Bpin)(3)] with arenes and the catalytic reaction of B(2)pin(2) with arenes catalyzed by [Ir(COD)(OMe)](2) and dtbpy occur faster with electron-poor arenes than with electron-rich arenes. However, both the stoichiometric and catalytic reactions also occur faster with the electron-rich heteroarenes thiophene and furan than with arenes, perhaps because eta(2)-heteroarene complexes are more stable than the eta(2)-arene complexes and the eta(2)-heteroarene or arene complexes are intermediates that precede oxidative addition. Kinetic studies on the catalytic reaction show that [Ir(dtbpy)(COE)(Bpin)(3)] enters the catalytic cycle by dissociation of COE, and a comparison of the kinetic isotope effects of the catalytic and stoichiometric reactions shows that the reactive intermediate [Ir(dtbpy)(Bpin)(3)] cleaves the arene C-H bond. The barriers for ligand exchange and C-H activation allow an experimental assessment of several conclusions drawn from computational work.

Most generally, our results corroborate the conclusion that C-H bond cleavage is turnover-limiting, but the experimental barrier for this bond cleavage is much lower than the calculated barrier.

Answer 147:

Bibliographic Information

Distinct mechanisms for the oxidative addition of chloro-, bromo-, and iodoarenes to a bisphosphine palladium(0) complex with hindered ligands. Barrios-Landeros Fabiola; Hartwig John F Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107, USA Journal of the American Chemical Society (2005), 127(19), 6944-5. Journal code: 7503056. ISSN:0002-7863. Journal; Article; (JOURNAL ARTICLE); (RESEARCH SUPPORT, N.I.H., EXTRAMURAL); (RESEARCH SUPPORT, U.S. GOV'T, P.H.S.) written in English. PubMed ID 15884925 AN 2005247158 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Answer 148:

Bibliographic Information

Mononuclear and dinuclear monoperoxovanadium(v) complexes with a hetero ligand. 1.(1) Self-decomposition reaction, detection of reactive oxygen species, and oxidizing ability. Kanamori Kan; Nishida Kazuya; Miyata Nanako; Shimoyama Toshiyuki; Hata Kaori; Mihara Chie; Okamoto Ken-Ichi; Abe Yuriko; Hayakawa Shingo; Matsugo Seiichi Department of Chemistry, Faculty of Science, Toyama University, Gofuku 3190, Toyama 930-8555, Japan. kanamori@sci.toyama-u.ac.jp Inorganic chemistry (2004), 43(22), 7127-40. Journal code: 0366543. ISSN:0020-1669. Journal; Article; (JOURNAL ARTICLE) written in English. PubMed ID 15500351 AN 2004562982 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

A mononuclear peroxovanadium(V) complex with histamine-N,N-diacetate (histada), K[VO(O(2))(histada)], and a dinuclear peroxovanadium(V) complex with 2-oxo-1,3-diaminopropane-N,N,N',N'-tetraacetate (dpot), Cs(3)[(VO)(2)(O(2))(2)(dpot)], were prepared and characterized. The self-decomposition reaction was examined for these peroxovanadium(V) complexes as well as for K[VO(O(2))(cmhist)] (cmhist = N-carboxymethylhistidinate). The reaction profiles depicted by the absorbance change in the UV-vis spectrum show a sigmoid shape with an induction period. The induction period is reduced by the addition of acid, fluoride, thiocyanate, VO(2+), VO(2)(+), and trolox compared to the solution containing perchlorate. On the other hand, the induction period was elongated by the addition of chloride, bromide, and 2-tert-butyl-p-cresol. These behaviors are discussed on the basis of a radical chain mechanism. The self-decomposition reactions have also been followed by the (1)H and (51)V NMR and EPR spectra. These spectral studies as well as the UV-vis spectral study indicate that vanadium(V) is partly reduced to vanadium(IV) in the self-decomposition process. The histada complex yields a mixed-valence dinuclear complex in a concentrated solution, and the dpot complex yields a mixed-valence tetranuclear complex. The reduction of vanadium ion suggests that the peroxo ligand may act as a reducing agent. In order to know the fate of the peroxo ligand, we tried to detect superoxide anion and hydroxyl radical, which were anticipated to be produced in the self-decomposition process. The formation of superoxide anion was spectrophotometrically confirmed using two independent methods, including the reduction of cytochrome c and the reduction of sodium 4-[3-(iodophenyl)-2-(4-nitrophenyl)-2H-5-tetrazolio]-1,3-benzene disulfonate (WST-1). The formation of hydroxyl radical was confirmed by an EPR spin trapping technique. The oxidizing abilities of the peroxovanadium(V) complexes toward bovine serum albumin (BSA) were also evaluated.

In the protein carbonyl assay, it was found that the total amount of protein carbonyl in BSA was increased by the reaction with the peroxovanadium complexes in the concentration-dependent manner. In addition, the oxidation of sulfhydryl group in BSA induced by the peroxovanadium complexes was confirmed.

Answer 149:

Bibliographic Information

Reductive elimination/oxidative addition of carbon-hydrogen bonds at Pt(IV)/Pt(II) centers: mechanistic studies of the solution thermolyses of Tp(Me2)Pt(CH3)2H. Jensen Michael P; Wick Douglas D; Reinartz Stefan; White Peter S; Templeton Joseph L; Goldberg Karen I Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700, USA Journal of the American Chemical Society (2003), 125(28), 8614-24. Journal code: 7503056. ISSN:0002-7863. Journal; Article; (JOURNAL ARTICLE) written in English. PubMed ID 12848569 AN 2003320731 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

Reductive elimination of methane occurs upon solution thermolysis of kappa(3)-Tp(Me)2Pt(IV)(CH(3))(2)H (1, Tp(Me)2 = hydridotris(3,5-dimethylpyrazolyl)borate). The platinum product of this reaction is determined by the solvent. C-D bond activation occurs after methane elimination in benzene-d(6), to yield kappa(3)-Tp(Me)2Pt(IV)(CH(3))(C(6)D(5))D (2-d(6)), which undergoes a second reductive elimination/oxidative addition reaction to yield isotopically labeled methane and kappa(3)-Tp(Me)2Pt(IV)(C(6)D(5))(2)D (3-d(11)). In contrast, kappa(2)-Tp(Me)2Pt(II)(CH(3))(NCCD(3)) (4) was obtained in the presence of acetonitrile-d(3), after elimination of methane from 1. Reductive elimination of methane from these Pt(IV) complexes follows first-order kinetics, and the observed reaction rates are nearly independent of solvent. Virtually identical activation parameters (DeltaH(++)(obs) = 35.0 +/- 1.1 kcal/mol, DeltaS(++)(obs) = 13 +/- 3 eu) were measured for the reductive elimination of methane from 1 in both benzene-d(6) and toluene-d(8). A lower energy process (DeltaH(++)(scr) = 26 +/- 1 kcal/mol, DeltaS(++)(scr) = 1 +/- 4 eu) scrambles hydrogen atoms of 1 between the methyl and hydride positions, as confirmed by monitoring the equilibration of kappa(3)-Tp(Me)()2Pt(IV)(CH(3))(2)D (1-d(1)()) with its scrambled isotopomer, kappa(3)-Tp(Me)2Pt(IV)(CH(3))(CH(2)D)H (1-d(1'). The sigma-methane complex kappa(2)-Tp(Me)2Pt(II)(CH(3))(CH(4)) is proposed as a common intermediate in both the scrambling and reductive elimination processes. Kinetic results are consistent with rate-determining dissociative loss of methane from this intermediate to produce the coordinatively unsaturated intermediate [Tp(Me)2Pt(II)(CH(3))], which reacts rapidly with solvent. The difference in activation enthalpies for the H/D scrambling and C-H reductive elimination provides a lower limit for the binding enthalpy of methane to [Tp(Me)2Pt(II)(CH(3))] of 9 +/- 2 kcal/mol.

Answer 150:

Bibliographic Information

Electronic and medium effects on the rate of arene C [bond] H activation by cationic Ir(III) complexes. Tellers David M; Yung Cathleen M; Arndtsen Bruce A; Adamson Dan R; Bergman Robert G Division of Chemical Sciences, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, USA Journal of the American Chemical Society (2002), 124(7), 1400-10. Journal code: 7503056. ISSN:0002-7863. Journal; Article; (JOURNAL ARTICLE) written in English. PubMed ID 11841308 AN 2002140909 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

A detailed mechanistic study of arene C [bond] H activation in CH(2)Cl(2) solution by Cp(L)IrMe(X) [L = PMe(3), P(OMe)(3); X = OTf, (CH(2)Cl(2))BAr(f); (BAr(f) = B[3,5-C(6)H(3)(CF(3))(2)](4))(-)] is presented. It was determined that triflate dissociation in Cp(L)IrMe(OTf), to generate tight and/or solvent-separated ion pairs containing a cationic iridium complex, precedes C [bond] H activation. Consistent with the ion-pair hypothesis, the rate of arene activation by Cp(L)IrMe(OTf) is unaffected by added external triflate salts, but the rate is strongly dependent upon the medium. Thus the reactivity of Cp(PMe(3))IrMe(OTf) can be increased by almost 3 orders of magnitude by addition of (n-Hex)(4)NBAr(f), presumably because the added BAr(f) anion exchanges with the OTf anion in the initially formed ion pair, transiently forming a cation/borate ion pair in solution (special salt effect). In contrast, addition of (n-Hex)(4)NBAr(f) to [CpPMe(3)Ir(Me)CH(2)Cl(2)][BAr(f)] does not affect the rate of benzene activation; here there is no initial covalent/ionic pre-equilibrium that can be perturbed with added (n-Hex)(4)NBAr(f). An analysis of the reaction between Cp(PMe(3))IrMe(OTf) and various substituted arenes demonstrated that electron-donating substituents on the arene increase the rate of the C [bond] H activation reaction. The rate of C(6)H(6) activation by

[Cp(PMe(3))Ir(Me)CH(2)Cl(2)][BAr(f)] is substantially faster than [Cp(P(OMe)(3))Ir(Me)CH(2)Cl(2)][BAr(f)]. Density functional theory computations suggest that this is due to a less favorable pre-equilibrium for dissociation of the dichloromethane ligand in the trimethyl phosphite complex, rather than to a large electronic effect on the C [bond] H oxidative addition transition state. Because of these combined effects, the overall rate of arene activation is increased by electron-donating substituents on both the substrate and the iridium complex.

Answer 151:

Bibliographic Information

Investigation of the mechanism of alkane reductive elimination and skeletal isomerization in Tp'Rh(CNneopentyl)(R)H complexes: the role of alkane complexes. Northcutt T O; Wick D D; Vetter A J; Jones W D Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627, USA Journal of the American Chemical Society (2001), 123(30), 7257-70. Journal code: 7503056. ISSN:0002-7863. Journal; Article; (JOURNAL ARTICLE) written in English. PubMed ID 11472153 AN 2001425332 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

Experiments are described that provide indirect evidence for the involvement of alkane sigma-complexes in oxidative addition/reductive elimination reactions of Tp'Rh(L)(R)H complexes (Tp' = tris-3,5-dimethylpyrazolylborate, L = CNCH(2)CMe(3)). Reductive elimination rates in benzene-d(6) were determined for loss of alkane from Tp'Rh(L)(R)H, where R = methyl, ethyl, propyl, butyl, pentyl, and hexyl, to generate RH and Tp'Rh(L)(C(6)D(5))D. The isopropyl hydride complex Tp'Rh(L)(CHMe(2))H was found to rearrange to the n-propyl hydride complex Tp'Rh(L)(CH(2)CH(2)CH(3))H in an intramolecular reaction. The sec-butyl complex behaves similarly. These same reactions were studied by preparing the corresponding metal deuteride complexes, Tp'Rh(L)(R)D, and the scrambling of the deuterium label into the alpha- and omega-positions of the alkyl group monitored by (2)H NMR spectroscopy. Inverse isotope effects observed in reductive elimination are shown to be the result of an inverse equilibrium isotope effect between the alkyl hydride(deuteride) complex and the sigma-alkane complex. A kinetic model has been proposed using alkane complexes as intermediates and the selectivities available to these alkane complexes have been determined by kinetic modeling of the deuterium scrambling reactions.

Answer 152:

Bibliographic Information

Further evidence for multiple pathways in soluble methane-monooxygenase-catalysed oxidations from the measurement of deuterium kinetic isotope effects. Wilkins P C; Dalton H; Samuel C J; Green J Department of Biological Sciences, University of Warwick, Coventry, England European journal of biochemistry / FEBS (1994), 226(2), 555-60. Journal code: 0107600. ISSN:0014-2956. Journal; Article; (JOURNAL ARTICLE); (RESEARCH SUPPORT, NON-U.S. GOV'T) written in English. PubMed ID 8001570 AN 95094813 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

The data from the deuterium isotope experiments in this study show that the primary kinetic isotope effect for methane oxidation catalysed by soluble methane monooxygenase from Methylococcus capsulatus (Bath) is very small, < 2. In contrast, the primary kinetic isotope effect for -CH3 group oxidation in toluene is large, > 7. A mechanistic pathway in which a substrate radical is formed from hydrogen atom abstraction by a ferryl species is believed to operate for CH4, the toluene -CH3 group and similar alkanes. Direct oxygen atom addition, rather than H atom abstraction, is indicated for aromatic ring oxidations in benzene and toluene and for styrene oxide formation from styrene. Thus, more than one

mechanistic pathway appears to operate in soluble methane-monooxygenase-catalysed reactions and, in some cases, the pathway chosen may be dictated by the substrate. In the soluble methane-monooxygenase-catalysed oxidation of toluene the rates of: (a) substrate dissociation from the enzyme-substrate complex, (b) product formation and (c) product release (benzyl alcohol and p-cresol) from the enzyme-product complex are comparable in magnitude. Therefore all three of these steps are partially rate-determining in the soluble methane monooxygenase catalytic cycle for toluene oxidation.

Answer 153:

Bibliographic Information

Molecular recognition in cytochrome P-450: mechanism for the control of uncoupling reactions. Loida P J; Sligar S G Department of Biochemistry, University of Illinois, Urbana 61801 Biochemistry (1993), 32(43), 11530-8. Journal code: 0370623. ISSN:0006-2960. Journal; Article; (JOURNAL ARTICLE); (RESEARCH SUPPORT, U.S. GOV'T, P.H.S.) written in English. PubMed ID 8218220 AN 94032274 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

The pathway for utilization of pyridine nucleotide derived reducing equivalents in the cytochrome P-450 monooxygenase systems has three major branch points. The first is a partitioning between autoxidation of a ferrous, oxygenated heme adduct and input of the second reducing equivalent required for monooxygenase stoichiometry. The second is between dioxygen bond scission and release of two-electron-reduced O2 as hydrogen peroxide. The third is between substrate hydrogen abstraction initiated by a putative higher valent iron-oxo species and reduction of this intermediate by two additional electrons to produce water in an overall oxidase stoichiometry. For all substrates investigated, the direct release of superoxide at the first branch point never competes with second electron input. In order to elucidate the aspects of molecular recognition of a substrate-P-450 complex which affect these individual branch points in the catalytic cycle, we have measured the NADH-derived reducing equivalents recovered in hydroxylated substrate, hydrogen peroxide, and water for a series of active-site mutants designed to alter the coupling of ethylbenzene hydroxylation. We find that the reaction specificity at the second and third branch points is affected by site-directed mutations that alter the topology of the binding pocket. The increased commitment to catalysis observed for all mutants suggests that active-site hydration is important in the uncoupling to form hydrogen peroxide at the second branch point. The liberation of hydrogen peroxide does not correlate with the location of the mutation in the pocket, as expected if the two-electron-reduced dioxygen-bound intermediate is not directly participating in the substrate activation step.(ABSTRACT TRUNCATED AT 250 WORDS)

Answer 154:

Bibliographic Information

Inhibition of dimeric dihydrodiol dehydrogenases of rabbit and pig lens by ascorbic acid. Hara A; Shinoda M; Kanazu T; Nakayama T; Deyashiki Y; Sawada H Department of Biochemistry, Gifu Pharmaceutical University, Japan The Biochemical journal (1991), 275 (Pt 1) 121-6. Journal code: 2984726R. ISSN:0264-6021. Journal; Article; (JOURNAL ARTICLE) written in English. PubMed ID 2018468 AN 91207278 MEDLINE (Copyright (C) 2008 U.S. National Library of Medicine on SciFinder (R))

Abstract

The dehydrogenase activity of dimeric dihydrodiol dehydrogenases (DD) purified from pig and rabbit lenses was inhibited by either L-ascorbic acid or its epimer, isoascorbic acid, at pH 7.5. Isoascorbate [IC50 (concn. giving 50% inhibition) = 0.043 mM for the pig enzyme; IC50 = 0.13 mM for the rabbit enzyme] was a more potent inhibitor than ascorbate (IC50 values 0.45 and 0.90 mM respectively), but 1 mM-dehydroascorbate gave less than 30% inhibition. Glucose, glucuronate, gulono-gamma-lactone, glutathione and dithiothreitol did not inhibit the enzyme activity. The inhibition by isoascorbate and ascorbate was instantaneous and reversible, and their inhibitory potency was decreased by addition of ascorbate oxidase. In the reverse reaction, isoascorbate and ascorbate gave low IC50 values of 0.013 and 0.10 mM respectively for the pig enzyme and 0.025 and 0.25 mM for the rabbit enzyme. The inhibition patterns by the two compounds were competitive with respect to dihydrodiols of naphthalene and benzene and uncompetitive with respect to NADP+, but those in the reverse reaction were uncompetitive with respect to both carbonyl substrate and NADPH. The steady-state kinetic measurements in the forward and reverse reactions by the pig enzyme were consistent with an ordered Bi Bi mechanism, in which NADP+ binds to the enzyme first and NADPH leaves last. The results indicate that ascorbate and its epimer directly bind to an enzyme: NADP+ binary complex as dead-end inhibitors. Thus ascorbate may be an important modulator of DD in the lens.