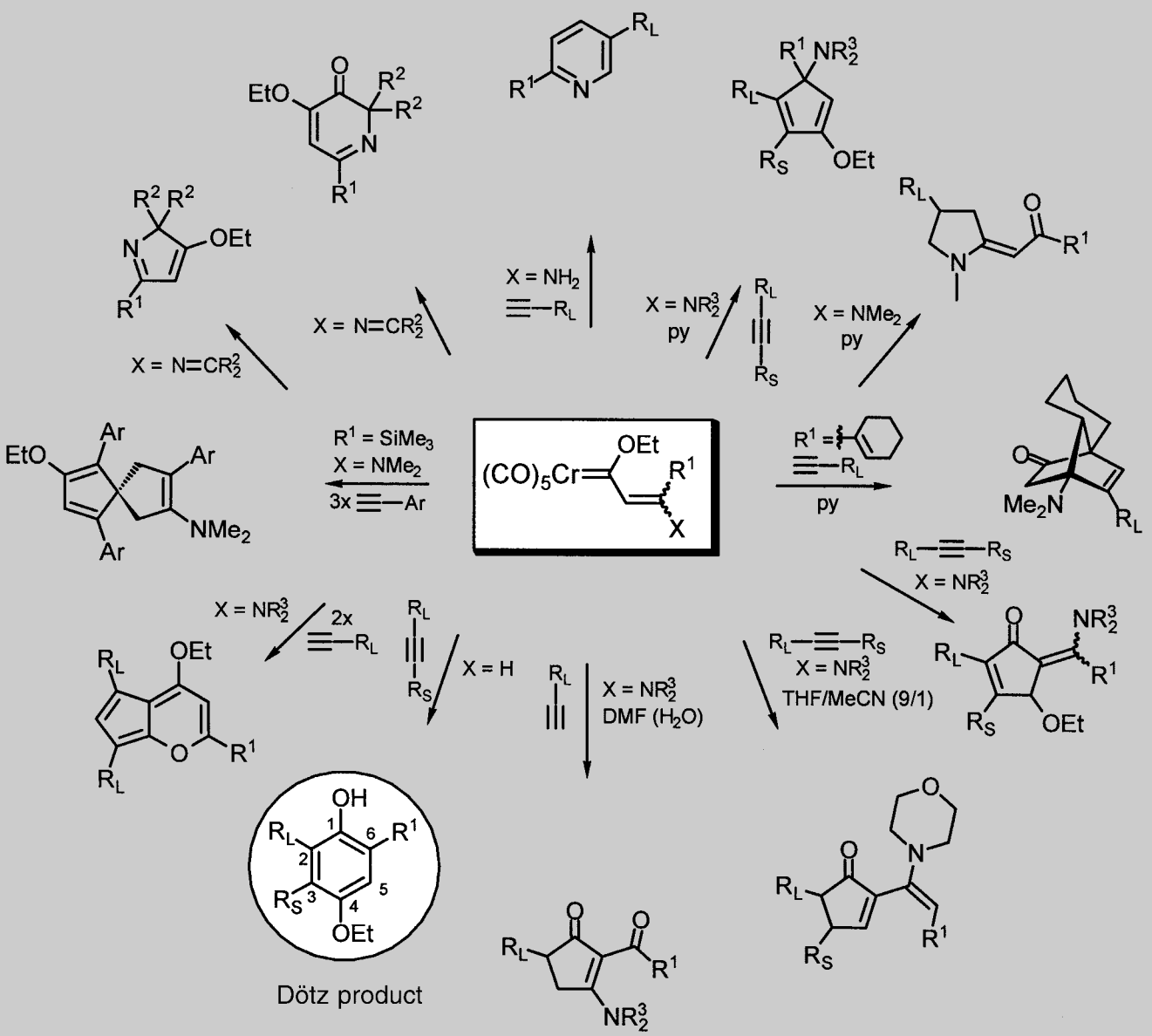
Just a Section of the Incredible Range of Products from α,β-Unsaturated Carbenepentacarbonylchromium Complexes



Fischer Carbene Complexes as Chemical Multitalents: The Incredible Range of Products from Carbenepentacarbonylmetal α,β-Unsaturated Complexes

Armin de Meijere,* Heiko Schirmer, and Michael Duetsch

Dedicated to Professor Henning Hopf on the occasion of his 60th birthday

The metal carbene complexes, discovered by E. O. Fischer at the start of the 1960s and carrying his name, have since proved themselves to be irreplaceable building blocks for organic synthesis. In particular, since the discovery of the Dötz reaction, a formal cycloaddition of Fischer α,β-unsaturated carbene complexes to alkynes with CO insertion, this area of chemistry has become increasingly interesting to organic chemists. In spite of the considerable diversity of reactions performed with these complexes, proper selection of substrates and careful adjustment of the reaction conditions have allowed, in most cases the perfectly selective preparation of individual compounds of this enormous range of products. The spectrum of new successes begins with the conventional Diels–Alder reaction of alkynylcarbene complexes and the formal regioselective [3+2] cycloaddition of alkenylcarbene complexes to alkynes. It extends much further, however, from cascade reactions with the formation of oligofunctional and oligocyclic products of impressive molecular complexity to complex, formal [3+6] cocyclizations in which six bonds are formed in a single operational step. Beyond doubt, the methodological arsenal of preparative organic chemistry cannot be imagined any more without the valuable transformations of the Fischer carbene complexes; it only remains to be seen whether one or other of the numerous new types of cocyclization products of these complexes can establish itself as a lead structure in the search for biologically active compounds.

Keywords: alkynes · carbene complexes · cycloadditions · domino reactions · insertion

1. Introduction

A feature of a whole series of organometallic compounds is their ability, with the same type of substituent, to afford a spectrum of product types under divers external conditions and with a range of different reaction partners. With proper selection of all variables the manifold reactions of such organometallic compounds can take place each time with high selectivity. Such classes of compounds can be justifiably described as "chemical multitalents". Their transformations are particularly valuable for the repertoire of synthetic methods whenever these reactive intermediates are readily available and manipulable. One example of such a class of organometallic compounds is beyond doubt that of the Fischer carbene complexes, which were first described by Fischer and Maasböl in 1964.[1, 2] Initially they were only hesitantly introduced into preparative organic chemistry, but eventually began to achieve an established place for themselves in synthetic strategies, particularly through the discovery of the so-called Dötz reaction in the middle of the 1970s.[3] Initially the Dötz reaction served mainly for the synthesis of naphthoquinone frameworks by the formal cycloaddition of phenylcarbene complexes to alkynes with CO insertion under very mild conditions. Since then a whole range of cocyclization products from the reactions of α,β-unsaturated carbene complexes with alkynes have been isolated and characterized. The range of 21 different product types obtained from the phenyl- and alkenylcarbene complexes of Group VI metals in reactions with alkynes mentioned by Wulff et al.[4] is by far no longer up to date. Moreover, even though a small change to the carbene ligand, the reaction conditions, or the alkyne used, can lead to different products, it is a feature of these reactions that with the proper combination of all these factors only one type of product is formed, usually with high selectivity in each case. It is precisely this which makes the reactions of the Fischer carbene complexes so interesting and so valuable for organic synthesis.

[*] Prof. Dr. A. de Meijere, Dr. H. Schirmer, Dr. M. Duetsch
Institut für Organische Chemie der Georg-August-Universität Göttingen
Tammannstrasse 2, 37077 Göttingen (Germany)
Fax: (+49) 551-399475
E-mail: Armin.deMeijere@chemie.uni-goettingen.de

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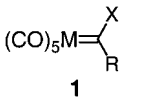


1
M = Cr, Mo, W

That with their help, that is, within the coordination sphere of the metals, the most varied of carbo- and heterocyclic compounds can be constructed has definitely contributed to the constantly increasing popularity of the Fischer carbene complexes **1**. However, it must not be overlooked that more conventional organic chemistry can also be readily carried out on the ligands. Because of the strong electron-withdrawing character of the pentacarbonylmetal group—this is a characteristic of the Fischer carbene complexes which at the same time differentiates them from the Schrock class of carbene complexes[5]—depending upon the nature of the heteroatom at the carbon center they can be regarded as analogues **2** of esters, thioesters, or amides.[6]

2
X = OR, SR, NR_2

A few of the typically ester-like features are the pronounced α-CH acidity—with a pK_a value of 8 for the pentacarbonyl(methoxymethylcarbene)chromium

A. de Meijere

M. Duetsch

H. Schirmer

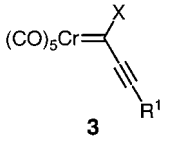
Armin de Meijere was born in Homberg (Niederrhein) in 1939. He studied chemistry at the Universities of Freiburg and Göttingen, and he obtained his doctorate under the supervision of Professor Dr. Wolfgang Lüttke in 1966. He spent a period of two years as a postdoctoral research fellow at Yale University in New Haven, CT, USA with Professor K. B. Wiberg, and he obtained his Habilitation at the Universität Göttingen in 1971. In 1977 he was appointed Ordentlicher Professor für Organische Chemie at the Universität Hamburg. In October 1989 he returned to the Universität Göttingen as Professor für Organische Chemie and successor to his former mentor. Over the years he has been Visiting Professor at the University of Wisconsin in Madison, WI, the IBM Research Laboratories in San José, CA, at the Technion in Haifa, Israel, Princeton University in Princeton, NJ, the Université d'Aix Marseille III, in Marseille, France, the Universitàdegli Studi in Firenze, Italy, the Ecole Normale Supérieur in Paris, France, the Université de Paris-Sud in Orsay, France, the University of Colorado in Boulder, CO, and the University of Florida in Gainesville, FL. Until 1963 he was Stipendiat der Studienstiftung des deutschen Volkes, he was awarded the Dozenten-Stipendium des Fonds der Chemischen Industrie in 1972, and in 1992 he was appointed a member of the Norwegian Academy of Sciences and Letters. He was awarded the Gay Lussac-Alexander von Humboldt Award of the French Ministère de l'Éducation National, de la Recherche et de la Technologie. In 1997 he was appointed as a member of the Braunschweigische Wissenschaftliche Gesellschaft, Honorary Professor of the St. Petersburg State University and Fellow of the Japan Society for the Promotion of Science. He is editor or member of the editorial board of a series of scientific journals, including Chemical Reviews, periodicals, and books. His scientific achievements have been published in over 420 original communications, review articles, and book contributions. His current research interests are: the development of new domino reactions for the efficient construction of complex structures and new small-ring compounds as synthesis building blocks including their use in the synthesis of natural and nonnatural compounds; new highly strained polycyclic compounds with interesting properties; the application of organometallic complexes and catalysts in organic synthesis, currently mainly palladium-catalyzed domino reactions as well as titanium induced cyclopropanations and other transformations of carbonyl compounds; carbon compounds and organometallic complexes with unconventional chemical and physical properties.

Michael Duetsch, born in Hamburg in 1966, concluded his studies at the Universität Hamburg under Professor Armin de Meijere with a Diplomarbeit on Michael additions to alkynylcarbene complexes. He followed Professor de Meijere to the Universität Göttingen where he received his doctorate with a dissertation on donor-substituted vinylcarbene and homovinylcarbene complexes of chromium and tungsten in 1993. He then held a postdoctoral research fellowship with Professor H. B. Kagan at the Université Paris-Sud with research work in the area of asymmetrically induced oxidation of sulfides to sulfoxides mediated by chiral titanium complexes. He joined the research department of Th. Goldschmidt AG, Essen in 1994.

Heiko Schirmer, born in Leinefelde (Thüringen) in 1971, studied chemistry at the Universität Göttingen and the Universidade Estadual de Campinas, in Campinas, Sao Paulo, Brazil. He gained his doctorate in 1999 under Professor Armin de Meijere with a dissertation on β-aminosubstituted α,β-unsaturated Fischer carbene complexes. He accepted a position at the Schering AG in Berlin.

complex[7a] it is even considerably greater than that of ethyl acetate ($pK_a = 24.5$[7b])—and nucleophilic substitution by addition/elimination at the carbene C atom by amines,[8] thiols, alcohols,[9] and also allyllithium compounds.[10] As would be expected, multiple bonds neighboring the carbene center, as in complexes **3**–**5**, are also activated towards attack by nucleophiles.

Particularly versatile are nucleophilic additions to the triple bond of the alkynylcarbene complexes **3** resulting in the α-alkenylcarbene complexes **4** which for their part can participate predominantly in formal cycloaddition reactions with alkynes with the inclusion of the carbene center and possibly a CO ligand. Whereas the reactions of complexes **3** are dominated by the strong polarization of the triple bond, in complexes **4** and the analogous aryl complexes **5** the metal center also always plays a role by coordinating with possible reaction partners or stabilizing reactive intermediates by coordination.



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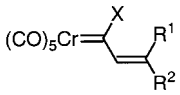

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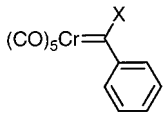


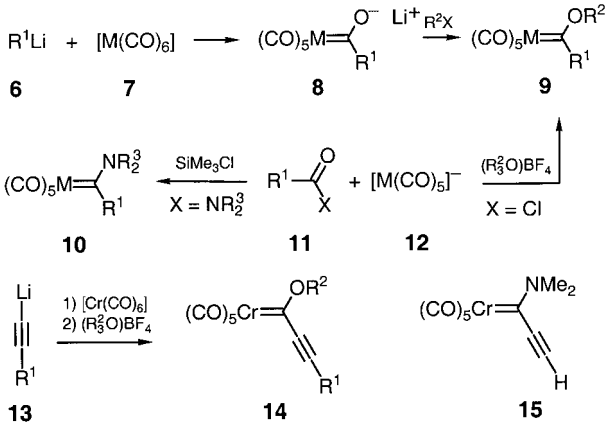
5

Thirty five years after the discovery of the Fischer carbene complexes and more than fifteen years after the last comprehensive review on this topic in this journal[2b] it appeared appropriate to us to summarize the rapidly growing amount of work in this area in an orderly fashion. This contribution should serve to lift the confusion caused by the manifold reactions of the multitalented Fischer carbene complexes from those less familiar with this chemistry, and to encourage others to consider the numerous novel possibilities of the readily assembled α,β-unsaturated Fischer carbene complexes for the elegant solution of synthetic problems.

Only the characteristic reactions of the three complex types **3**, **4**, and **5** will be treated in this review, and only those of the respective chromium complexes. On the one hand, their reactions are almost certainly the most extensively investigated, and on the other the change to molybdenum or tungsten complexes usually brings about only a change in the distribution of the product types known from the chromium complexes.[4]

2. Alkynylcarbenechromium Complexes

Carbene complexes of the Group VI metals are prepared almost exclusively by two procedures. Either an alkyllithium compound **6** is added to the respective hexacarbonylmetal complex **7**[11] and the metallaacylate **8** thus formed is trapped with an electrophile,[12] or an alkali metal or ammonium pentacarbonylmetalate **12** is reacted with the corresponding carboxylic acid chloride or amide.[13]. After addition of the Meerwein salt the adduct from the acid chloride eliminates chloride to form the alkoxycarbene complexes, whereas trapping the amide adduct with chlorotrimethylsilane leads to the aminocarbene complex. Alkynylcarbenechromium complexes of type **14** are accordingly obtained easily by reaction of the particularly readily available 1-lithio-1-alkynes

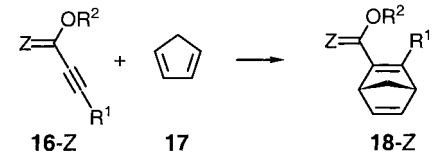


13 with hexacarbonylchromium with subsequent alkylation with trimethyl- or triethyloxonium tetrafluoroborate.[14, 15] A large number of such α-alkynylcarbene complexes **14** with a wide variety of substituents R^1 have since been prepared, but the isolation of a terminally unsubstituted propynylidene complex has only relatively lately been achieved along an indirect route, and then only in the form of the 1-dimethylamino derivative **15**.[16]

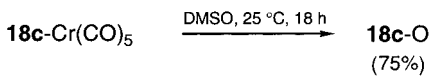
2.1. [4+2] and [2+2] Cycloadditions

2.1.1. With Dienes and Electron-Rich Alkenes

In view of the strong electron withdrawing influence of the pentacarbonylmetal moiety on the carbene ligand in Fischer carbene complexes it appeared obvious to use α,β-unsaturated complexes of this type as dienophiles in Diels–Alder reactions. The investigations concerning the dienophilic nature of 1-alkenylcarbene complexes and the regioselectivity of their Diels–Alder reactions with dienes extend until well into the 1990s.[17] 1-Alkynylcarbene complexes are also significantly better dienophiles than the corresponding esters of propynoic acid (Scheme 1).[18–20] Thus, the propynylidenechromium complexes **16** [$Z = Cr(CO)_5$] add to cyclopentadiene (**17**) in yields of 73–91%, even at room temperature, whilst the esters **16** ($Z = O$) only react above 170 °C, if at



16-Z **17** **18**-Z

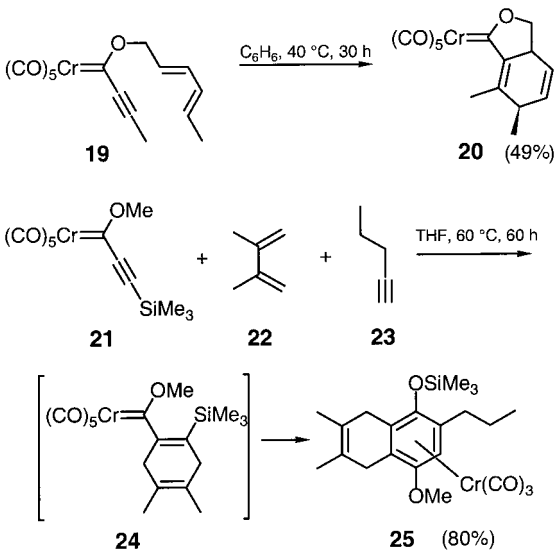


16	R^1	T [°C]/t [h]	Z	18-Z [%]	T [°C]/t [h]	Z	18-Z [%]
a	Me	170/1	O	22	25/2	$Cr(CO)_5$	85
b	$SiMe_3$	190/24	O	66	25/0.75	$Cr(CO)_5$	91
c	*c*Pr	180/24	O	0	25/17	$Cr(CO)_5$	73

Scheme 1. Comparative reactivities of 1-alkynylcarbene complexes and the corresponding esters. R^2 = Me, Et.

all.[18, 19] Such comparisons are legitimate precisely because Fischer carbene complexes may be oxidized to the corresponding carboxylic acid derivatives under very mild conditions.[21] Thus, for example the cyclopropyl substituted norbornadienylcarbenechromium complex **18c**-Cr(CO)$_5$ is transformed into the ester **18c**-O in a yield of 75% simply by stirring in dimethylsulfoxide.[20a]

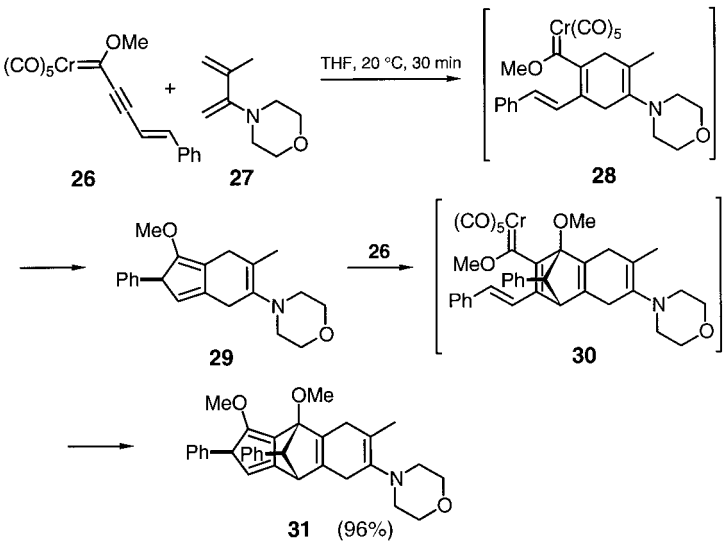
Intramolecular variants of such Diels–Alder reactions lead to bicyclic compounds with a pentacarbonylcarbenechromium moiety.[17g–i, 21a, 22] In the example of the hexadienyloxypropynylidene carbene complex **19** the dienyl group is connected by way of the oxygen substituent on the carbene C atom; in benzene solution **19** gives the Diels–Alder product **20** in a yield of 49% after 30 h at 40 °C.[19a] The combination of different types of reactions in reaction



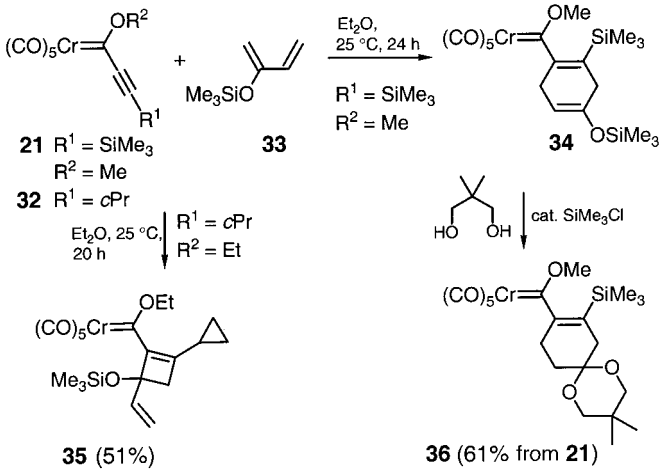
cascades is also possible with carbene complexes. Thus, cycloaddition of the alkynylcarbene complex **21** to 2,3-dimethylbutadiene (**22**) gives the α,β-unsaturated carbene complex **24** with a cyclohexa-1,4-diene moiety which immediately reacts with the added 1-pentyne (**23**) in a Dötz-type reaction. In this one-pot transformation the complexed dihydronaphthalene derivative **25** could be obtained by crystallization from the crude product in a yield of 80%.[18]

A further increase in the number of interconnected reaction steps is demonstrated by the sequential transformation beginning with the [4+2] cycloaddition of 2-methyl-3-morpholinobuta-1,3-diene (**27**) to the alkenynylcarbene complex **26** reported by Barluenga et al.,[23] in which the initial product **28** cyclizes to the cyclopentadiene derivative **29**. This adds to a further molecule of **26** in a [4+2] cycloaddition, and the product cyclizes once more to afford the cyclopentadiene derivative **31**. The highly substituted tetracycle **31** results with formation of six new C–C bonds, and is isolated in 96% yield.

However, 2-(trimethylsilyloxy)butadiene (**33**), known for its high diene reactivity, can react differently with alkynylcarbene complexes depending on the nature of their terminal substituent. With the (trimethylsilylethynyl)carbene complex **21** it forms the expected [4+2] cycloadduct **34**,[19a] which

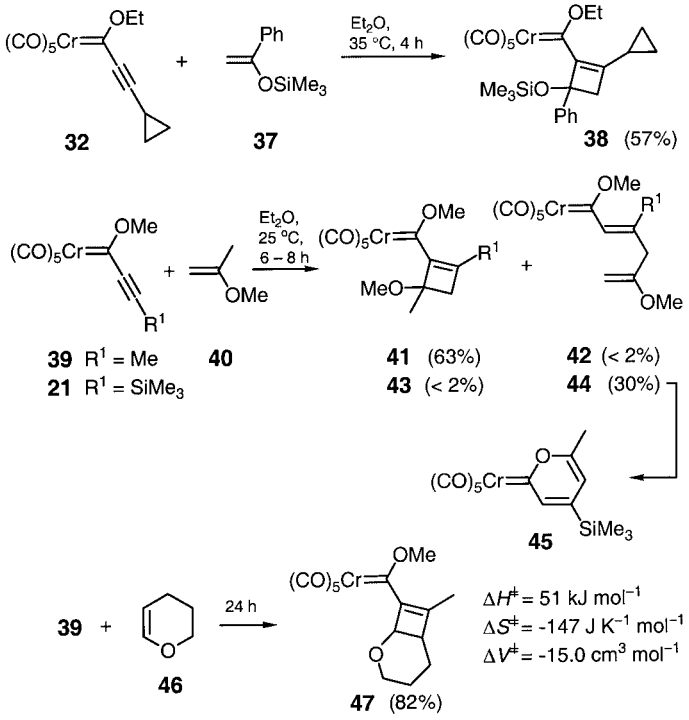


before further use in a Dötz reaction had to be converted into the acetal compound **36**. In contrast, the cyclopropyl-substituted complex **32** reacts regioselectively with the electron-rich double bond in **33** (R^2 = Et) in a [2+2] cycloaddition.[20, 24] This is analogous to the [2+2] addition of 2,3-bis(*tert*-butyldimethylsilyloxy)butadiene to the complex **32** (R^2 = Me) observed by Faron and Wulff.[25]

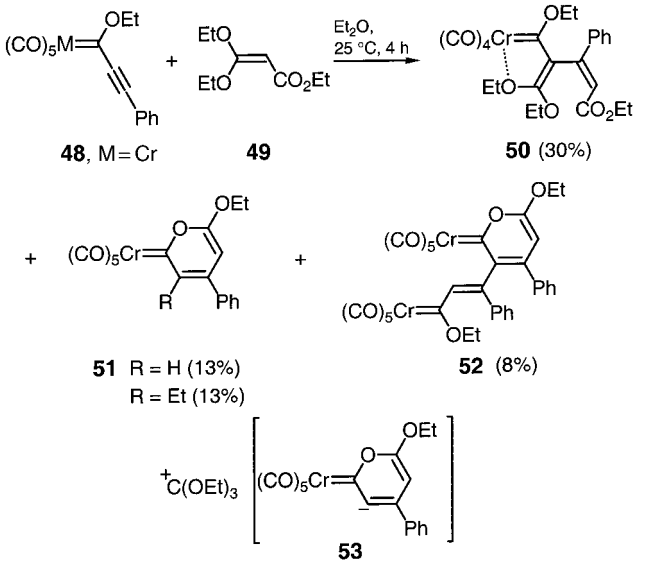


Meanwhile, it has been shown that enol ethers generally react with alkynylcarbene chromium and tungsten complexes by [2+2] cycloaddition.[20–29] 2-Alkoxycyclobutenylcarbene complexes are formed with diverse enol ethers, as is demonstrated by the reaction of the cyclopropyl-substituted complex **32** (R^2 = Et) with α-trimethylsilyloxystyrene (**37**) to form **38**, and the reaction of the butynylidene complex **39** with 2-methoxypropene (**40**) to form **41**, as well as with dihydropyran (**46**) to afford **47**.[25, 26] One exception arises again, however, with the trimethylsilyl-substituted complex **21**, which mainly undergoes an ene reaction with 2-methoxypropene (**40**) to form the (methoxypenta-1,4-dienyl)carbene complex **44**; compound **44** is for its part highly labile and cyclizes to the pyranylidene complex **45**.[25] It was concluded

from kinetic measurements on the temperature and pressure dependence that the model reaction of dihydropyran (**46**) with **39** involves a synchronous, single-step process with a nonpolar transition state.[28]

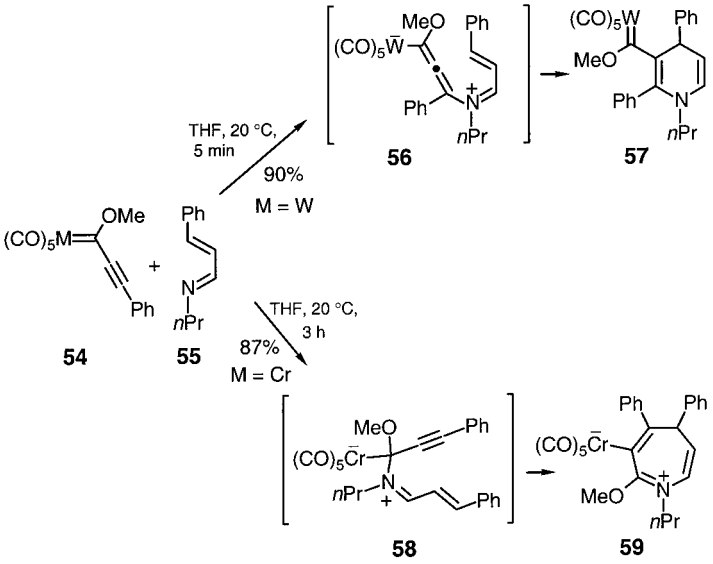


A spontaneous cycloreversion[30] to butadien-2-ylcarbene complexes is sometimes observed after a successful [2+2] cycloaddition,[25, 26, 29, 31] as for example in the reaction of **48** (M = Cr) with ethyl 3,3-diethoxyacrylate (**49**), which leads to the complex **50**.[29] The total product spectrum from **48** (M = Cr) and **49** appears somewhat bizarre, for in addition to **50** two pyranylidene complexes **51** (R = H, Et) analogous to product **45** (see above), and the binuclear biscarbene complex **52** are found.[31] It is assumed that the three compounds **51** (R = H, Et) and **52** arise from one and the same ionic intermediate **53**.

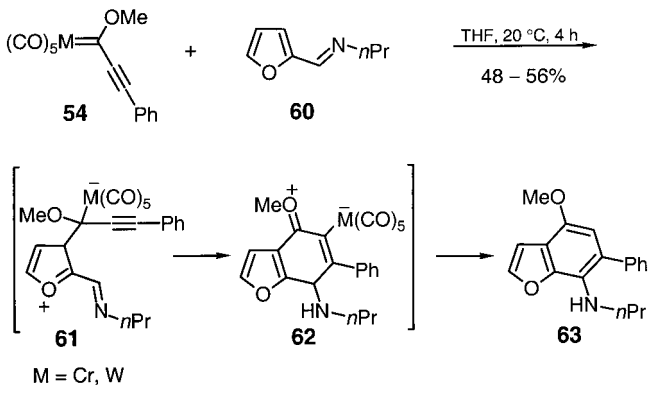


2.1.2. With Azadienes and Enamines

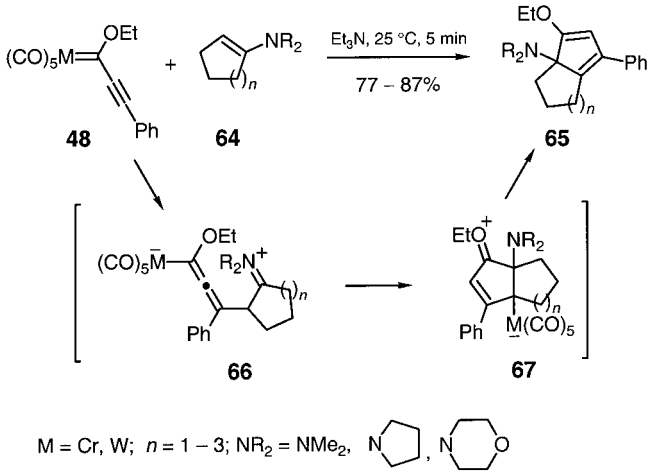
The reaction of alkynylcarbene complexes **54** with azadienes may take rather different courses depending upon the metal.[32, 33] The alkynylcarbene tungsten complex **54** (M = W) affords the corresponding [4+2] cycloadduct **57** upon reaction with 4-phenyl-1-propyl-1-azabutadiene (**55**). The zwitterionic intermediate **56** was identified by NMR spectroscopy.[32a] In contrast, with the identically substituted alkynylcarbene chromium complex **54** (M = Cr) cyclization of the zwitterion **58** with migration of the metal-complex fragment and formation of the azepine **59** follows a nucleophilic attack of the azadiene **55** at the carbene center.[33]



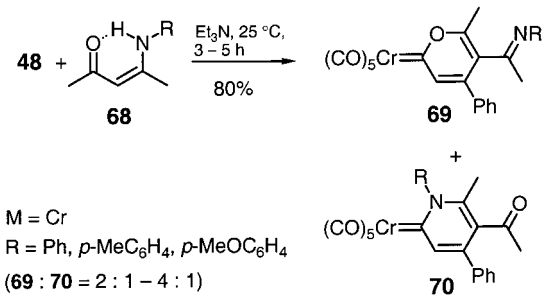
The direction of the reaction depends, however, not only upon the constitution of the alkynylcarbene complex,[32, 33] but also upon the nature of the azadiene used.[34] Thus, the tungsten and chromium complexes **54** described above do not react in a [4+2] or [4+3] cycloaddition with the N-substituted furan derivative **60**. Here too, the sequence begins with a nucleophilic attack, albeit of the furan fragment of **60** at the carbene center of **54**, and cyclization of **61** with [1,2] migration of the metal fragment leads to **62** with a furan-annelated six-membered ring. The trisubstituted benzofuran **63** results from the zwitterion **62** by protiolysis.[34]



According to these examples it does not require too great an imagination to think of a plethora of possible products for the reactions of alkynylcarbene complexes with enamines.[35] Aumann and co-workers have shown impressively that alkynylcarbene complexes of type **48** react with cyclic enamines **64** in a formal [3+2] cycloaddition with the formation of ring-annelated cyclopentadienes **65**. A large number of products could be synthesized from five-, six- and seven-membered cyclic enamines using this reaction principle.[35a,b]

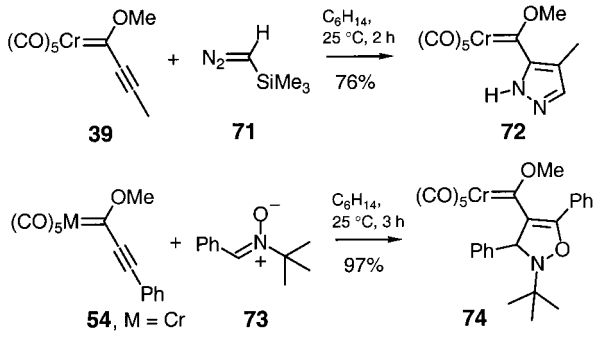


Solely the pyran-2-ylidene and 1,2-dihydropyridin-2-ylidene complexes **69** and **70**, respectively, were formed in the base-catalyzed reaction of the secondary enamin-3-ones **68** with chromium complex of **48**.[35]



2.2. [3+2] Cycloadditions with 1,3-Dipoles

In view of the high reactivity of alkynylcarbene metal complexes in [4+2] and [2+2] cycloadditions the question of their behavior towards 1,3-dipoles is an obvious one. In fact, only a few investigations on this topic have been carried out. In an early study solely metal-free compounds were obtained in the reaction of pentacarbonyl(1-ethoxy-3-phenylpropynylidene) tungsten with diazomethane.[36] This is not surprising since in reactions with ylids, metal carbene complexes also show a similar behavior to the esters and amides of carboxylic acids to form alkenes.[37] It was over a decade later that Chan and Wulff were successful in observing a smooth cycloaddition of trimethylsilyldiazomethane (**71**) to **39**.[14b] At 25 °C the pyrazolyl(methoxy)carbenechromium complex **72** was obtained in a yield of 76 % with a strikingly high regioselectivity of more than 300:1. The almost quantitative formation of the 2,3-dihydroisoxazolyl(methoxy)carbenechromium complex **74** by addition of the nitrone **73** to the chromium complex of **54** was later reported.[38]



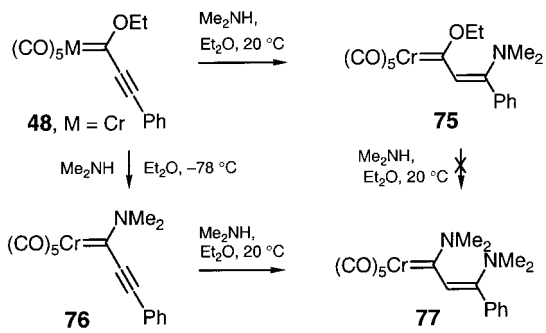
Azides, however, do not undergo 1,3-dipolar cycloadditions with alkynylcarbene complexes. Instead, after thermal release of nitrogen a nitrene is formed which, by hydrogen atom abstraction from the solvent, forms the primary amine. This then adds to the triple bond of the alkynylcarbene complex (see Section 2.3.1.).[39]

2.3. Michael Additions

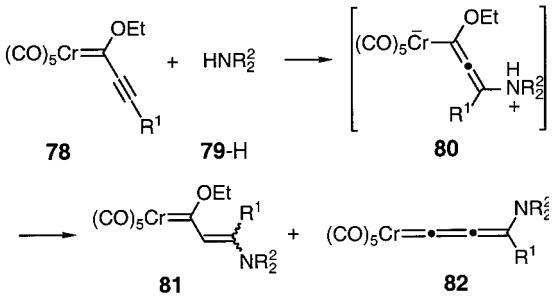
2.3.1. Addition of Amines, Ammonia, Imines, Hydrazine, and Phosphanes

In 1972 the facile 1,4-addition of a secondary amine to an alkynylcarbene complex was first described in the literature by Fischer and Kreissl.[14a] Five years later came a report on the temperature dependence of the product distribution,[40] for in addition to the 1,4-attack, 1,2-attack at the carbene C atom is also possible, which after rapid elimination of ethanol corresponds to simple substitution.

Fischer and Kalder found that the reaction of **48** (M = Cr) with dimethylamine at −78 °C gives solely the substitution product **76**, whereas at room temperature only the Michael adduct **75** is formed.[40] However, at that time the configuration of the newly formed double bond was unclear. The further reaction of **76** with dimethylamine at 20 °C leads smoothly to the dimethylamino(dimethylaminoethenyl)carbene complex **77**, whereas **75** does not react further to **77** under these conditions, even over an extended period.



A series of rules were uncovered by de Meijere and co-workers for this type of reaction during the investigation of a large number of differently substituted complexes **78** with divers secondary amines **79**-H.[15, 41] At 20 °C the reaction generally leads to the Michael adducts **81** in good, usually quantitative yields. The occurrence of the iminium ylid intermediate **80** could also be confirmed by isolation and X-ray structure analysis.[42, 43]



Almost without exception the products **81** are formed as a single diastereomer, usually as the *E*-isomer, if R^1 is not too large and the amine is a secondary amine. In this case a coplanar arrangement with optimal conjugation including that of the lone electron pair on the nitrogen atom is possible (Figure 1). If R^1 is tertiary or otherwise extremely sterically demanding (e.g. $R^1 = CH(Me)OSiMe_2tBu$), the products **81** with *Z*-configuration are formed.[15] In (*Z*)-**81** the substituents on the amino group are rotated out of the plane so that the interaction of the lone electron pair with the 1-metalla-1,3-diene system is greatly reduced.

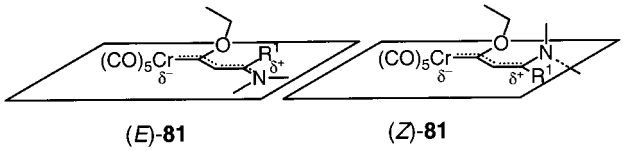
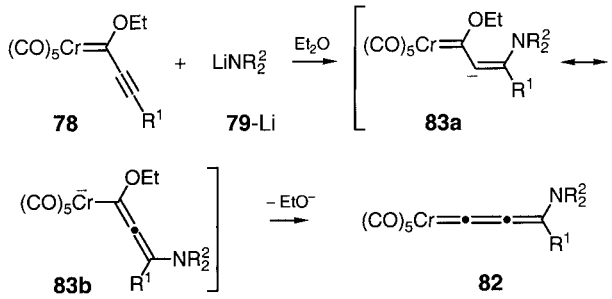


Figure 1. Steric relationships in *E*- and *Z*-configured pentacarbonyl(3-dialkylamino-1-ethoxyprop-2-enylidene)chromium complexes **81**.

Where R^1 represents large tertiary substituents in **78** side products are formed in the reaction with secondary amines which, with suitable choice of amine and/or temperature, can become the main products.[41]. In contrast to the findings of Fischer and Kalder with the phenyl-substituted complex **78** ($R^1 = Ph$),[40] the 1,4 adduct is favored with all other substrates of type **81** when the temperature is reduced.[41] The products of a new type formed at higher temperatures have proved to be the allenylidene complexes **82**,[44] isomeric with the substitution products **76** (see above), as was recognized by X-ray structure analysis. They are even formed as sole products if the complexes **78** are treated with the lithium amides **79**-Li at low temperatures (Scheme 2).[41]

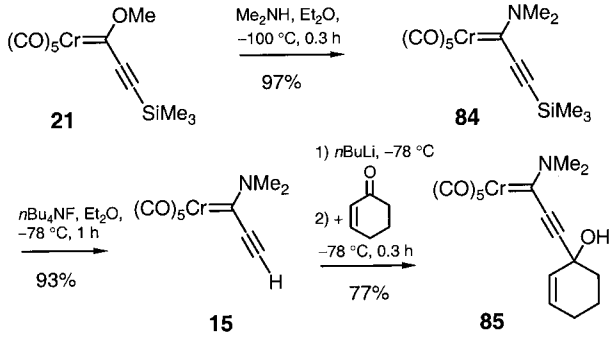
In this case the anionic complex **83** must be formed directly by nucleophilic attack of the amide at the alkyne terminus from which the 1-metallacumulene **82** then results by elimination of ethanolate. Allenylidene complexes of the type **82** are also formed by elimination of ethanol from the β-amino-substituted alkenylcarbene complexes **78** by treatment with Lewis acids such as BF_3 or $AlCl_3$.[45]



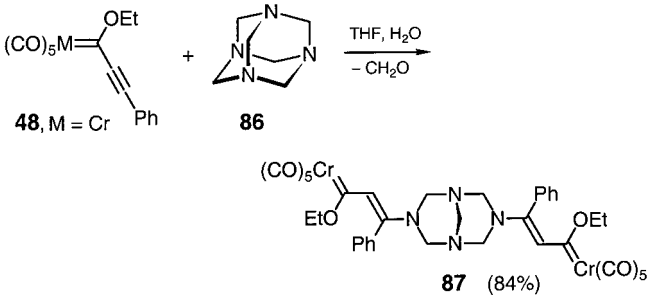
	R^1	R^2	**82** [%]
a	Ph	Me	94
b	Ph	Bn	99
c	Ph		98
d	CMe_2OEt	Me	79
e	CMe_2OSiMe_3	Me	87
f	CMe_2OSiMe_3	Et	60
g	CMe_2OSiPh_2tBu	Me	95

Scheme 2. Formation of allenylidene complexes **82** with the lithium amides **79**-Li.

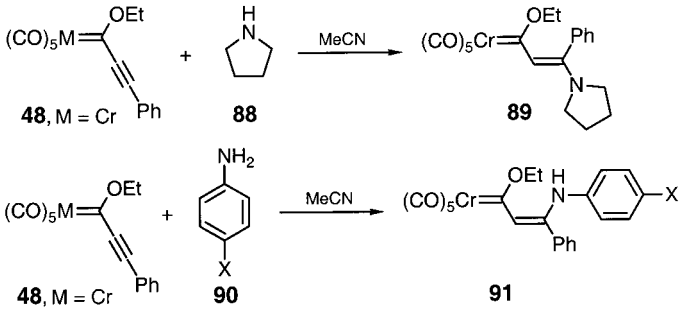
Because the trimethylsilyl substituent in **21** is sterically highly demanding, the 1-dimethylaminocarbene complex **84** is formed by reaction with dimethylamine, the addition product (28% at 20 °C) is also formed, but not the respective allenylidene complex of type **82**.[16] The trimethylsilyl group may be removed from **84** by treatment with fluoride; in this way Wulff and co-workers obtained the first unsubstituted derivative **15** of this class of compounds. This could develop into a valuable synthetic building block, as it has been shown that **15** also reacts smoothly with electrophiles such as cyclohexenone to carbene complexes like **85** after conversion into the lithium derivative.[16]



From any point of view, the result of the reaction of the phenylethynylcarbene complex **48** (M = Cr) with urotropine (**86**) is surprising.[42] In aqueous THF the binuclear adduct **87** is formed in a surprisingly high yield (84%). Clearly the urotropine residue is partially hydrolyzed with removal of formaldehyde, and the resulting two secondary amino functions each add spontaneously to the triple bond in **48** (M = Cr) with formation of the binuclear complex **87**.

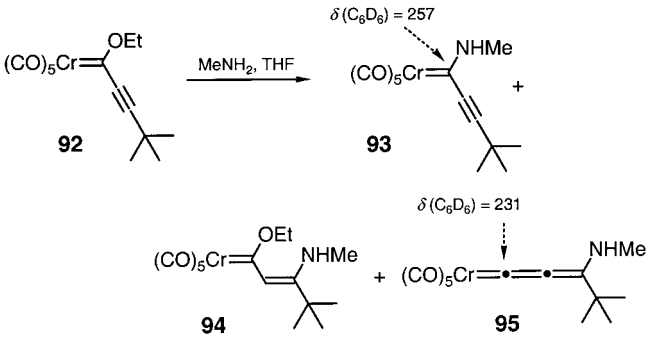


Kinetic investigations on the pressure dependence of the addition of pyrrolidine (**88**)[43] and *para*-substituted anilines **90**[46] to the phenylethynylcarbene complex **48** (M = Cr) by van Eldik et al. (Scheme 3) gave negative activation volumes with values between -16.6 and $-27.9\ cm^3 mol^{-1}$; this and the increase of -2.95 ± 0.14 found in the Hammett plot for the addition of the aniline groups confirm a two-stage process with significant C–N bond formation in the polar transition structure (similar to the intermediate **83**) of the rate-determining reaction step.



Scheme 3. X = CN, MeCO, Cl, F, H, Me, MeO.

Michael adducts such as **94**, from the reaction of primary amines to alkynylcarbene complexes, are formed exclusively with *Z*-configuration.[14, 47–50] The considerations regarding the configuration of the double bond and the orientation of the amino groups described above (see Figure 1) do not apply to complexes **94**. Rathermore these *Z*-configured complexes are

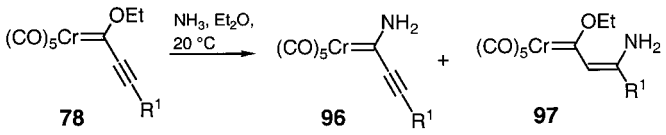


also coplanar with optimal conjugation precisely because of the hydrogen bond from the amine hydrogen to the oxygen atom of the 1-alkoxy group. Aumann obtained chirally modified 2-aminoethenylcarbene complexes by addition of enantiomerically pure galactopyranosylamines;[49] it has also been shown that the secondary amino group in such complexes may be acylated.[50] Formal substitution (1,2-addition/elimination) occurs to a greater extent as a side reaction to the 1,4-addition of primary amines,[47, 48] although allenylidene complexes are also found in reactions with amines such as isopropylamine.[41] The reaction of the (3,3-dimethylbutynyl)-carbene complex **92** with methylamine is currently the only known example in which, in addition to Michael addition to give **94**, both formal substitution to give **93** and addition/elimination to give the allenylidene complex **95** occurs. The two isomeric compounds **93** and **95** are readily differentiated because of the considerable difference between the chemical shifts of the carbene C atoms in the ^{13}C NMR spectrum. The temperature dependence of the product distribution (Table 1) shows very clearly that low temperatures favor 1,2-addition/elimination (formal substitution), medium temperatures 1,4-addition, and higher temperatures 1,4-addition/elimination.

Table 1. The effect of temperature on product distribution in the reaction of **92** with methylamine.[47]

T [°C]	Fraction [%]		
	93	**94**	**95**
−17	97	3	0
+3	88	12	0
+25	59	30	11
+41	26	46	28
+65	17	44	39

The reactions of various alkynylcarbene complexes **78** with ammonia always give considerable proportions of the respective formal substitution products **96** (Scheme 4). When R^1 = Ph, *t*Bu **96** is even the major product.[15, 48, 51] The 1,4-addition products **97** exist as primary enamines, which is clearly shown by the two signals of the two NH_2 protons that are observed the ^1H NMR spectrum, and exclusively as the *Z*-isomers in all cases.

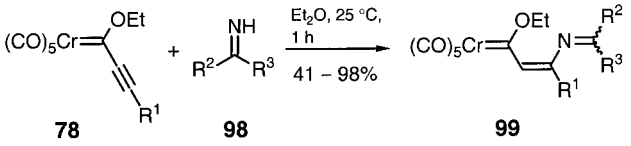


	R^1	**96** [%]	**97** [%]
a	Ph	86	13
b	*n*Pr	31	63
c	*c*Pr	28	70
d	*t*Bu	60	35

Scheme 4. Reactions of the alkynylcarbene complexes **78** with ammonia and product ratios.

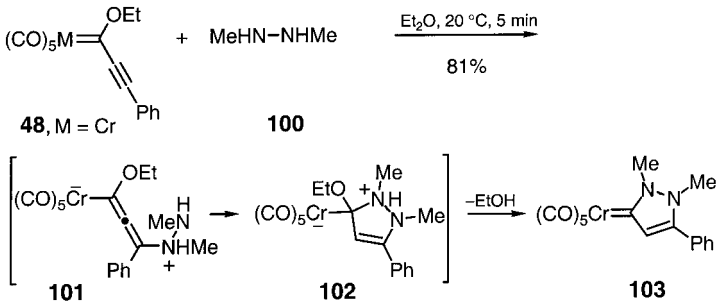
The addition of imines **98** to the triple bond of **78** leads directly to the interesting 5-aza-1-chroma-1,3,5-hexatrienes **99** (Scheme 5).[52] Unlike the additions of amines this reaction takes place distinctly more slowly, but totally selectively to the 1,4-adducts **99**.

1,2-Dimethylhydrazine (**100**) reacts with alkynylcarbene-chromium complexes such as **48** (M = Cr) with formation of a

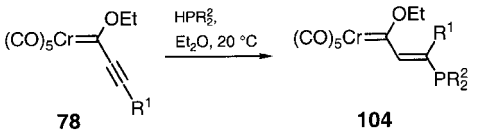


Scheme 5. For transformations of **99** see Scheme 28 and Table 8.

dihydropyrazolinylidenechromium complex **103**. Here, a formal substitution on the carbene carbon atom by the second secondary amino group to form the betaine complex **102** follows a Michael addition of **100** onto the triple bond of **48** (→**101**). The analogous tungsten complexes also gave formal substitution products as well as the pyrazolinylidene complexes on the addition of **100**.[53]



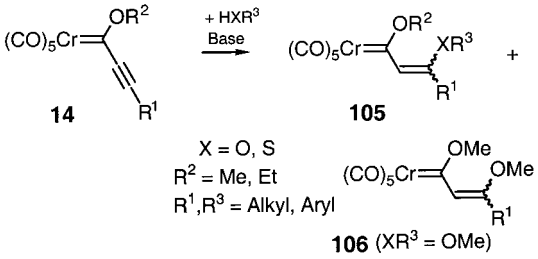
E-Configured 3-(diorganophosphanyl)propenylidenechromium complexes **104** could also be prepared for the first time by the Michael addition of secondary phosphanes to alkynylcarbene complexes (Scheme 6).[54]

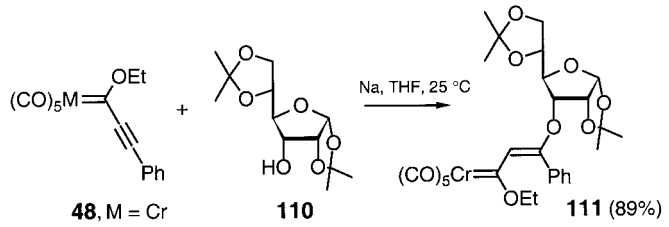


Scheme 6. R^1=Ph; R^2 = *t*Bu, *c*-C_6H_{11}.

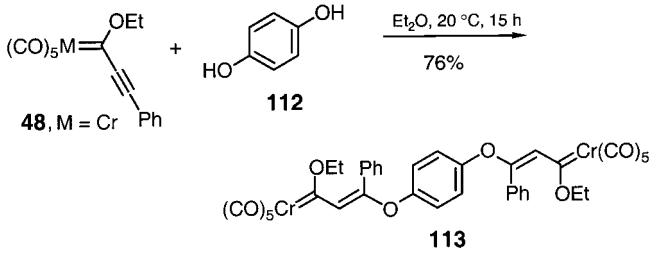
2.3.2. Additions of Alcohols, Thiols, and Carboxylic Acids

The addition of alcohols and thiols to alkynylcarbene complexes **14** generally furnishes *E*/*Z*-diastereomeric mixtures.[15, 55, 56a] Furthermore, the addition of these nucleophiles takes place far more slowly than those of amines,[15, 55] but can be accelerated by the addition of bases. Small amounts of the respective sodium alcoholate[15, 56a] or 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU)[55] have proved to be effective catalysts. In the reaction with methanol the 1,3-dimethoxypropenylidene complex **106** was also found as a byproduct in addition to the monoaddition product **105**.[15, 55] The unsubstituted 1,3-diethoxypropenylidenechromium complex **109** was formed by the addition of ethanol to **107** and subsequent protiodesilylation.[15] In this way Aumann incorporated sugar moieties into carbene ligands for the first time.[56b] The 1,2:5,6-protected α-D-allofuranose **110** gives the sugar adduct **111** as a single stereoisomer in a yield of 89% after addition of 0.2 equivalents of sodium in THF and subsequent addition of **48** (M = Cr).

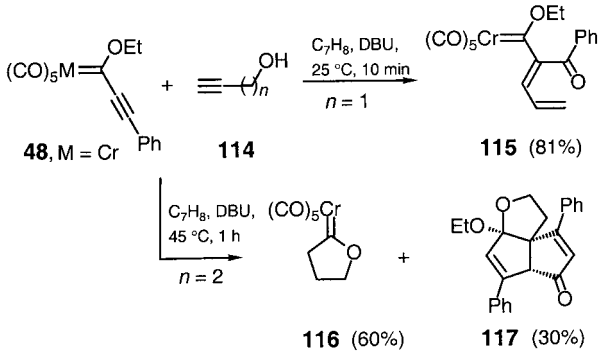




Phenols react with alkynylcarbene complexes in an analogous 1,4-addition. In this way the binuclear complex **113** could also be obtained, prepared by the addition of hydroquinone (**112**) to **48** (M = Cr).[57]

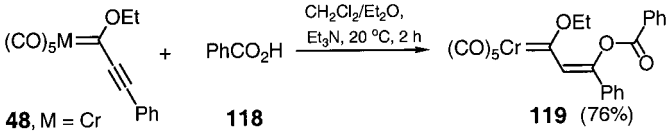


The reaction of **48** (M = Cr) with hydroxyalkyl-substituted alkynes leads to unexpected products. The Michael adduct was at best found in traces. Propargyl alcohol (**114**, $n = 1$) reacts with **48** (M = Cr) to form the butadienyl complex **115**, whereas 3-butyn-1-ol (**114**, $n = 2$) gives the tricycle **117** as a single diastereomer in a yield of 30%.[58] Compound **115** is most probably formed from the Michael adduct by [3,3] sigmatropic rearrangement with a subsequent [1,3] proton



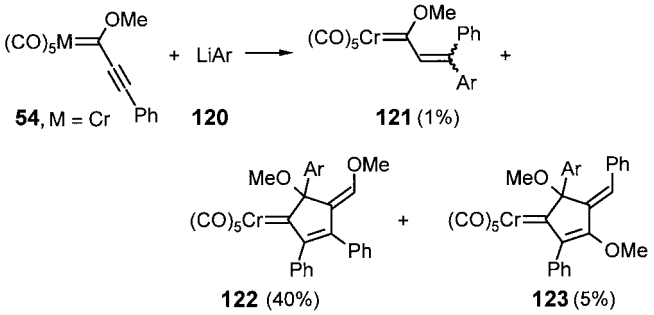
shift. At least two molecules of the starting complex **48** (M = Cr) are involved in the formation of **117**; the authors assume a sequence of intra- and intermolecular [4+2] cycloadditions. The major product in this case, however, was the tetrahydrofuranylidene complex **116**.

The Michael addition of carboxylic acids to alkynylcarbene complexes also proceeds smoothly.[59] Benzoic acid (**118**) reacts uniformly with **48** (M = Cr) in the presence of triethylamine to form the *Z*-isomer **119** in 76% yield.



2.3.3. Addition of Aryllithium Derivatives

The additions of secondary and primary amines, ammonia, imines, alcohols, and thiols[55] are reactions which are easy to carry out and usually give the desired Michael adducts in good to very good yields, and frequently even in essentially quantitative yields. Adducts of type **82** from secondary amines can even be prepared in a one-pot reaction by deprotonation of terminal alkynes with *n*-butyllithium, addition of hexacarbonylchromium, addition of triethyloxonium tetrafluoroborate, and finally addition of the secondary amine. However, attempts at 1,4-addition of *p*-tolyllithium (**120**) proved to be rather disappointing (Scheme 7).[60] Compound **121** was isolated in a yield of only 1%. It is difficult



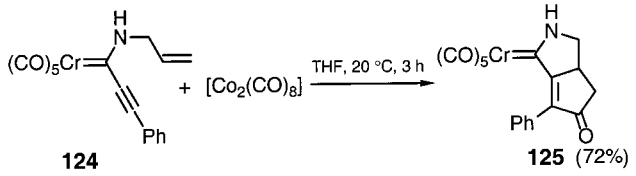
Scheme 7. Ar = *p*-MeC_6H_4.

even to recognize the starting material in the main product **122** (yield 40%). The intermediate formed after an initial 1,2-attack of the lithium compound has clearly attacked another molecule of the alkynyl complex **54** (M = Cr). The additional product **123** (5%) had to have formed analogously but with reversed regiochemistry during the attack on the second molecule of the starting complex.

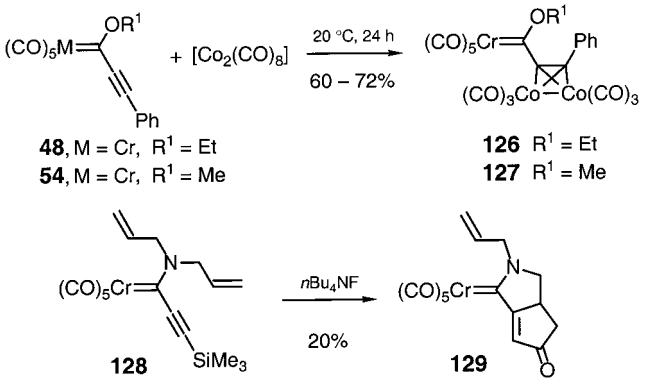
The addition of organozinc compounds to the alkynylcarbene complexes has been reported. In this case a product of type **122** was formed selectively.[61]

2.4. Reactions of Octacarbonyldicobalt—Intramolecular Pauson–Khand Reactions at Room Temperature

Simultaneously, but independently of each other, the groups of Moretó and Dötz discovered that 1-(allylamino)alkynylidenechromium and -tungsten complexes undergo Pauson–Khand reactions at surprisingly low temperatures upon treatment with octacarbonyldicobalt.[62, 63] After only 3 h at 20 °C **124** had reacted completely, via the corresponding alkynehexacarbonyldicobalt complex, and the cyclization product **125** was isolated in a yield of 72%.[62a]



Alkynylcarbenechromium complexes without an allyl group, such as **48** (M = Cr) and **54** (M = Cr), smoothly form the alkynehexacarbonyldicobalt complexes **126** and **127** which could be isolated and investigated by X-ray crystallography.[64, 65] Complicated metal cluster compounds are obtained



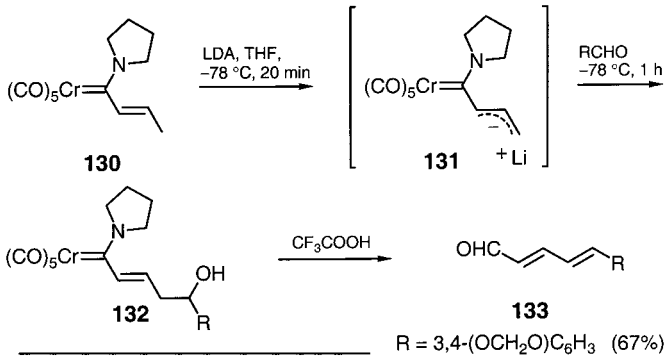
on heating these complexes.[65] In this type of reaction too, a (trimethylsilylethynyl)carbene complex represents an exception. Compound **128** does not react, or at the best unconventionally, with octacarbonyldicobalt, although both intramolecular and intermolecular Pauson–Khand reactions usually give particularly good yields with trimethylsilyl-substituted alkynes. However, Moretó and co-workers obtained the cyclization product **129** in a yield of 20% by treatment of **128** with tetrabutylammonium fluoride without addition of octacarbonyldicobalt (the corresponding tungsten complex gave a better yield).[66] The mechanism of this reaction is unclear, although the incorporated carbonyl group must have arisen from the decomposition of a further molecule of the carbenepentacarbonylchromium complex.

3. Aryl and Alkenylcarbenechromium Complexes

3.1. Aldol Reactions of Alkenylcarbenechromium Complexes

The 1-pyrrolidinylbutenylidenechromium complex **130** represents a synthetic equivalent of an α,β-unsaturated amide. As Maiorana and co-workers have demonstrated, the complex

130 can be converted into the allyl anion **131**, equivalent to an amide enolate, with a base such as lithium diisopropylamide (LDA). This then reacts regioselectively with an aldehyde functionality with the formation of a δ-hydroxy-substituted alkenylcarbenechromium complex **132**. After removal of the chromium complex fragment with trifluoroacetic acid and concomitant dehydration, the substituted butadienylaldehydes **133** are obtained (Scheme 8).[67]

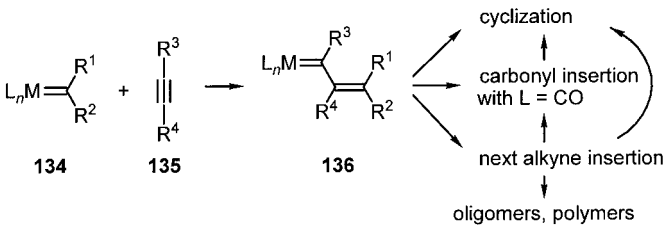


	R	132 [%]
a	Me	79
b	*n*-C_6H_{13}	80
c	$(CH_2)_2Ph$	77
d	HC=$CHCH_3$	72
e	HC=CHPh	72
f	η^6-$(C_6H_5)Cr(CO)_3$	98
g	3,4-$(OCH_2O)C_6H_3$	95

Scheme 8. Reactions of the allyl anion **131** with aldehydes.

3.2. Reactions with Alkynes

Carbene complexes **134** of Group VI metals insert alkynes **135** into the metal–carbene double bond to form the alkenylcarbene complexes **136**. Depending upon the nature



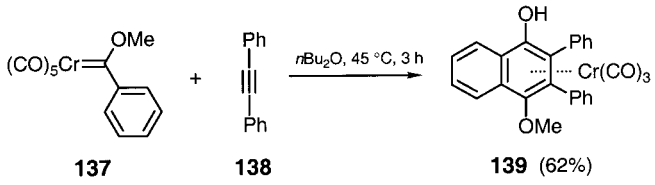
of the complex, this alkyne insertion can be either repeated reiteratively or multiply, leading finally to alkyne oligomers or polymers.[68] Alternatively, one of the intermediates cyclizes—possibly with the insertion of a carbonyl ligand—to afford an organic product after reductive elimination of the metal fragment.

Examples of all three follow-up reactions after the first alkyne insertion illustrated above are known for alkenyl- and phenylcarbenepentacarbonylchromium complexes. They may be classified as formal [k+m+n] cycloadditions, where k, m, and n represent the respective number of atoms from the carbene ligand (k), the alkyne (m), and the carbonyl ligand (n) which form the ring. The following section will describe first those cases in which $k > 1$, namely where more than only the carbene C atom of the carbene ligand is found in the ring system of the product.

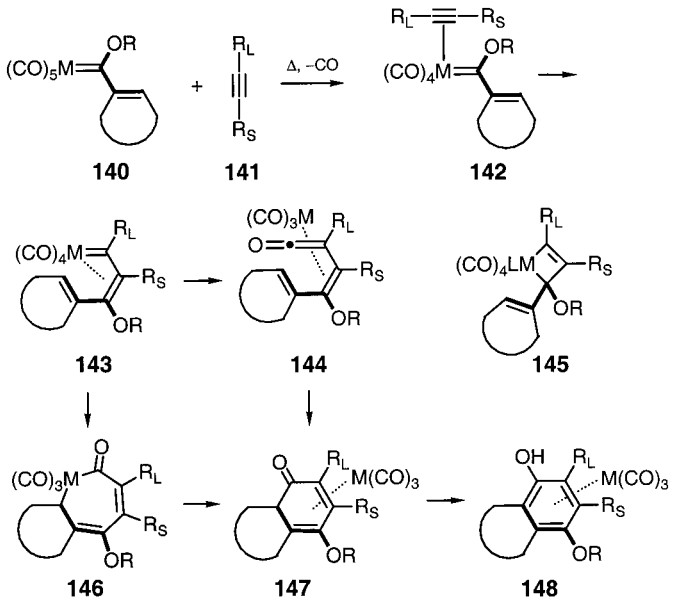
3.2.1. Formal [3+2+1] Cycloadditions: The Now Classical Dötz Reaction

3.2.1.1. Arylcarbenechromium Complexes

In 1975 a benzene annelation by formal cycloaddition of the phenylcarbene complex **137** with diphenylethyne (**138**) was reported for the first time by Dötz.[3, 69] In the meantime more than 100 reports on this reaction have been published.[2] It is



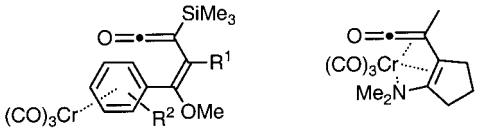
not possible to discuss all aspects within the scope of this review; instead, plausible ideas concerning the mechanism of the Dötz reaction will be discussed, followed by a number of substituent, solvent, and temperature effects. Finally, several new applications of this reaction in organic synthesis will be described (Scheme 9).



Scheme 9. The mechanism of the Dötz reaction (R_L = larger, R_S = smaller substituent).[19a, 70–82]

The initiating and rate-determining step of this reaction must be the dissociation of one of the carbonyl ligands located *cis* to the carbene moiety.[70] An alkyne molecule can then coordinate onto the coordinatively unsaturated complex, and then be inserted into the metal–carbon bond. The photochemically induced CO expulsion and the coordination of an

alkyne with subsequent phenol formation can be followed directly by on-line FT IR spectroscopy.[71] According to this there is only one intermediate, which lies in a pronounced energy minimum and is thus relatively stable. The originally assumed pathway via the metallacyclobutene **145** was recognized as unfavorable by Hofmann et al. on the basis of semiempirical MO calculations.[72, 73] The selectivity with which the diastereomer **143**, capable of cyclization, is formed during alkyne insertion was originally explained by the stereochemistry typical of an electrocyclic ring opening of a cyclobutene.[74] However, this stereoselectivity can be explained satisfactorily by direct insertion via a η^3-vinylcarbene complex, the pathway most favored by calculation.[72b] Meanwhile the isolation and characterization of a carbene complex analogous to the intermediate **143** has been successful, as has that of the complex which is formed after the expulsion of a CO ligand from a 1-amino-substituted alkenylcarbene complex of type **140**.[75] Two different pathways have been discussed for the formation of the coordinated cyclohexadienone **147** from **143**. According to a proposal of Casey, **143** must cyclize to a metallacyclohexadiene. This forms the 7-metallacycloheptadienone **146** by carbonyl insertion, leading to **147** after reductive elimination.[76] In the opinion of Dötz, [77a] the carbonyl ligand is first inserted into **143** to form the alkadienylketene complex **144**, and an electrocyclic ring closure then occurs leading to **147**. In support of the second pathway is the isolation of the alkenylketene complexes **149**[77] and **150**[78] which are formed in the reaction of Fischer carbene complexes with alkynes. Moreover, against the first suggestion is the observation that 5-metalla-1,3-cyclohexadienes,



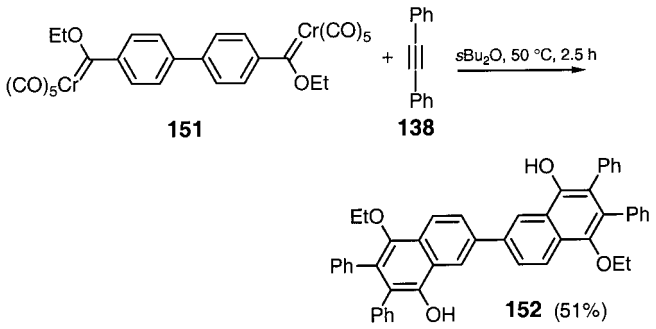
149 R^1 = H, $SiMe_3$; R^2 = H, Me **150**

which can form preferentially from 1-metalla-1,3,5-hexatrienes under certain conditions, clearly lose the metal fragment by reductive elimination without insertion of CO to form cyclopentadienes (see below). The complexed cyclohexadienone **147**, which is accordingly formed via **144**, finally tautomerizes to the complexed *para*-alkoxyphenol **148**[79] if this is not blocked by twofold substitution in the six position.

Whereas pentacarbonyl[(*o*-methoxyphenyl)propylthiomethylene]chromium gave the naphthol derivative in only moderate yield,[80] the Dötz reaction tolerates different substituents on the aryl moiety of alkoxyarylcarbene complexes, as the reactions of a whole series of alkoxy-[19a, 81] and alkyl-substituted[72, 81a, 82] phenyl- and naphthylcarbene complexes[82] with alkynes confirm.

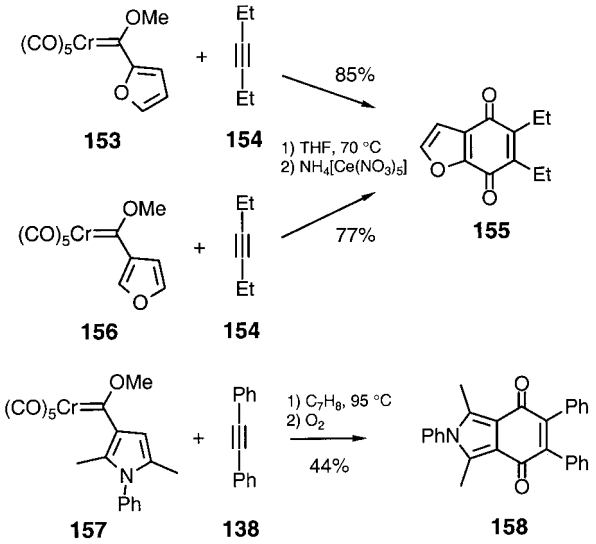
Whereas a phenylcarbenechromium complex with a second carbenechromium group in the *para* position reacts with only one molecule of tolane (**138**) in the usual way,[83] the binuclear biphenyl complex **151**[84] gave the binapthol derivative **152** with **138** in a yield of 51 %.[83]

Heteroarylcarbene complexes with furan,[74, 82a, 85] thiophene, [82a, 85a,e] pyrrole,[85c, 86] or pyrazole residues also undergo



151 **138** **152** (51%)

Dötz reactions. The benzo ring is here generally annelated across the *b* side of the heterocycle, regardless of whether the carbene center is bound to the heterocycle at C-2 or C-3. Thus, both **153** and **156** afford the same furo-*p*-benzoquinone **155** in yields of 85 and 77 %, respectively, after addition of 3-hexyne (**154**) and oxidative work-up.[85a] A different observation was made with carbene complexes with 3-pyrrolyl substituents. Depending upon the position of further substituents on the heterocycle either annelation occurs across the *b* side,[86b] or an isoindoquinone is obtained, such as in the formation of **158** from **157** and tolane (**138**).[87]



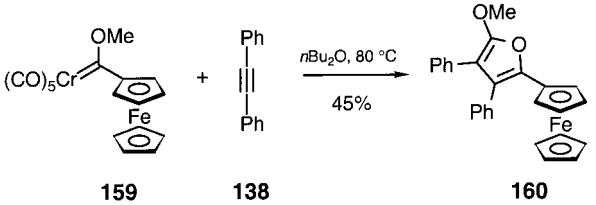
153 **154** **155**

156 **154**

157 **138** **158**

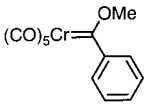
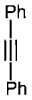
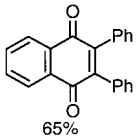
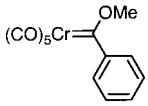
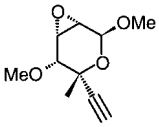
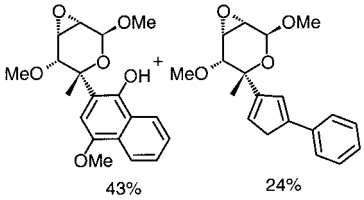
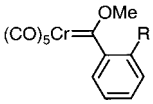
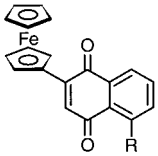
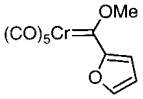
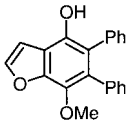
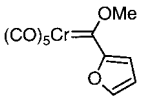
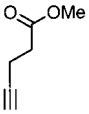
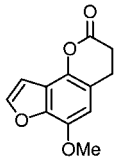
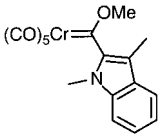
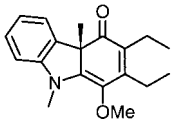
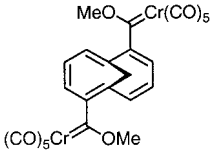
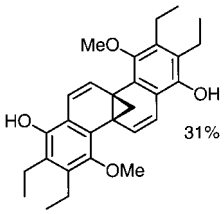
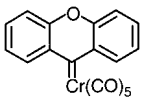
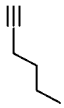
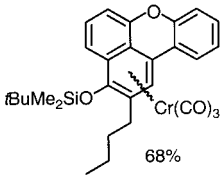
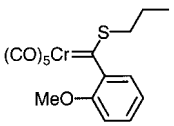
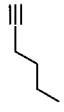
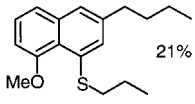
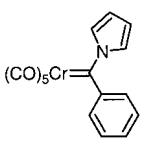
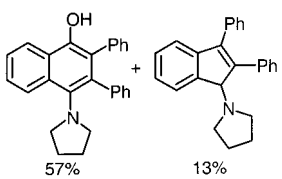
The efficiency and scope of the Dötz reaction has been impressively confirmed by numerous examples in earlier reviews[2] and by more recent work (see Table 2).

Benzoannelation of arylcarbenechromium complexes first reaches a limit when the ferrocenylcarbene complex **159** reacts with tolane (**138**) under standard conditions. Dötz et al. isolated only the furan derivative **160**.[94] Furans of this type, which are normally formed from iron and cobalt carbene



159 **138** **160**

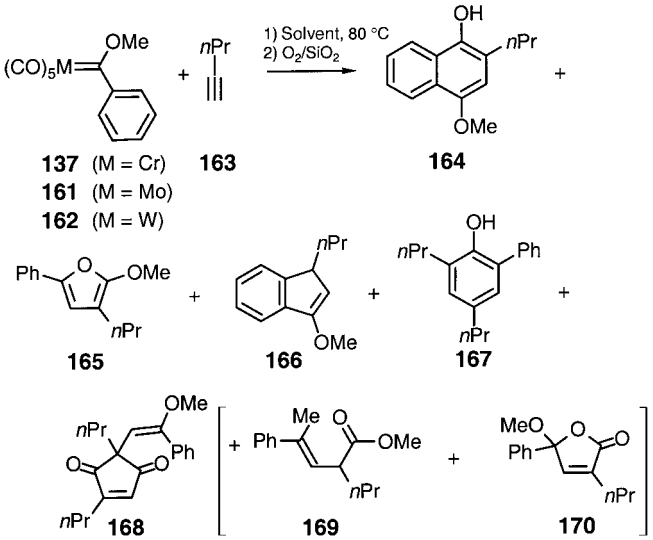
Table 2. Recent examples of the formal cycloaddition of arylcarbenechromium complexes with CO insertion into alkynes.

Carbene complex	Alkyne	Conditions[a]	Product and yield	Ref.
		1) Ultrasound, 20 min; 2) CAN	 65%	[85h]
		1) SiO_2, without solvent, 3 h; 2) CAN	86 %	[85g,h]
		THF, 60 °C, 12 h	 43% 24%	[88]
 R = H, OMe		1) THF, 55 °C, 2 d; 2) PbO_2, CH_2Cl_2	 63-61%	[89]
		300 W Xe lamp, Pyrex, THF, 5.5 h	 88%	[90]
		1) THF, 65 °C, 18 h; 2) O_2, 85 °C, PhH, molecular sieve 4 Å	 55%	[85a]
		1) hexane, 50 °C, 24 d; 2) CAN	 95%	[86b]
		1) SiO_2, 60 °C, 20 h; 2) SiO_2	 31%	[91]
		1) *t*BuOMe, 20 °C, 2 h; 2) *t*BuMe$_2$SiCl, NEt$_3$, 20 °C, 2 h	 68%	[92]
		$BF_3 \cdot Et_2O$, C_7H_8, 65 °C, 3 d	 21%	[80]
		1) THF, 65 °C, 1.5 h; 2) O_2	 57% 13%	[93]

[a] CAN = cerium(IV) ammonium nitrate.

complexes and alkynes,[95] have also been observed in part as main products or byproducts in other Dötz reactions.[4, 19a, 74, 81d, 96] By the use of a carbene complex with a labeled ($^{13}CO)_5Cr$ fragment in such transformations Wulff and co-workers were able to show that the alkoxy-substituted C atom in the furan originates from a carbonyl ligand.[74]

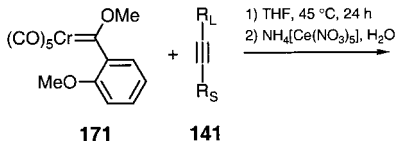
Even though the Dötz reactions normally proceed smoothly, byproducts also occur in a few cases. Of the numerous investigations carried out on this topic, the work of Wulff et al. on the product distribution in the reaction of arylcarbene complexes with alkynes stands out.[4, 81d,i] Exemplary are the cocyclizations of the three phenylcarbene complexes **137**, **161**, and **162** of chromium, molybdenum, and tungsten, respectively, with pentyne (**163**; Scheme 10).[4] Under standard

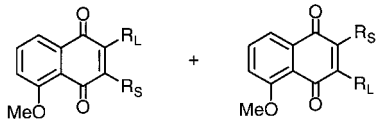


Scheme 10. Solvent = MeCN, C_6H_6, THF. Compounds **169** and **170** are only formed with the tungsten complex **162**.

conditions (THF, 0.1M complex, 24 h) the naphthol **164** is formed from **137** in 84% (GC, isolated yield 66%); the type of furan **165**, is known from the reaction of **159** with **138**, is formed in 10% yield (6%). The formal [3+2] cycloadduct **166** (2%) and the phenol **167** (0.5%) play only minor roles. Lower complex concentrations lead to a higher proportion of **166**; however, in benzene (in this case **168** is also formed in 10% yield) or acetonitrile as solvent, **164** remains the main product. This high selectivity in the reactions of the chromium complex **137** does not apply to the molybdenum and tungsten complexes **161** and **162**. In THF (0.1M, 27 h) the molybdenum complex **161** yields only 5% **164**, and instead **165**, **166**, **167**, and **169** are formed each in about 20%. In benzene **165** becomes the main product (65%). The tungsten complex **162** requires the longest reaction times (8 days), and gives mixtures of all seven products (**164**–**170**) unselectively. The product distribution was found to be dependent on the solvent, the concentration of the arylcarbenechromium complex used, and the constitution of the alkyne.[4, 81d,i]

There has also been a series of investigations into the question of regioselectivity (see mechanism in Scheme 9).[81a, 97] Whereas in the cocyclization with terminal alkynes the regioisomer with the largest residue next to the C atom of the inserted carbonyl ligand is formed almost exclusively, in reactions with nonterminal alkynes, of the two possible regioisomers one is formed preferentially in each case, though only with moderate selectivity (Scheme 11).[81]

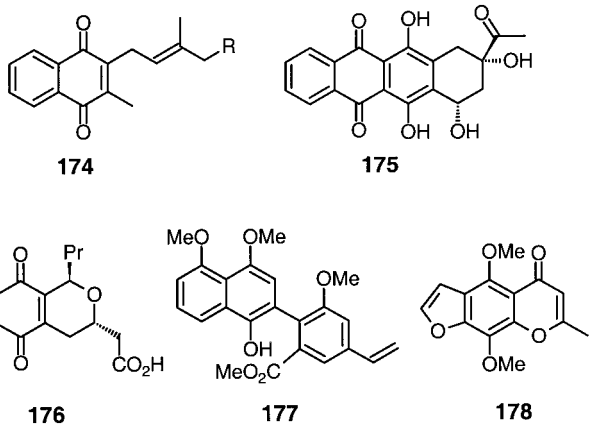




R_L	R_S	172		173
Et	Me	1.5	:	1
*n*Pr	Me	2.9	:	1
*i*Pr	Me	4.8	:	1
*n*Pr	H	>111	:	1

Scheme 11. Examples of the regioselectivity observed with nonterminal alkynes (R_L = larger, R_S = smaller substituent).

In view of the wide synthetic potential of the Dötz reaction it is not surprising that it finds use in the key steps of numerous natural-product syntheses. Representative examples are the elegant synthesis of vitamins E and K **174**,[98] daunomycin **175**,[81f,g, 99] desoxyfrenolycin **176**,[81b] 1-*O*-methyldefucogilvocarin V **177**,[100] and khellin **178**.[101]

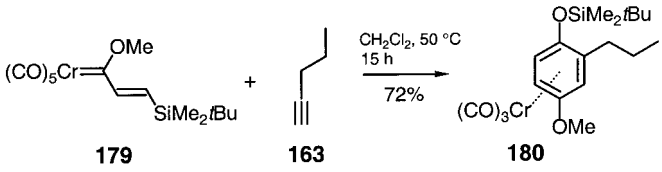


3.2.1.2. *Alkenylcarbenechromium Complexes*

Most alkenylcarbenechromium complexes react with alkynes according to the same principle as arylcarbenechromium complexes, that is they furnish in each case the respective hydroquinone monoethers in a Dötz reaction.[102]

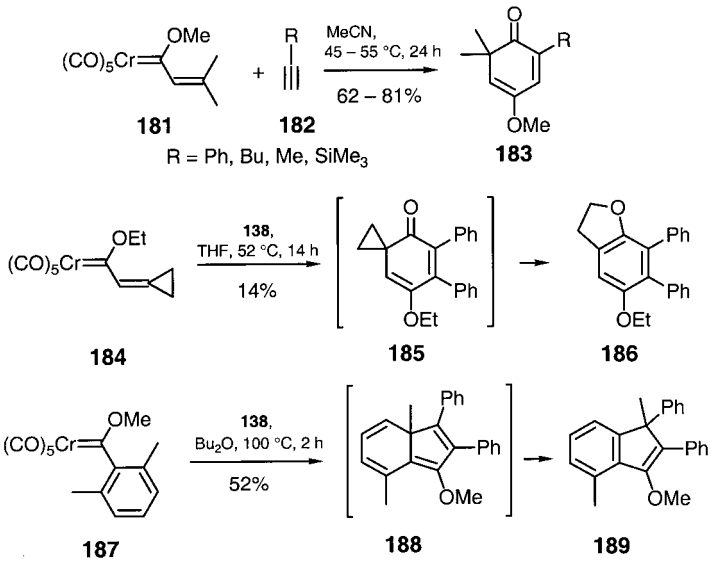
The simplest representative of the 1-alkenylcarbene complexes, the terminally unsubstituted alkoxyethenylcarbenechromium complex, is unstable and polymerizes as soon as the solvent is distilled off at room temperature.[17f, 103] As Chamberlin and Wulff have shown, the formal products of the Dötz reaction of the unsubstituted ethenylcarbene complexes may

still be prepared.[104] In the reaction of (2-trialkylsilylethenyl)carbene complexes such as **179** with alkynes, the silyl group migrates to the oxygen atom so that hydroquinone-diethers such as **180** are formed.



179 **163** **180**

What should be formed with the use of 2′,2′-disubstituted ethenylcarbene complexes may be inferred from the mechanism of the Dötz reaction (see Scheme 9), for in the last step of the Dötz reaction the tautomerization of **147** to **148** cannot occur in a 6,6-disubstituted derivative of **147**. In the simplest case, as illustrated with the cocyclization of **181** and alkynes **182**, tautomerization does not occur, and the 6,6-disubstituted cyclohexa-2,4-dienones **183** are isolated.[77b] The reaction of the cyclopropylidene(methyl)carbene complex **184**, analogous to the isobutenylcarbene complex, with tolane (**138**) gave in contrast the benzodihydrofuran derivative **186** which apparently is readily formed under the influence of the tricarbonylchromium residue from the initially formed complex of spiro[2.5]octa-5,7-dien-4-one **185**, analogous to the tricarbonylchromium complexes of dimethylcyclohexadienones **183**, by heteroanalogous vinylcyclopropane-cyclopentene isomerization.[20a] Moreover, in the cyclization of (2,6-dimethylphenyl)carbene complex **187** with tolane (**138**)



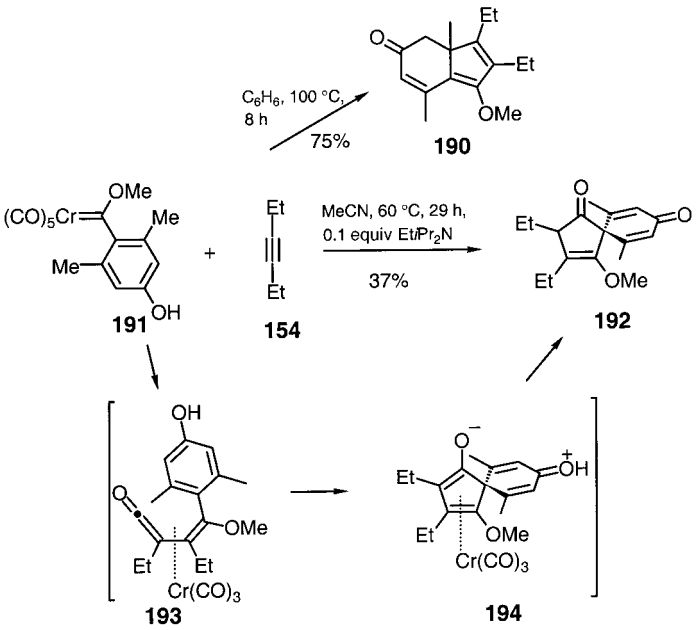
181 **182** **183**

184 **185** **186**

187 **188** **189**

investigated by Dötz et al., tautomerization of type **147** → **148** cannot occur. However, a benzoannelated cyclohexadienone of type **183** is not formed; instead CO insertion does not occur, and after cyclization to a cyclohexadiene-annelated, methoxymethyldiphenylcyclopentadiene derivative **188**, the indene derivative **189** is formed by sigmatropic 1,5-methyl shift.[105]

A really unusual reaction course was observed by Wulff and co-workers in the cocyclization of the (4-hydroxy-2,6-dimethylphenyl)carbene complex **191** with 3-hexyne (**154**). In benzene **191** reacts essentially to form the corresponding indene derivative **190** in a formal [3+2] cycloaddition. Only with the use of acetonitrile as solvent was a change in the



190 **191** **154** **192** **193** **194**

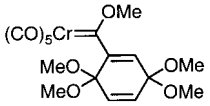
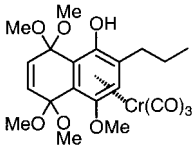
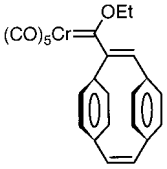
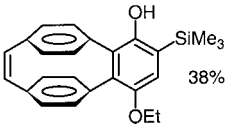
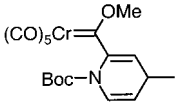
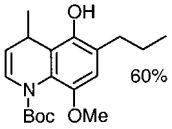
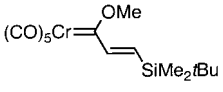
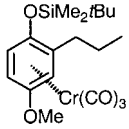
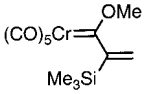
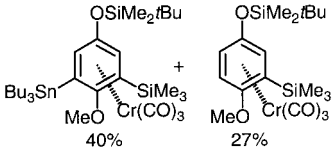
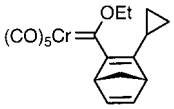
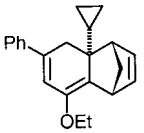
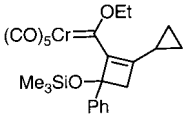
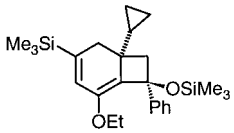
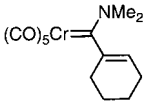
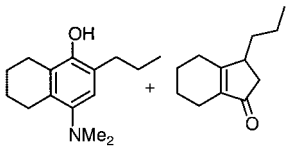
course of the reaction observed, with preference for CO insertion. However, the formation of the normal [3+2+1] cocyclization product (Dötz product) does not occur, instead the intermediate (arylethenyl)ketene complex **193** cyclizes by electrophilic *ipso* attack of the carbonyl group on the electron-rich aryl residue with formation of the spiro[4.5]decatrienone **192**.[106]

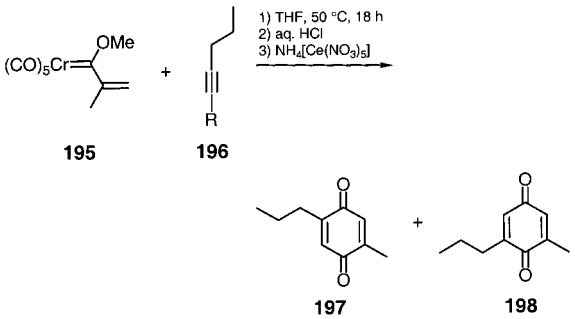
As Wulff and Yang have found, alkynylcarbene complexes react with dienes and alkynes in a one-pot reaction to form dihydronaphthohydroquinone derivatives (see **21** – **25**).[18] In actual fact *O*-alkyl-*O*′-trialkylsilyl hydroquinones such as **25** are formed by this route[18, 19a, 81j] if (2-trialkylsilylethynyl)carbenechromium complexes are used. In these reactions (2-alkylethynyl)carbenechromium complexes naturally give the respective bicyclic cyclohexadienone derivatives because the alkyl group does not migrate as readily as the silyl group.[18, 19a, 20a, 81j]

Further examples of the Dötz reaction of alkenylcarbenechromium complexes are summarized in Table 3.

The same rules apply for the regioselectivity of the incorporation of the alkyne as in the Dötz reaction (see above) as long as stannyl or silyl-substituted alkynes are not used.[112] According to Wulff and co-workers the 2-methylpropenylidene complex **195** reacts with 1-pentyne **196** (R = H)[111] and also with 1-trialkylstannylpentynes **196** (R = $SnBu_3$, $SnMe_3$)[112] to give, after oxidative work-up, mainly 2-methyl-5-propyl-*p*-benzoquinone (**197**) with the same position of the propyl group (Scheme 12). This means that factors other than exclusively steric effects must play a role here.

Table 3. Recent examples of the formal cycloaddition of alkenylcarbenechromium complexes with CO insertion into alkynes.

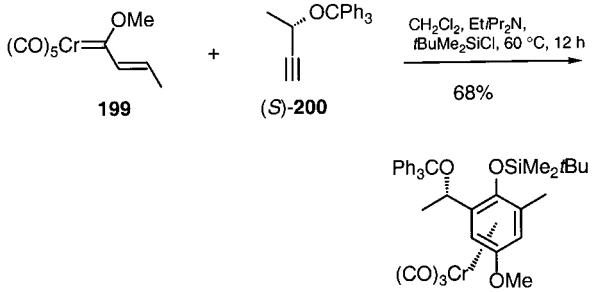
Carbene complex	Alkyne	Conditions	Product, Yield	Ref.
		*tert*-butyl methyl ether, 55 °C, 30 min		[107]
		1) THF, 40 °C, 3 d; 2) pyridine	 38%	[108]
		THF, 60 °C, 42 h	 60%	[109]
		CH_2Cl_2, 50 °C, 20 h	 68%	[104]
		1) THF, 50 °C; 2) *t*BuMe$_2$SiOTf, Et$_3$N	 40% 27%	[112]
		THF, 50 °C, 20 h	 33%	[20]
		THF, 52 °C, 14 h	 65% (70 : 30)	[20]
		1) THF, 80 °C, 3 d; 2) 1N HCl, THF, H_2O, 25 °C, 1 h	 57% 12%	[110]



R	197 : 198	[%]
H	13.3 : 1	51
$SnBu_3$	34.1 : 1	68
$SnMe_3$	34.3 : 1	—

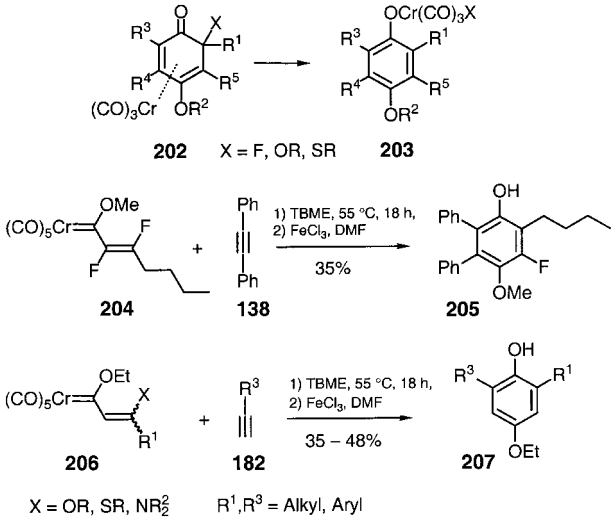
Scheme 12. The effect of stannylalkynes on regioselectivity; for R = $SnMe_3$ no yield was reported.

Wulff and et al. have also carried out the first stereoselective synthesis of an aryltricarbonylchromium complex with the aid of the Dötz reaction.[113] By cocyclization of the (*S*)-1-butyn-3-yltriphenylmethyl ether ((*S*)-**200**) with the but-



2-enylidene complex **199**, the complex **201** was formed with a diastereoselectivity of more than 92%.

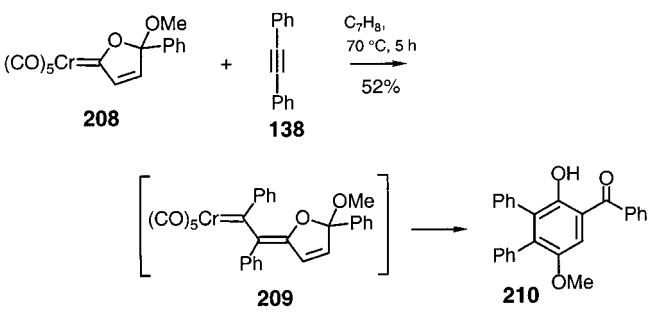
Heteroatom- and in particular donor-substituted alkenylcarbene complexes frequently deviate extensively from the "normal" Dötz reaction in their reactions with alkynes (see Sections 3.2.2–3.2.7). Even 2-fluoro-, 2-alkoxy-, and 2-alkylthioalkenyl substituted carbene complexes show a remarkably different mode of reaction with alkynes (Scheme 13).



Scheme 13. TBME = *tert*-butyl methyl ether.

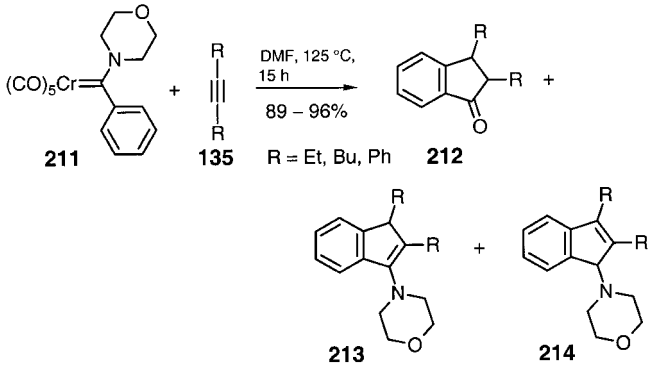
The actually expected cyclohexadienone of type **202** is not found in any instance, rather the respective hydroquinone monoether **203** is formed by loss of the heteroatom group. Thus, for example the 2,3-difluoroheptenylidene complex **204** affords the monofluorohydroquinone monoether **205** with tolane (**138**).[114] The alkenylidene complexes of type **206**, obtained particularly readily by Michael addition of the respective nucleophile to alkynylcarbene complexes (see Section 2.3.2), give hydroquinone monoethers of type **207** with alkynes **182**.[115]

An interesting result is obtained if an oxacycloalkenylidenechromium complex such as **208** is reacted with an alkyne, for example **138**, for after alkyne insertion the intermediate **209** clearly cannot cyclize. Thanks to the acetal group the ring in intermediate **209** can open so that after CO insertion and renewed cyclization the acylhydroquinone monoether **210** is obtained.[116] Such a product cannot be readily formed directly by a Dötz reaction because the corresponding starting complex would be very difficult to prepare.

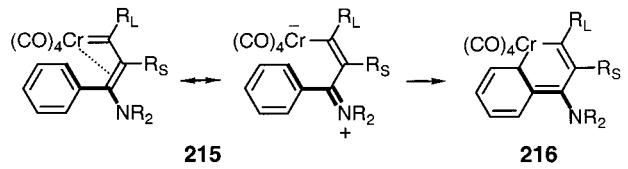


3.2.2. *Formal [3+2] Cycloadditions*

In one respect 1-aminoarylcarbene and 1-aminoalkenylidene complexes behave decisively differently than the previously and exclusively discussed α,β-unsaturated 1-alkoxycarbene complexes.[2g] Thus Yamashita et al. found that the morpholinophenylcarbene complex **211** gives exclusively the indene derivatives **213** and **214** in very good yields with symmetrically substituted alkynes **135**, as well as the hydrolysis product **212** of the enamine **213**.[117a] Dialkylaminofuranylcarbene complexes also react in the same way.[117b]

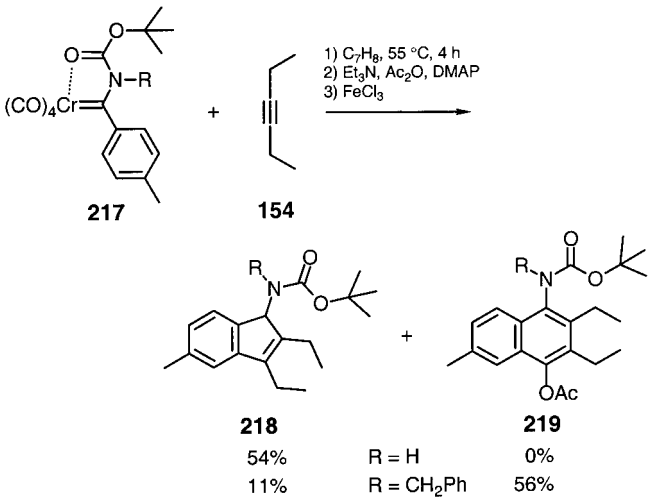


The formation of the indenes almost certainly takes place by 6π-electrocyclization of the 1-chroma-1,3,5-triene **215**, formed from **211** by alkyne insertion, followed by reductive elimination of the metal fragment from **216** (Scheme 14). According to Wulff and co-workers, amino substituents stabilize intermediate **215**;[81d] the increased electron density at the chromium atom brought about by the conjugated amino group results in a strengthening of the Cr–CO bond as a result of which the insertion of a *cis*-CO ligand occurs less readily.



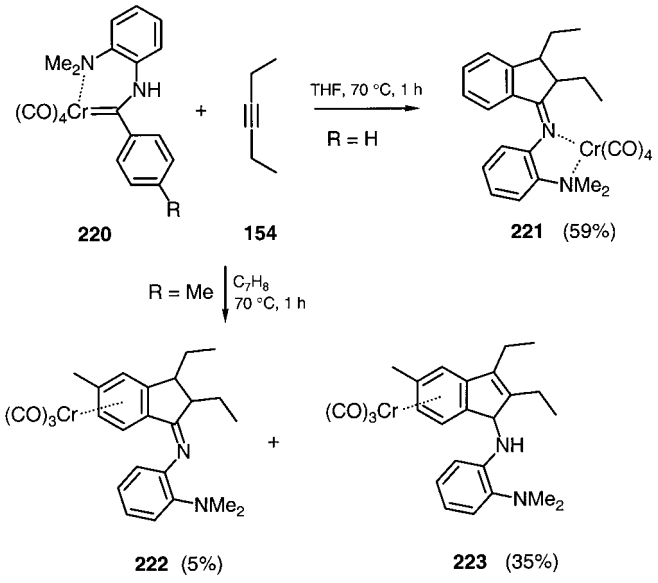
Scheme 14. R_L = larger, R_S = smaller substituent.

That the relative donor ability of the amino substituent in complexes of type **211** or the intermediates of type **215** derived from them is actually responsible for such reaction behavior is demonstrated by the results of Dötz and coworkers (Scheme 15).[118] This donor ability is clearly reduced by the *tert*-butoxycarbonyl group on the substituents, as in **217**, and, with an additional benzyl substituent on the nitrogen atom mixtures of products with and without CO insertion are formed (**219** and **218**, respectively).[118] The reaction of **217** is moreover an example of the formal cycloaddition of a chelated carbene chromium complex. Comparative investigations have shown that frequently carbenetetracarbonyl complexes such as **217** are particularly reactive towards alkynes.[81e, 107, 119]

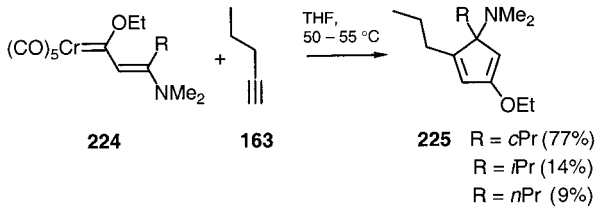


Scheme 15. DMAP = 4-dimethylaminopyridine.

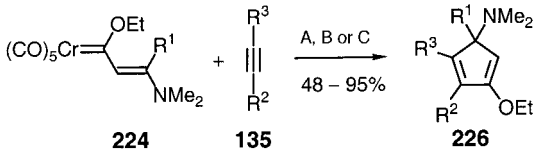
Both aminoindenes and iminoindanes can be formed by the reaction of N-monosubstituted 1-aminocarbenechromium complexes.[120, 121] Iminoindane- and aminoindenechromium carbonyl complexes are obtained as products from a 1-(2-aminoaryl)aminocarbenechromium complex with a six-membered chelate ring such as **220**.[121] Depending upon the solvent, the chromium fragment is bound across the two nitrogen atoms as in **221** (formed in THF) or to the aromatic nucleus as in **222** and **223** (formed in toluene), the R groups do not appear to have any influence.[121]



In the case of 1-alkoxycarbene complexes formal [3+2] cycloadducts in significant quantities were, for a long time, observed only starting from *o*,*o*′-dialkylarylcarbene complexes (see **187** → **189**).[105] Subsequently de Meijere and coworkers found that with donor substituents in vinyl-analogous α-position to the chromium atom (2-aminoethenyl)carbene complexes such as **224** (readily available from the addition of secondary amines to alkynylcarbene complexes,[15, 41] see Section 2.3.1) also react under normal reaction conditions without CO insertion to form 3-alkoxy-5-(dialkylamino)-cyclopentadienes **225**.[119, 122] The yields however, with tetrahydrofuran as solvent were surprisingly highly dependent upon the nature of the substituent R on the ethenyl terminus of the carbene complex. Only cyclopropyl-substituted complexes gave the corresponding cyclopentadienes in good yields.[119]



After detailed investigations of all the factors (type of substituent, degree of substitution, solvent, solvent additives) which could influence this reaction, a complete generalization and optimization of this novel five-membered ring synthesis was achieved (Scheme 16).[2l, 123] Cyclopropyl-substituted



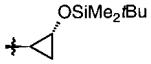
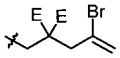
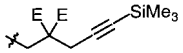
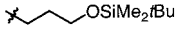
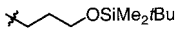
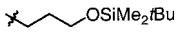
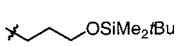
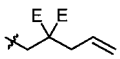
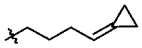
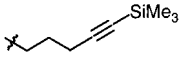
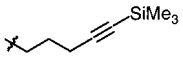
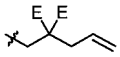
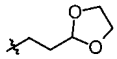
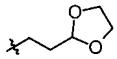
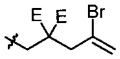
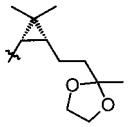
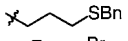
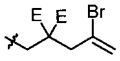
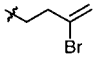
Scheme 16. A: hexane, 55 °C; B: pyridine, 55 – 80 °C; C: MeCN 80 °C, low alkyne concentration (for details see Table 4).

complexes of the type **224** in *n*-hexane as solvent give the correspondingly substituted cyclopentadienes **226** in very good yields (92 – 95 %, see Table 4). Generally good to very good yields are obtained with a wide spectrum of substituents both in the alkenylcarbene complex **224** and in the alkyne component **135** with the use of pyridine as solvent (Table 4).

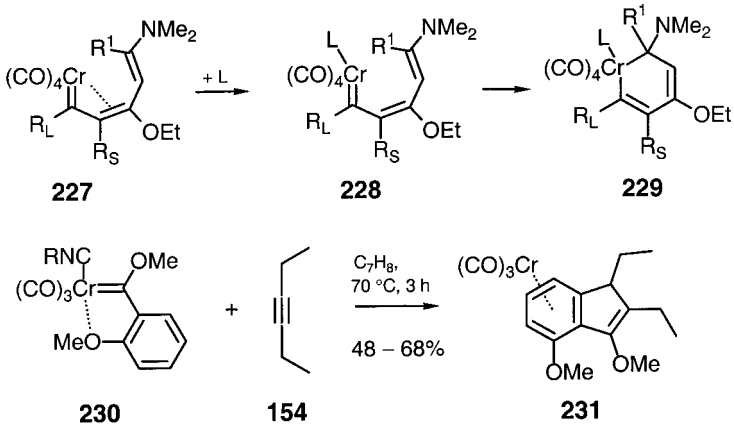
This is particularly surprising for previously pyridine had been thought of as a "poison" for Fischer carbene complexes, and it was rarely considered as a solvent for their reactions. Clearly, however, pyridine as a good donor ligand stabilizes coordinatively unsaturated intermediate complexes such as **227** and **228**. The increase in the strength of the Cr–CO bond associated with the increased electron density at the chromium atom retards CO insertion and thus favors the direct cyclization of the 1-metalla-1,3,5-triene **227** to a 5-metalla-1,3-cyclohexadiene **229** (Scheme 17).

The cyclopentadiene compounds **226** were also formed in high yield in acetonitrile, although only when a constantly low concentration of the alkyne **135** was maintained by slow addition. At a higher alkyne concentration there is increased CO insertion, although without formation of the Dötz product.[124] Dötz and Christoffers were able to show that an isocyanide ligand previously introduced into the coordination sphere of the chromium, as in **230**, has exactly the same effect so that indenes **231** are preferentially formed from alkoxy-(aryl)carbenechromium complexes by cyclization to a five-membered ring (Scheme 17).[125]

Table 4. 5-Dialkylaminocyclopentadienes **226** from β-dialkylamino-substituted carbenechromium complexes **224** and alkynes **135** (see Scheme 16).[a]

224	R^1	**135** R^2	R^3	Conditions[b]	Product	Yield [%]
a	*c*Pr	*c*Pr	H	A	**226a**-*c*Pr	95
b		*n*Pr	H	A	**226b**-*n*Pr	92
c	Me	Me	Me	B	**226c**-Me,Me	56
c	Me	CH_2OSiMe_2tBu	H	B	**226c**-CH_2OSiMe_2tBu	86
d	*n*Pr	Me	Me	C	**226d**-Me,Me	95
d	*n*Pr	Ph	Ph	C	**226d**-Ph,Ph	80
d	*n*Pr	$SiMe_3$	H	C	**226d**-$SiMe_3$	53
d	*n*Pr		H	B	**226d**-E,E,Br	69
d	*n*Pr	CH_2SiMe_3	H	C	**226d**-CH_2SiMe_3	53
d	*n*Pr		H	B	**226d**-E,E,$SiMe_3$	81
e		Me	Me	B	**226e**-Me,Me	91
e			H	B	**226e**-$(CH_2)_3OSiMe_2tBu$	77
e			H	B	**226e**-E,E,Br	51
f		Me	Me	B	**226f**-Me,Me	94
g		Me	Me	B	**226g**-Me,Me	69
h		Me	Me	B	**226h**-Me,Me	46
h			H	B	**226h**-E,E	50
i		Ph	Ph	B	**226i**-Ph,Ph	81
i			H	B	**226i**-E,E,Br	48
j		Me	Me	B	**226j**-Me,Me	81
k		Me	Me	B	**226k**-Me,Me	85
l		Me	Me	B	**226l**-Me,Me	74
m		Me	Me	B	**226m**-Me,Me	79

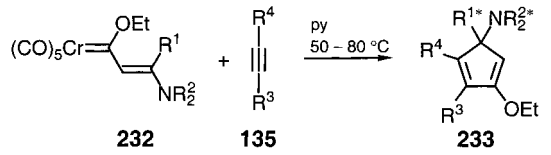
[a] E = CO_2Me or CO_2Et. [b] For conditions see Scheme 16.

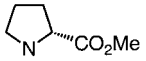
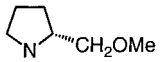
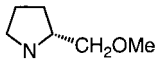
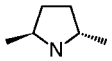
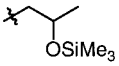
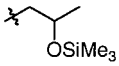


Scheme 17. L = pyridine, MeCN.

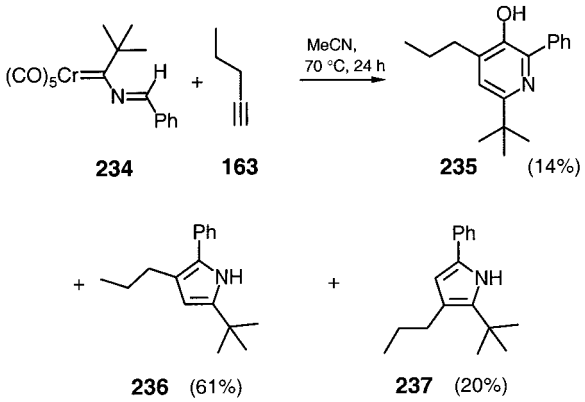
Attempts at the stereoselective control of the formation of cyclopentadienes of type **233** by induction through chiral centers in the carbene ligand (**232**) have been only moderately successful. In cocyclization with alkynes **135**, the cyclopentadienes **233** were obtained as mixtures of two diastereomers with diastereomeric excesses of up to 80% (Scheme 18).[126]

Alkylideneaminocarbene complexes such a **234**[127] are aza analogues of alkenylcarbene complexes and react correspondingly with alkynes. According to the groups of Wulff[128] and Aumann[129] these complexes give primarily formal [3+2] cycloadducts analogous to the 1-aminocarbene complexes. The product composition from **234** and 1-pentyne (**163**) is highly solvent dependent.[128] Although the ratio of the [3+2+1] adduct **235** to [3+2] adducts **236**+**237** changes little in the change from acetonitrile to hexane as solvent, the



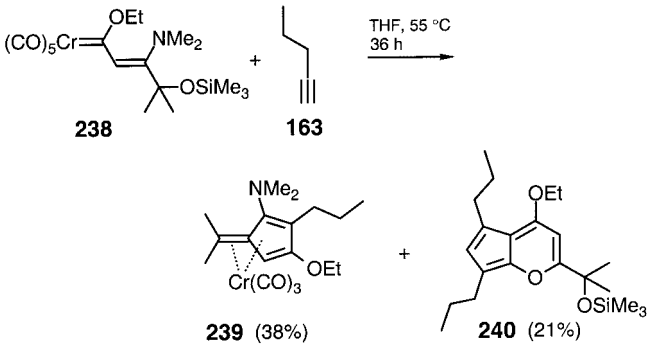
	R^1	NR_2^2	R^3	R^4	**233** [%]	*de* [%]
a	*n*Pr		Me	Me	78	23
b	*n*Pr		Me	Me	98	31
c	*n*Pr		Me	Me	22	50
d	*n*Pr		H	Ph	73	56
e		NMe_2	H	Ph	48	31
f		NMe_2	H	*t*Bu	43	44
g		NMe_2	H	*t*Bu	29	75
h		NMe_2	H	Ph	21	82

Scheme 18. Stereoselective control of the formation of the cyclopentadienes of type **233**.



regiochemistry of the alkyne incorporation, that is, the ratio **236**:**237** reverses.

The formation of the complexed fulvene **239**[130] from **238** and 1-pentyne (**163**) also formally follows a [3+2] cycloaddition, even if the mechanism is still obscure. Particularly

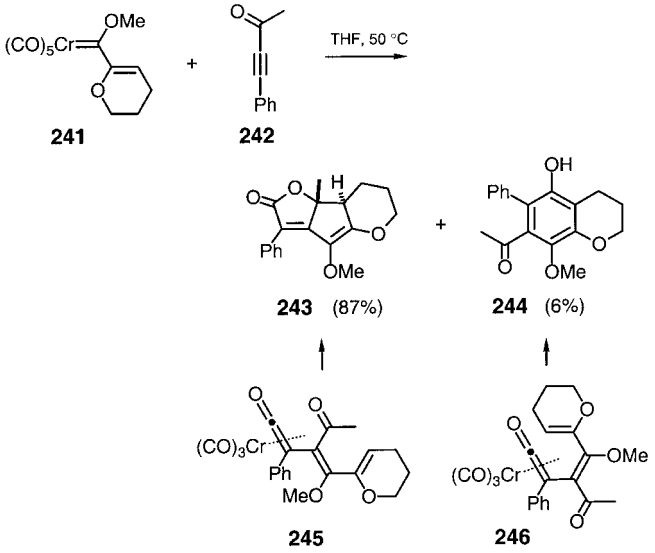


conspicuous here is that the alkyne is inserted contrary to the normal regiochemistry, and in addition, during the reaction the dimethylamino substituent must have migrated. The formation of cyclopenta[*b*]pyrans of type **240** from *Z*-configured complexes such a **238** tends to be the norm (see Section 3.2.3).

3.2.3. [3+4+1] and [3+2+2+1] Cycloadditions

Both the incorporation of two alkyne molecules each with two C atoms and also that of an alkyne with a total of four C atoms can lead to formal [3+4+*n*] cycloadditions. There are in fact examples of both variants.

Conjugated nonterminal alkynones react with alkenyl(alkoxy)carbene complexes only to a limited extent to form hydroquinone monoethers in the sense of the normal Dötz reaction. For example, **241** gives only 6% of the Dötz product **244** with 4-phenyl-3-butyn-2-one (**242**).[111a] The main product is the tricycle **243** (87%) formed as the result of a formal [3+4+1] cocyclization. The insertion of the alkyne to the *E*-configured intermediate **245**, the diastereoisomer of the



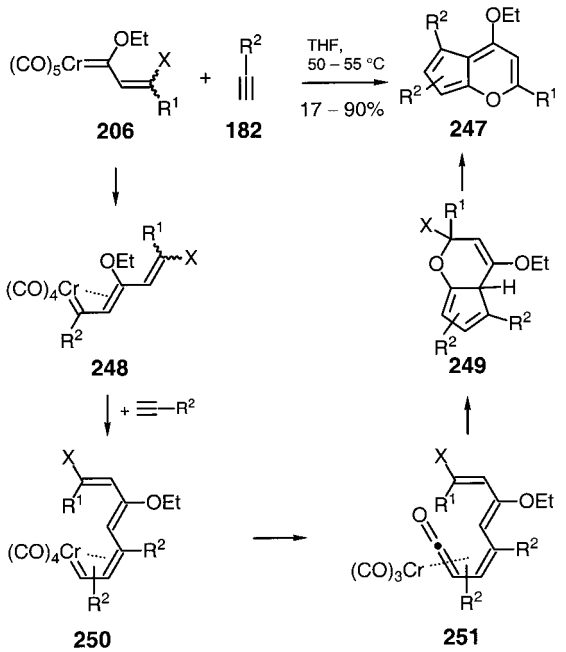
"normal" Dötz intermediate **246**, is held responsible for this unusual reaction course. One special feature is that this acyldienylketene can react further in a Halban–White type cyclization[131] to form a stable product. Moreover, electronic factors are responsible for the regiochemistry of the insertion, not the size of the substituents on the alkyne, as Wulff et al. were able to demonstrate.[111a]

In contrast, steric effects may be the reason that in the reaction of 2′-donor-substituted ethenylcarbenechromium complexes **206** with terminal alkynes **182**, cyclopenta[*b*]pyrans **247** are formed, and in yields of up to 90% (Table 5).[132, 133] An indication for this is primarily that high yields of **247** are obtained particularly when R^1 in **206** is a tertiary or a large secondary substituent. Normally in such cases the Michael adducts of nucleophiles onto alkynylcarbene complexes (type **206)** are not *E*- but *Z*-configured, and

Table 5. Cocyclization of (*E*)- and (*Z*)-(2-dialkylaminoethenyl)carbene-chromium complexes **206** with terminal alkynes **182** (see Scheme 19).

Complex	R^1	R^2	X	Product	Yield [%]
206a	Ph	Ph	NMe_2	**247a**-Ph	24
206a	Ph	Ph	NBn_2	**247a**-Ph	48
206a	Ph	Ph	$N(\sim\!\!=)_2$	**247a**-Ph	43
206a	Ph	Ph	$NiPr_2$	**247a**-Ph	17
206a	Ph	*n*Pr	NMe_2	**247a**-*n*Pr	19
206b	$C(CH_3)_2OEt$	Ph	NMe_2	**247b**-Ph	51
206b	$C(CH_3)_2OEt$	Ph	NBn_2	**247b**-Ph	68
206b	$C(CH_3)_2OEt$	Ph	$N(\sim\!\!=)_2$	**247b**-Ph	42
206b	$C(CH_3)_2OEt$	*n*Pr	NMe_2	**247b**-*n*Pr	59
206c	$C(CH_3)_2OSiMe_3$	Ph	NMe_2	**247c**-Ph	90
206c	$C(CH_3)_2OSiMe_3$	Ph	NBn_2	**247c**-Ph	78
206c	$C(CH_3)_2OSiMe_3$	Ph	NEt_2	**247c**-Ph	87
206c	$C(CH_3)_2OSiMe_3$	*n*Pr	NEt_2	**247c**-*n*Pr	25
206d		Ph	NMe_2	**247d**-Ph	41
206d		Ph	NBn_2	**247d**-Ph	47
206d		*n*Pr	NMe_2	**247d**-*n*Pr	17
206e		Ph	NMe_2	**247e**-Ph	84
206f	Adamantyl	Ph	NMe_2	**247f**-Ph	56
206f	Adamantyl	Ph	NBn_2	**247f**-Ph	47

the alkyne insertion leads then to a 1-chroma-1,3,5-hexatriene **248** with a *Z*-configured central double bond which is not capable of 6π-electrocyclization (Scheme 19). Therefore a second molecule of the alkyne and finally CO are inserted, and the resulting hexatrienylketene complex **251** can then

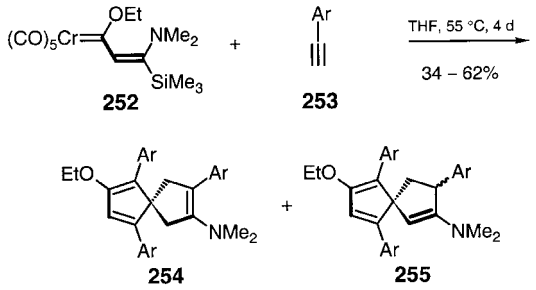


Scheme 19. X = NR_2, OR, SR. For details see Table 5.

participate in an intramolecular [4+2] cycloaddition. The resulting heterobicycle **249** finally furnishes the end product **247** by 1,4-elimination of HX. The yields with better leaving groups (e.g. NBn_2 (Bn = benzyl) compared with NMe_2) are thus generally higher. Because of the lower regioselectivity in the insertion of the second alkyne molecule the cyclopenta[*b*]pyrans are formed in part as a mixture of two regioisomers.

3.2.4. [3+2+2+2] Cocyclizations

A quite unusual mode of reaction was displayed by the 2′-trimethylsilyl-substituted (2-dimethylaminoethenyl)carbene-chromium complex **252**. On heating **252** with an excess of phenylethyne (six equivalents) in THF at 55 °C a yellow solid, which fluoresces strongly in solution, was obtained after purification by column chromatography (Scheme 20). ^1H and ^{13}C NMR spectra suggested that it was a mixture of three



Scheme 20. For details see Table 6.

isomeric compounds (ratio 3.6:1:1) none of which possessed a trimethylsilyl group. Assuming that the highest positioned peak in the mass spectrum at *m*/*z* 433 corresponded to the molecular ion, a compound had been formed in a yield of 62 % in this reaction from the protiodesilylated carbene ligand and three molecules of phenylethyne without carbonyl insertion. However, the three isomers could neither be separated, even by repeated column chromatography, nor was it possible to deduce the correct constitutions from the NMR spectra.[47a, 115a] Eventually a single crystal of the quaternary ammonium iodide of the main isomer could be obtained and thus the compound could be characterized by X-ray structural analysis as the spiro[4.4]nonatriene **254** (Ar = Ph).[134]

To probe the scope of this reaction **252** was treated with a series of alkynes. It was thus shown that only arylacetylenes gave spiro[4.4]nonatrienes **254** and **255**. The isomer ratios of the products obtained varied according to the type of substitution of the arylacetylene used (Table 6).[134b] Terminal alkynes such as 1-pentyne and nonterminal alkynes such as 2-butyne react in the normal manner to form the respectively substituted cyclopentadienes.[123]

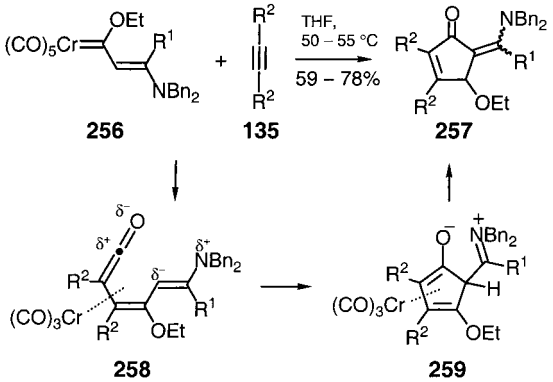
Table 6. Spiro[4.4]nonatrienes **254** and **255** (see Scheme 20) formed by the reaction of three molecules of an arylethyne **253** with the (3-dimethylamino-3-trimethylsilylalkenylidene)chromium complex **252** and subsequent cyclization.

	Ar	Yield [%] **254** + **255**	Ratio **254**:**255**
a	C_6H_5	62	1.8:1
b	4-PhC_6H_4	34	4.5:1
c	4-$OMeC_6H_4$	37	2.5:1
d	3,5-$(Me)_2C_6H_3$	48	1.6:1

For some of the originally merely speculative concepts concerning the mechanism of formation of these novel cocyclization products of arylethynes with the chromium complex **252** the first experimental evidence has been collected.[134b] The observation that a ^{13}C-labeled carbene carbon atom in the complex **252** ends up as the spirocarbon in the products **254** and **255** consistantly demonstrates that the original connectivity of the carbene ligand in **252** is retained in the products **254** and **255** (Scheme 20) just as in all the previously known products from β-dialkylamino-substituted α,β-unsaturated carbenechromium complexes.[21] This means that at the same time the ethoxy group must have migrated from its original position in **252** to a different carbon atom in the products.[134b]

3.2.5. [2+2+1] Cocyclizations

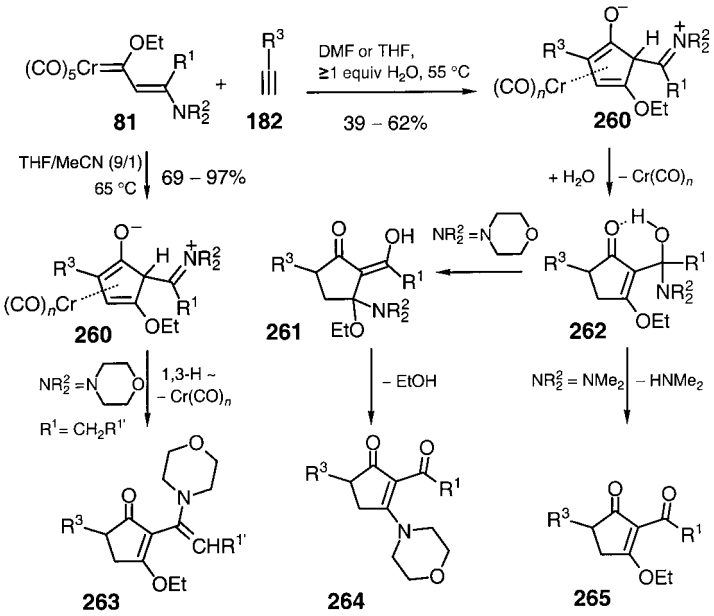
In the classical Dötz reaction (see Section 3.2.1), its analogues, and also the formal [3+2] cycloadditions of (2-dialkylaminoalkenyl)carbene complexes with alkynes, three carbon atoms of the carbene complex reappear in the cyclic system of the product. A further cyclization variant has been described by de Meijere and co-workers in which only the carbene carbon atom and its directly neighboring C atom in the carbene complex are found in the five-membered ring of the product, the amino-substituted β-C atom is in contrast exocyclic. It was first found that nonterminal alkynes do not react with (2-dibenzylaminoalkenyl)carbenechromium complexes of type **256** in tetrahydrofuran to give formal [3+2] cycloadducts of type **226**, but react smoothly with CO insertion to produce 5-(1-dibenzylaminoalkylidene)cyclopent-2-enones **257** (Scheme 21).[135] Since CO insertion is effectively suppressed with the concurrent presence of two good electron-donor groups in the β position of the complex, or in the presence of a solvent with good donor properties such as pyridine or acetonitrile (see Section 3.2.2), the formation of an intermediate ketenyl complex **258** is understandable. Surprisingly however, **258** apparently does not cyclize to form a cyclohexadienone of type **147** as in a Dötz reaction, but clearly cyclizes as a 1,5-dipole to form a five-membered ring. The resulting intermediate **259** can be transformed into the end product **257** by a [1,5] hydrogen shift and loss of the tricarbonylchromium moiety. The (dibenzylaminoalkylidene)cyclopentenones occur as mixtures of *E*- and *Z*-isomers, and the diastereomeric ratio depends upon the nature of the substituent, although the barrier to *E*/*Z*-isomerization is so low that rapid interconversion of the two isomers occurs at room temperature.



Complex	R^1	R^2	**257** [%]
256a	*n*Pr	Ph	68
256a	*n*Pr	Me	78
256a	*n*Pr	$-(CH_2)_6-$	75
256b	*c*Pr	Ph	59
256b	*c*Pr	$-(CH_2)_6-$	62

Scheme 21. Substituent effects on the formation of compounds **257**; Bn = benzyl.

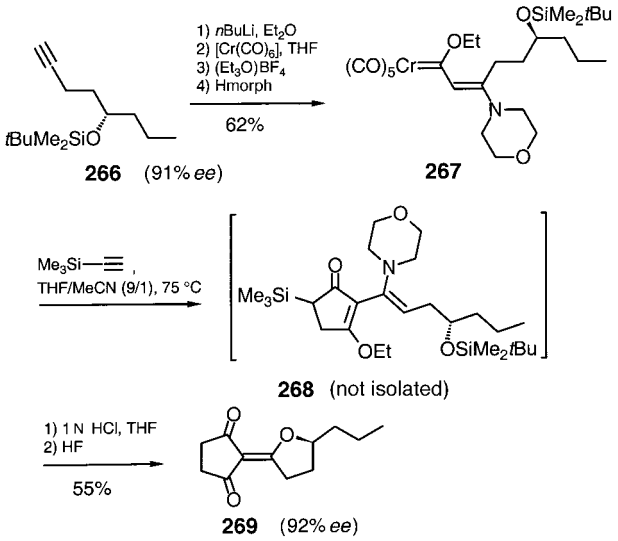
Terminal alkynes **182** also react with complexes of type **256** in this manner under CO insertion to afford [2+2+1] cocyclization products of type **257** if the reaction is carried out in dimethylformamide (DMF).[21] Two other types of [2+2+1] cocyclization products are obtained, sometimes in very good yields, if carbenechromium complexes **81** with a β-morpholinoethenyl substituent are reacted with alkynes **182**. Here the constitution of the products depends upon the



reaction conditions. In aqueous DMF or THF 2-acyl-3-morpholinocyclopent-2-enones **264** are formed,[136] and—in the case of **81** with the dimethylamino substituents (entry 7 in Table 7) in aqueous THF— also the 2-acyl-3-ethoxycyclopent-2-one **265a**.[137] In contrast, however, in a mixture of THF and acetonitrile (9:1), 2-(1-morpholino-1-alkenyl)cyclopent-2-enones **263** are formed.[138] Clearly, in a manner similar to the formation of the methylenecyclopentenones **257** an intermediate of type **260** must arise on the way to these cocyclization products. In the case of the alkenylcyclopentenones **263**, a [1,3] hydrogen shift with subsequent tautomerization and loss of the carbonylchromium fragment leads to the cyclopentenone. The acylcyclopentenones **264** and **265** arise through 1,4-addition of water to **260**. On the way to **264** the amino group must migrate from the exocyclic to the endocyclic 3-position, which can occur through elimination–readdition. Subsequent 1,4-elimination of ethanol from **261**

leads to **264**, whereas **265** is formed directly by the elimination of dimethylamine from **262** (Table 7).[136]

Cyclopentenones of type **263**, **264**, and **265** are protected 2-acylcyclopentane-1,3-diones which should have significant synthetic potential. Since the mild reaction conditions are compatible with a series of functional groups in both starting materials, namely the complexes **81** and the alkynes **182**, the use of this type of reaction in natural-product synthesis is obvious. A simple example was demonstrated by de Meijere and co-workers in the synthesis of (−)-oudenone **269** in essentially two steps from the nonracemic octyn-5-yl silyl ether **266** and trimethylsilylacetylene. Since the stereogenic center in **266** is not affected throughout the whole transformation the enantiomeric purities of the product **269** and of the starting material **266** are essentially identical.[138]



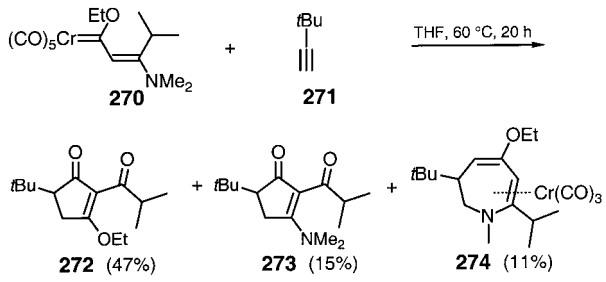
266 (91% *ee*) **267**

268 (not isolated)

269 (92% *ee*)

3.2.6. [5+2] Cocyclizations

In the reaction of the isopropyl-substituted alkenylcarbenechromium complex **270** with sterically demandingly substituted terminal alkynes such as 3,3-dimethylbutyne (**271**), the seven-membered heterocycle **274** was obtained as a byproduct in addition to the two acylcyclopentenones **272** and **273**, which are formed by formal [2+2+1] cycloaddition. In the new cocyclization product **274** five atoms of the (dialkylaminoethenyl)carbene complex and the two atoms of the triple bond are involved in the formation of the ring. The



270 **271**

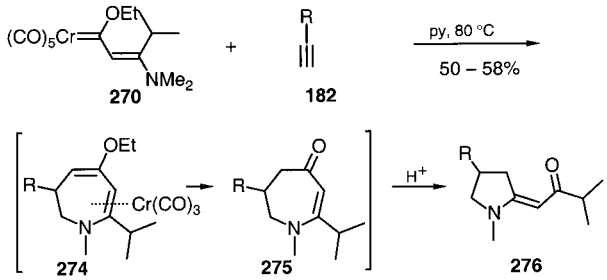
272 (47%) **273** (15%) **274** (11%)

tricarbonylchromium fragment is coordinated η^5 with the aminodienyl unit of the dihydroazepine **274**.

The formation of **274** almost certainly begins in the same way as the Dötz reaction with a regioselective insertion of the alkyne into the chromium–carbon double bond. The result is most readily explained if it is assumed that first the free carbene is formed from the insertion product, possibly facilitated by the bulky *tert*-butyl substituent, and the free carbene then inserts intramolecularly into one of the C–H bonds of the aminomethyl groups.

To favor formation of the dihydroazepine **274** possibly still further two equivalents of triphenylphosphane were added to the reaction mixture, for triphenylphosphane as a donor ligand leads to an increased electron density at the chromium center, which retards CO insertion during cyclization.[139] Indeed, in this way the yield of **274** could be increased to 23%.

Even more effective is the use of the donor solvent pyridine, as in the synthesis of the 3-alkoxy-5-dimethylaminocyclopentadienes **226**.[123] In the reaction of **270** with **182** in pyridine the product ratio was shifted towards the dihydroazepine **274**, and at the same time under these conditions the tricarbonylchromium fragment was cleaved off. After purification by column chromatography the methylenepyrrolidine **276** was formed, not the azepinone **275** (Scheme 22). The former is formed



270 **182**

274 **275** **276**

Scheme 22. R = *t*butyl, adamantyl, CMe_2NMe_2; py = pyridine.

Table 7. Highly-substituted cyclopentenones **263**–**265** from (2-dialkylaminoethenyl)carbenechromium complexes **81** and alkynes **182**.

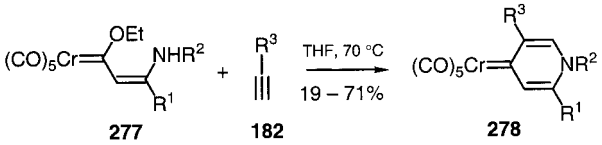
Entry	R^1	NR^2_2[a]	R^3	Conditions[b]	Product	[%]	Product	[%]
1	*n*Pr	morph[b]	*n*Pr	A	**264a**	54	–	
2	*n*Pr	morph	*t*Bu	A	**264b**	51	–	
3	*n*Pr	morph	$SiMe_2tBu$	A	**264c**	62	–	
4	Ph	morph	*n*Pr	A	**264d**	39	–	
5	Ph	morph	*t*Bu	A	**264e**	54	–	
6	Ph	morph	$SiMe_2tBu$	A	**264f**	48	–	
7	*i*Pr	NMe_2	*t*Bu	A	**264g**	15	**265a**	47
8	*n*Pr	morph	*n*Pr	B	**263a**	82	–	
9	*n*Pr	morph	Ph	B	**263b**	97	–	
10	Me	morph	$SiMe_2tBu$	B	**263c**	72	–	
11	$(CH_2)_4OSiMe_2tBu$	morph	$SiMe_2tBu$	B	**263d**	69	–	

[a] morph = morpholino. [b] A: DMF (1 equiv H_2O) or THF (1 equiv H_2O), 55 °C; B: THF/MeCN 9:1, 65 °C.

most probably by ring-opening hydrolysis of the cyclic enamine **275**, and subsequent ring closure by the addition of the secondary amino group onto the δ-oxo function.[137] Methylenepyrrolidines **276** are produced in this way only with sterically demandingly substituted alkynes **182**, with sterically less congested alkynes only the 3-alkoxy-5-dialkylaminocyclopentadienes of type **226** are formed.[123]

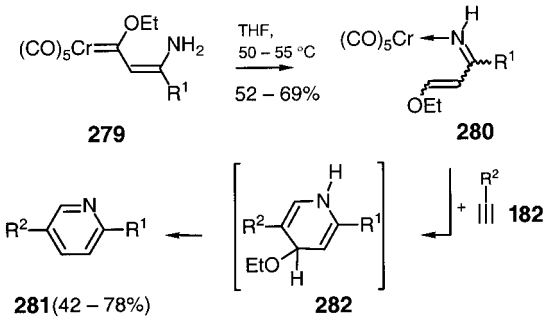
3.2.7. [4+2] Cocycloadditions

3-Aminoalkenylidenechromium complexes such as **277** with a secondary amino group, react with alkynes in a totally different way compared to those with tertiary amino groups. When **277** and terminal alkynes **182** are heated in THF, 4-(1*H*)-pyridinyl complexes of type **278** are formed (Scheme 23),[48a, 111a, 130] the stability of which arises from the nitrogen atom in the ring. Four sequential atoms of the 3-aminoalkenylidene moiety from **277** are thus found in the formal cycloadduct **278**.



Scheme 23. $R^1 = n$Bu, Ph; R^2 = Me, *i*Pr, Bn; $R^3 = n$Bu, Ph.

(2-Aminoalkenyl)carbenechromium complexes **279** with a primary amino group behave quite differently (Scheme 24). When heated in THF they rearrange into pentacarbonylchromium-coordinated 1-azabutadienes **280** which may actually be isolated.[51] In the presence of alkynes, complexes **280** react



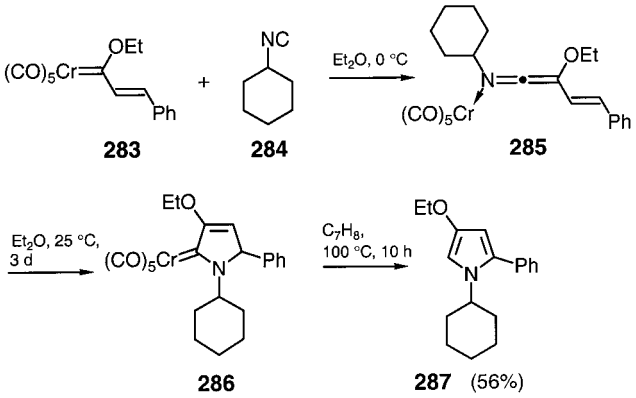
Scheme 24. $R^1 = n$Pr, *c*Pr, Ph; R^2 = Ph, *n*Pr.

in a [4+2] cycloaddition to form dihydropyridines **282**, which give pyridines **281** by 1,4-elimination of ethanol. Thus, the mechanism of the previously observed[48a] formation of pyridines from (β-aminoethenyl)carbenechromium complexes is also explained, for until then it was not understandable why in the formation of the pyridine almost exclusively that regioisomer is formed which contradicts the usual regioselectivity of an alkyne insertion into an ethenylcarbenechromium complex.

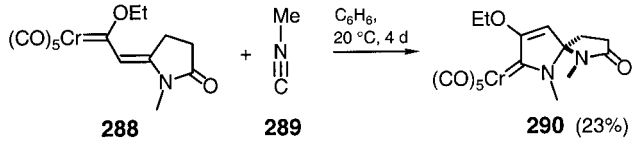
3.2.8. Cocyclizations with Aza- and Phosphalkynes

3.2.8.1. 2-Aza-1-alkynes (Isocyanides)

Carbene complexes react quite generally with isocyanides to form keteneimine complexes;[140] this also applies to α,β-unsaturated carbene complexes such as **283** which at 0 °C first form the 3-ethoxy-3-styrylketeneimine complex **285**. On warming to room temperature it produces the 3-ethoxy-2,5-dihydro-2-pyrrylidene complex **286** from which the pyrrole derivative **287** is released on heating to 100 °C.[141]



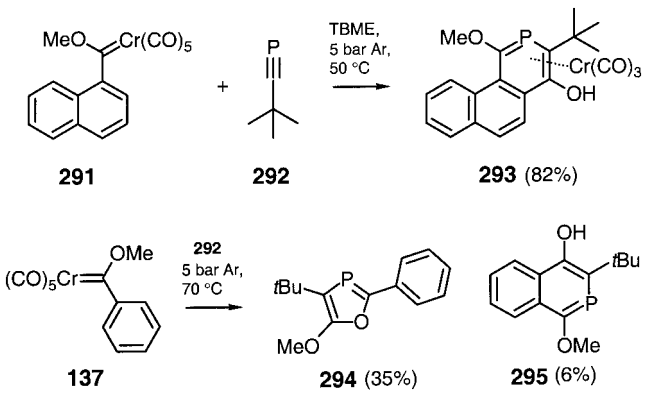
Only a small number of similar cases are known in which the α,β-unsaturated ligand is ultimately included into a cycloadduct by reaction with an isocyanide. One further interesting example of this type of reaction is the formation of the 1,6-diazaspiro[4.4]non-3-en-2-ylidene complex **290** from the β-donor-substituted ethenylcarbenechromium complex **288** and methyl isocyanide (**289**).[142]



3.2.8.2. Phosphaalkynes

As soon as isolable, kinetically stabilized phosphaalkynes were first known[143] they were also treated with unsaturated Fischer carbene complexes.[2f, 144] What effects the presence of the phosphorus atom as a potential electron-donor ligand would have on the course of the reaction was certainly eagerly awaited.

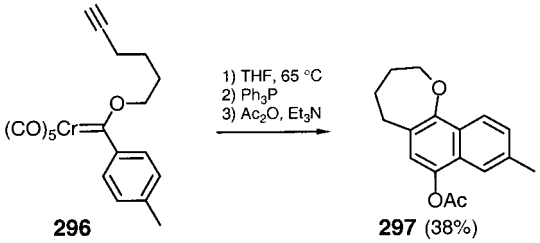
In actual fact, 3,3-dimethyl-1-phosphabutyne (**292**) adds to the (1-naphthyl)carbenechromium complex **291**[144] as in a Dötz reaction and the 3-phosphaphenanthrene derivative **293** is formed in very good yield. In a competition reaction between **292** and 3,3-dimethylbutyne **271** with the complex **291** the phosphalkyne **292** was found to react six times faster than the alkyne.[144] A side reaction in which oxaphospholes **294** are formed—corresponding to furan formation during a Dötz reaction—cannot always be suppressed, and frequently even becomes the main reaction, as in the example of the phenylcarbenechromium complex **137**.[144]



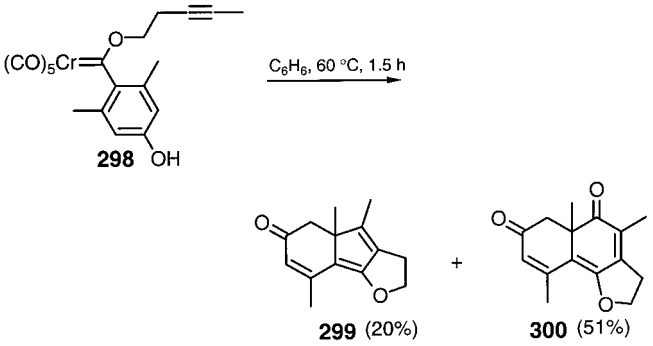
3.2.9. Intramolecular Cocyclization of Carbene Complexes with Alkynyl Groups

There have been only a few investigations of intramolecular variants of the Dötz reaction. In view of the steric demands on alkyne insertion the connection of the alkyne unit only appears useful when through the heteroatom at the carbene center. This principle has been used mainly to control the regioselectivity of ring annelation.[81b,c, 85a, 145–147]

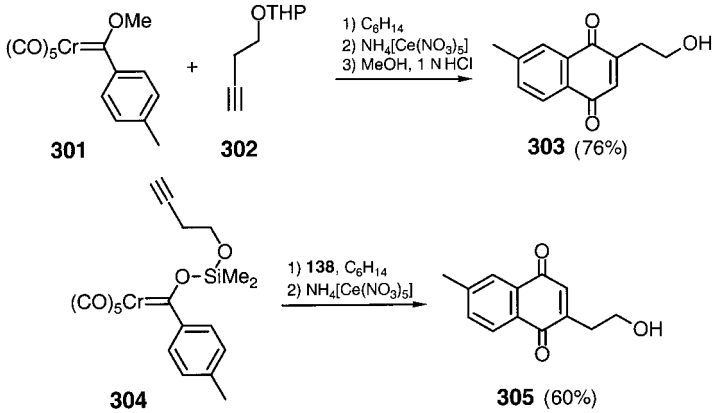
Annelation follows the classical Dötz reaction when a THF solution of the complex **296** with a 5-hexynyl chain on the oxygen atom is heated under reflux.[146] Neither added 1-hexyne nor diphenylacetylene (tolane (**138**)) could suppress the intramolecular reaction or influence it in any way. However, the product **297** was isolated in only 38% yield



following acetylation of the phenol hydroxyl group. A significantly better yield was obtained in the intramolecular cycloaddition of the complex **298**, in which in addition to the formal Dötz product **300** the indene derivative **299**, arising from a formal [3+2] cycloaddition, was also obtained.[106]

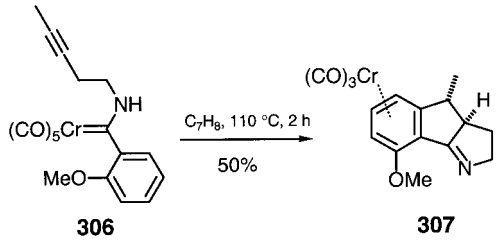


With this principle Gross and Finn developed a method for the preparation of quinones with a regiochemistry of alkyne insertion contrary to that of the normal Dötz reaction (Scheme 25).[146] The handle with the O–Si–O group in **304** can be readily cleaved after successful annelation so that after oxidation with cerium(IV) ammonium nitrate the (hydroxyethyl)naphthoquinone **305** is formed. This is a regioisomer of the normal oxidized Dötz product **303** from **301** and protected 3-butynol **302**. Unlike the intramolecular reaction of **296** the addition of tolane (**138**) dramatically favors the intramolecular cycloaddition of silyloxycarbenechromium complexes such as **304**.[146]



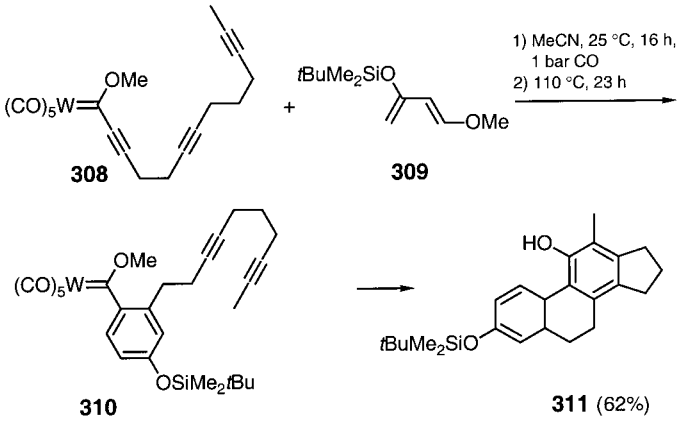
Scheme 25. Reversal of the regioselectivity in the Dötz reaction by intramolecularization.

The intramolecular formal [3+2] cycloaddition of 1-amino-substituted carbene complexes to alkynes has also been carried out. One example is the transformation of the 1-(alkynylamino)carbene complex **306** into the benzotetrahydrazoazapentalene derivative **307** by heating to 110 °C. As in



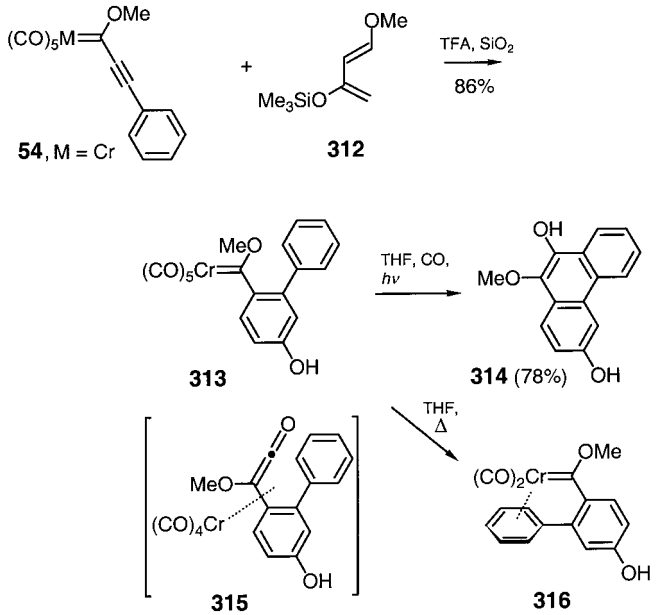
the intermolecular cycloaddition of 1-aminocarbene complexes, CO insertion is suppressed.[147, 148] The *cis* arrangement of the tricarbonylchromium fragment and methyl substituent in the five-membered ring was established by X-ray structural analysis,[147] thus the double ring annelation takes place diastereoselectively.

Particularly impressive is the cascade reaction of the tungsten alkynylcarbene complex **308** described by Wulff and co-workers which leads to a one-step construction of the steroid framework **311** in 62% yield. The sequence begins with a [4+2] cycloaddition of the diene **309** to the alkynylcarbene complex **308** with subsequent aromatization and generation of the arylcarbene complex **310**. Similar to the formation of the cyclopenta[*b*]pyrans[132] (Section 3.2.3.), a double alkyne insertion into the metal–carbene carbon bond, CO insertion, and electrocyclic ring closure then follow.[149]



3.3. [5+1] and [4+1] Cocyclizations with Carbon Monoxide and Isocyanides

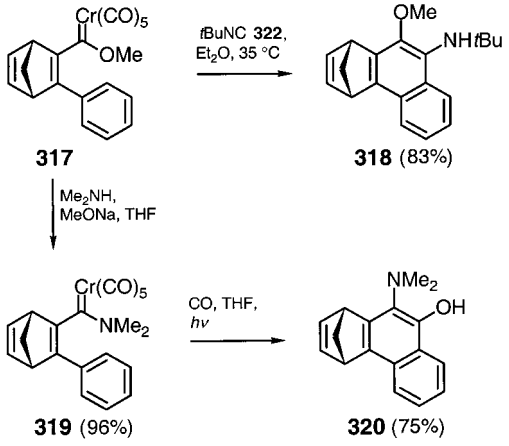
In the normal Dötz reaction alkyne insertion generally leads to a butadienylcarbene complex of type **143** which inserts a *cis*-positioned carbonyl ligand to form a butadienylketene complex **144** (see Scheme 9). Merlic et al. have developed a procedure for the synthesis of *o*-alkoxyphenols and *o*-quinones[150] in which external CO is inserted into a stable dienylcarbene complex analogous to **143**. This transformation begins (Scheme 26) with the [4+2] cycloaddition of



Scheme 26. TFA = trifluoroacetic acid.

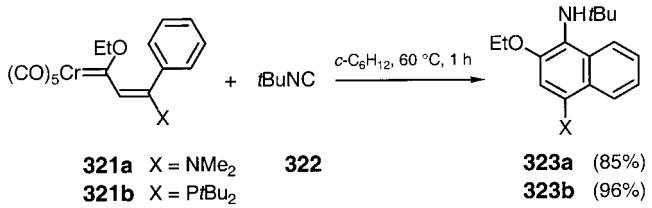
1-methoxy-3-trimethylsilyloxy-1,3-butadiene (**312**) to the (phenylethynyl)carbenechromium complex **54** (M = Cr) in which the stable biphenylcarbene complex **313**, formally a dienylcarbenechromium complex analogous to **143**, is formed (see Section 2.2). The *o*-methoxyphenol **314** (78% yield) is produced smoothly by irradiation of **313** in a CO atmosphere.[150a] It can be safely assumed that—as in the Dötz reaction—a dienylketene complex occurs as an intermediate, in this case it contains a methoxyketenyl moiety **315**. Derivatives of **54** with a *meta*-substituted aryl residue lead to products of type **314** with astonishingly high regioselectivities.[150b] The reaction proceeds surprisingly differently if the solution of **313** in THF is not irradiated but is heated under reflux,[151] then a carbenedicarbonylchromium complex **316**, chelated to a phenyl ring, is formed (Scheme 26).

In contrast, the [5+1] cocyclizations of complexes such as **313** with isocyanides also occur purely thermally.[54, 152, 153] On heating complex **317**, analogous to **313** and formed by cycloaddition of cyclopentadiene to **54** (M = Cr), with *tert*-butylisocyanide, the naphthonorbornadiene derivative **318** is formed.[152a] Merlic et al. showed impressively that by simple



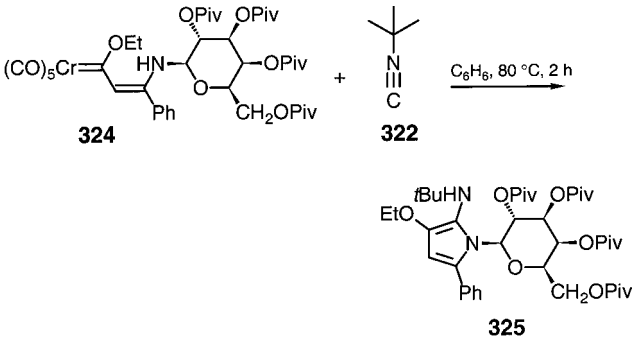
manipulations a product of type **318** with reversed positioning of the oxygen and the nitrogen substituent (**320**) can be obtained.[152a] Thus, if **317** is first treated with dimethylamine and the resulting 1-dimethylaminocarbene complex is irradiated in a carbon monoxide atmosphere, the naphthonorbornadiene **320** is formed smoothly.

Whereas (3-dialkylaminoalkenylidene)chromium complexes differ in their reactions with alkynes from other α,β-unsaturated carbene complexes, this does not apply to their reactions with isocyanides. Aumann et al. have shown that alkoxydiaminonaphthalenes such as **323a** are accessible from (3-dialkylamino-3-phenylpropenylidene)carbene complexes of the type **321a** and the isocyanide **322**.[50, 153] β-Phosphanyl-substituted ethenylcarbene complexes such as **321b** also react with isocyanides in the same manner to yield alkyloxyaminophosphanylnaphthalenes such as **323b**.[54]



Stable butadienylcarbenechromium complexes can not only form *o*-alkoxy- or *o*-aminophenol derivatives by [5+1] cocyclization with CO or isocyanides, but react in the manner of [4+1] cocyclizations. In the reaction of (β-aminoethenyl)-

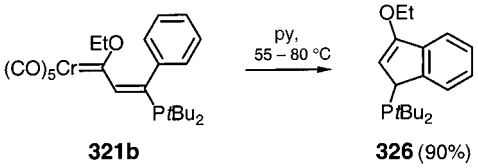
carbene complexes with secondary amino groups such as **324** with an isocyanide such as **322**, a keteneimine complex analogous to **285** is first formed, which has two possibilities for cyclization.[49] Of these the one with inclusion of the phenyl substituent would give a formal [5+1] cocyclization product. However, the other variant is preferred, in which clearly the secondary amino group attacks the keteneimino group as a nucleophile so that the pyrrole **325** is formed.[49b]



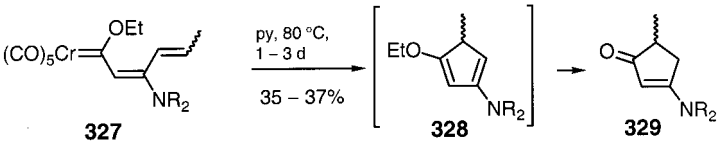
3.4. Intramolecular Cyclizations and Rearrangements of the Carbene Ligand

In addition to the intermolecular reactions of α,β-unsaturated carbenechromium complexes described above, in which—apart from the intramolecular variants of the Dötz reaction—one, two, or even three external partner molecules are involved, there are also reactions with ethenyl- and phenylcarbenechromium complexes in which only the carbene ligand cyclizes or rearranges.

With the [5+1] cocyclizations (see Section 3.3) of the stable butadienylcarbene complexes a kind of side entry into the Dötz reaction occurs which—as is usual after the insertion of carbon monoxide—concludes with the cyclization of a dienylketene complex. The formal [3+2] cycloadditions to indene and cyclopentadiene derivatives are examples of how butadienylcarbenechromium complexes, formed as intermediates by alkyne insertion, can also cyclize directly (see Section 3.2.2). That stable butadienylcarbenechromium complexes also cyclize to five-membered rings was eventually demonstrated by Aumann et al.[54] If the 3-di-*tert*-butylphosphanyl-3-phenylpropenylidene complex **321b** is not heated with *tert*-butylisocyanide in cyclohexane, but simply warmed in pyridine, the phosphanylindene **326** is formed. What special

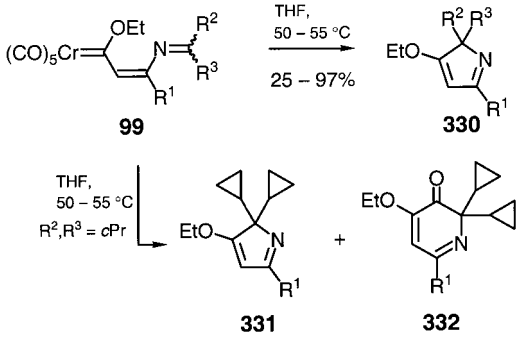


role pyridine as solvent plays has already been demonstrated by de Meijere and co-workers with the broadly applicable synthesis of 5-dialkylaminocyclopentadienes (see Section 3.2.2).[123] Thus, the relatively unstable 4-aminochromahexatrienes of type **327** also react intramolecularly to the corresponding cyclopentadienes **328**, which upon aqueous work-up hydrolyze to 3-dialkylaminocyclopentenones **329** (Scheme 27).[154]



Scheme 27. R = Me, Et.

1-Chroma-1,3,5-hexatrienes evidently have a fundamental reaction pathway which leads to formation of a five-membered ring. In this case it does not matter how the 1-chroma-1,3,5-hexatriene is assembled, or whether it contains further heteroatoms, as the example of 5-aza-1-chroma-1,3,5-hexatrienes **99** shows. These complexes, which are readily obtained by the addition of imines to alkynylcarbene complexes (see Scheme 5), cyclize on warming in THF—even in the presence of alkynes without their incorporation—to 2*H*-pyrroles **330**, mostly in good yields. With two cyclopropyl substituents in **99**, the pyridone **332** might be formed as a byproduct along with the 2*H*-pyrroles **331** on heating (Scheme 28 and Table 8).[52, 155]

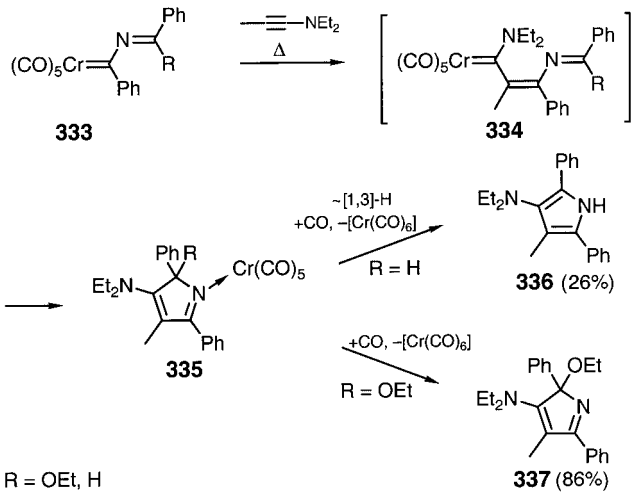


Scheme 28. For details see Table 8.

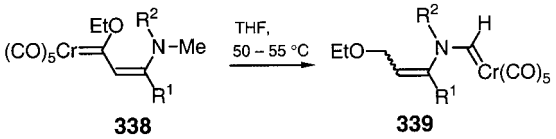
Table 8. Reactions of 5-aza-1-chroma-1,3,5-hexatrienes **99** according to Scheme 28.

Complex (yield [%])	R^1	R^2	R^3	Product	[%]	Product	Yield [%]
99a (41)	Ph	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**330a**	25	–	–
99b (63)	*n*Pr	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**330b**	57	–	–
99c (64)	*c*Pr	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**330c**	65	–	–
99d (59)	*t*Bu	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**330d**	78	–	–
99e (72)	Ph	Ph	*c*Pr	**330e**	62	–	–
99f (88)	*n*Pr	Ph	*c*Pr	**330f**	88	–	–
99g (98)	*c*Pr	Ph	*c*Pr	**330g**	97	–	–
99h (85)	*t*Bu	Ph	*c*Pr	**330h**	85	–	–
99i (63)	Ph	*c*Pr	*c*Pr	**331a**	45	**332a**	21
99j (81)	*n*Pr	*c*Pr	*c*Pr	**331b**	63	**332b**	22
99k (84)	*c*Pr	*c*Pr	*c*Pr	**331c**	81	**332c**	0
99l (86)	*t*Bu	*c*Pr	*c*Pr	**331d**	92	**332d**	0

The 2-dialkylamino-5-aza-1-metalla-1,3,5-hexatrienes **334**, which arise from alkyne insertion into 1-(methyleneamino)-alkylidenemetal complexes **333**, cyclize similarly and give pyrroles of type **336** and **337**.[35b, 129]



The rearrangement to the pentacarbonyl(ethenylamino)-methylenechromium complexes **339**, observed with (β-aminoethenyl)carbene complexes of the type **338** with a tertiary substituent R^1 in the β position, appears particularly bizarre (Scheme 29 and Table 9).[156] The mechanism of this transformation, which in view of the β-lactam synthesis developed by Hegedus et al. with aminocarbene complexes[157] could achieve preparative significance, is still open to speculation.



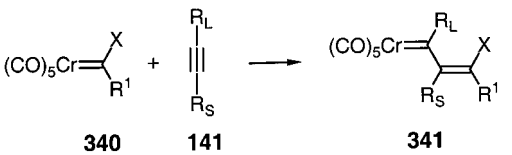
Scheme 29. For details see Table 9.

Table 9. Rearrangement of β-aminoethenylcarbene complexes **338** (see Scheme 29.

Complex	R^1	R^2	Product	[%]	Ratio *E*:*Z*
338a	*t*Bu	Me	**339a**	59	13:1
338b	CMe_2OEt	Me	**339b**	54	5:1
338c	$SiMe_3$	Me	**339c**	20	9:1
338d	*t*Bu	*c*Hex	**339d**	74	19:1

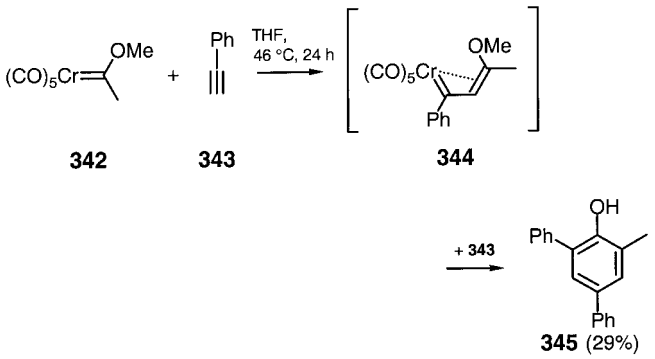
4. Reactions of α,β-Unsaturated Carbenechromium Complexes Prepared in situ from Alkynes and Alkylcarbene Complexes

The insertion of alkynes into a chromium–carbon double bond is not restricted to α,β-unsaturated carbene complexes. Simple alkylcarbene complexes **340** also react with alkynes primarily to form unstabilized alkenylcarbene complexes **341** (Scheme 30),[158] which can react further in a number of ways, both intermolecularly as well as intramolecularly.

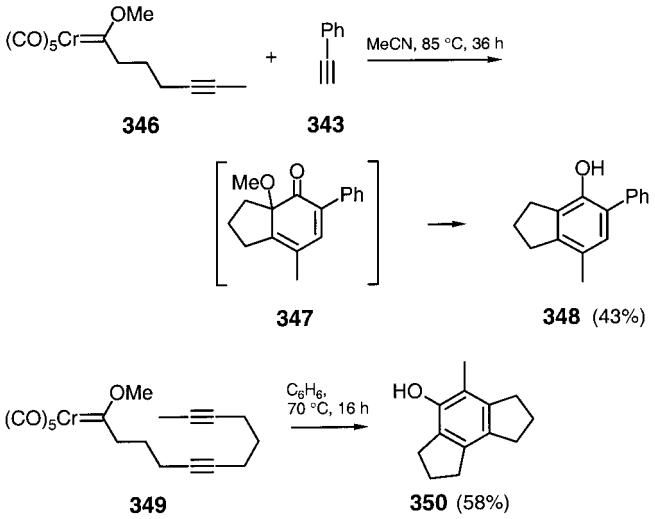


Scheme 30. R_L = larger, R_S = smaller substituent; X = OR, NR_2.

In the simplest case the carbene complex **344**, formed initially from **342** with phenylethyne (**343**), can react with a further molecule of the added alkyne by insertion. In this way the substituted phenol **345** is produced after CO insertion and cyclization, in what is a classical Dötz reaction.[159]



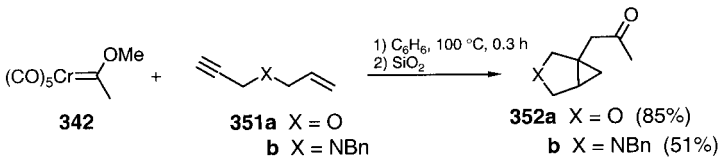
The sequence of an intramolecular and a subsequent intermolecular insertion of an alkyne into an alkylcarbene complex is even more clever, although a wide spectrum of products often ensues.[160] However, the indane derivative **348** is formed in moderate yield (43%) by heating the (4-hexynyl)carbene complex **346** with phenylethyne (**343**) in acetonitrile.[160a] That the obviously formed intermediate **347** cannot be isolated is in agreement with the behavior of the similarly substituted intermediate **202** with a heteroatom leaving group (see Scheme 13).



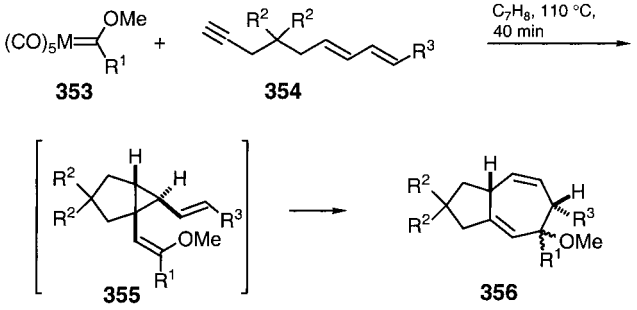
The reaction cascade which is initiated by heating the diynylcarbene complex **349** in benzene is also impressive. The methylphenol derivative **350** with two annelated five-membered rings is formed by two sequential intramolecular alkyne insertions and subsequent elimination of methanol (see earlier).[161]

A combination of alkyne insertion and [2+1] cycloaddition with cyclopropane formation has also been reported. Harvey et al.[162] and Katz and Yang[163] have shown that the allylpropargyl ether **351a** and the allylpropargylamine **351b** react

with the complex **342** to furnish the 1-(2-oxopropyl)-3-oxabicyclo[3.1.0]hexane **352a** and 1-(2-oxopropyl)-3-azabicyclo[3.1.0]hexane **352b**.



Dienynes of the type **354** react analogously with complexes **353** by alkyne insertion with subsequent intramolecular cyclopropanation to 1,6-dialkenylbicyclo[3.1.0]hexanes **355**, which then immediately undergo a [3,3] sigmatropic rearrangement under the conditions employed (110 °C) to form hexahydroazulenes **356** (Scheme 31).[164]



M	R^1	R^2	R^3	[%]	(*E*:*Z*)
Mo	*n*Bu	H	CO_2Et	87	1 : 4.8
Mo	*n*Bu	CO_2Me	CO_2Me	81	1 : 4.8
Cr	Me	H	CO_2Et	24	1 : 2.1
Cr	*n*Bu	H	CO_2Et	22	1 : 2.1

Scheme 31. The formation of hexahydroazulenes from a variety of dienynes and complexes **353**.

Disubstituted alkynes of type **141** insert a second time, only slowly, into the intermediates from complexes of the type **353**; instead, other reaction pathways are followed. The cyclopentenones **358** and **359** are formed, for example, from **357** by insertion of a carbonyl ligand in the second step, and subsequent cyclization (Scheme 32 and Table 10).[165] This reaction resembles the cyclopentenone formation by [2+2+1] cocyclization of (2-aminoalkenyl)carbenechromium complexes **256** with nonterminal alkynes under CO insertion discovered by de Meijere et al.[135] (see Scheme 21). The difference lies only in that R^1 in **357** corresponds to a substituted methylene group, the product of type **257** corresponds accordingly to **359**.

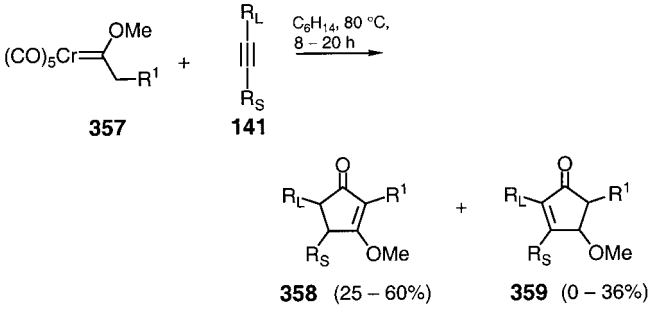
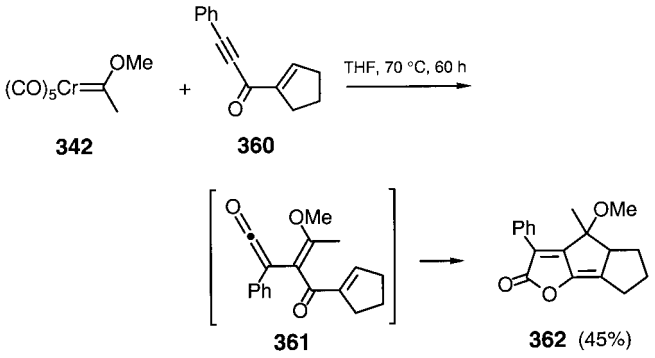


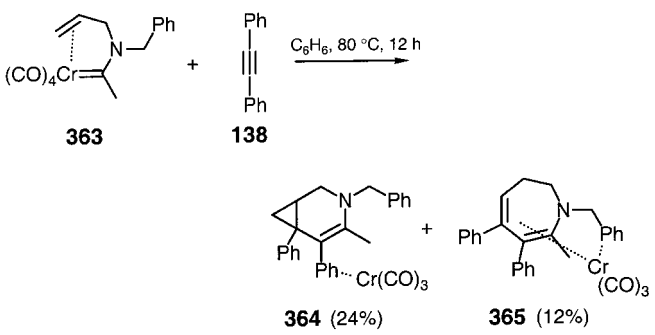
Table 10. Cyclopentenones **358** and **359** by cocyclization of **357** with alkynes **141** (Scheme 32).

Complex	R^1	R_L	R_S	Product	[%]	Product	[%]
357a	Ph	*n*Pr	H	**358a**	28	**359a**	0
357b	*n*Pr	Et	Et	**358b**	42	**359b**	18
357c	*c*Pr	*n*Pr	*n*Pr	**358c**	57	**359c**	33
357d	*t*Bu	Ph	Ph	**358d**	36	**359d**	36
357a	Ph	*n*Pr	H	**358e**	25	**359e**	8
357b	*n*Pr	Ph	Ph	**358f**	38	**359f**	24
357c	*c*Pr	*t*Bu	H	**358g**	28	**359g**	0
357d	*t*Bu	*t*Bu	H	**358h**	34	**359h**	0
357a	Ph	Ph	Ph	**358i**	60	**359i**	20

A particularly interesting reaction product is obtained on heating the methoxymethylcarbene complex **342** with the cyclopentenyl(phenylethynyl)ketone (**360**).[111b] The cross-conjugated ketene **361**, formed by alkyne and carbonyl insertion, cyclizes in a criss-cross fashion with the inclusion of five atoms from **360** to give the tricycle **362** in a yield of 45 %.

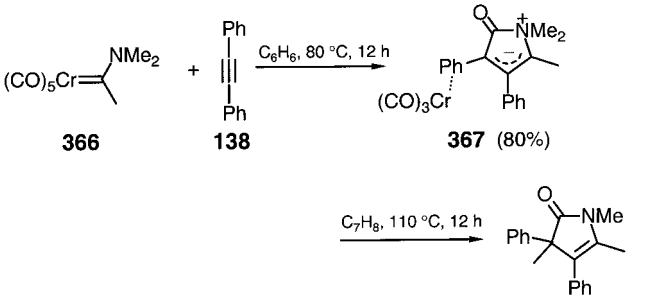


After alkyne insertion, (allylamino)carbenechromium complexes such as **363** react by intramolecular carbene transfer with cyclopropane formation.[111b, 166, 167] However, as well as the bicyclic cyclopropane derivative **364** the dihydroazepine derivative **365** (which must have arisen through opening of the cyclopropane ring in **364**[168]) and other ring-expansion products are also found.[169]

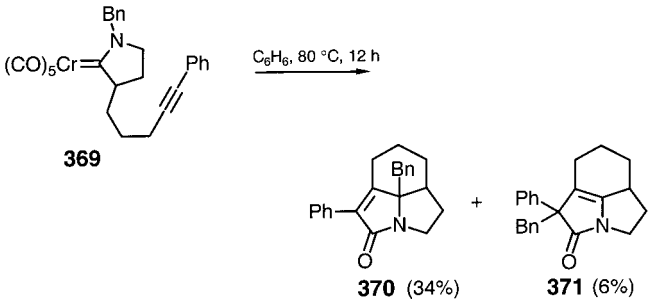


Scheme 32. For details see Table 10.

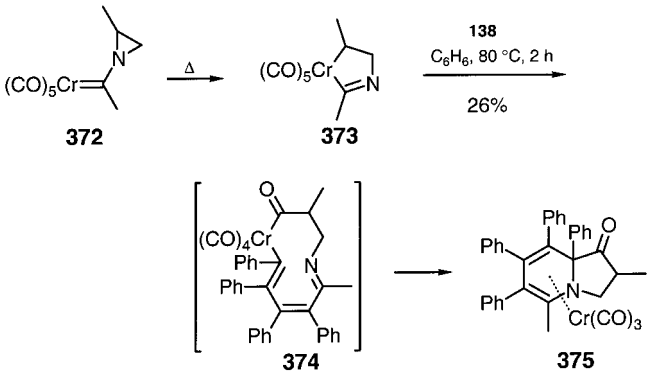
If, however, after alkyne insertion of, for example, tolane (**138**) into the complex **366**, there is no double bond for further reaction, a carbonyl ligand is inserted and the vinylketene complex thus formed cyclizes to a zwitterion of the type **367**,[170–172] which on heating to 110 °C is stabilized as the γ-lactam **368** after methyl migration.[171]



By proper selection of substituents in the starting material this type of reaction can be carried to extremes. Thus, the pyrrolidinylidene complex **369**, with the phenylpentynyl side chain, affords the tricyclic lactams **370** and **371** on heating in benzene.[172] Clearly in this reaction a [1,3] benzyl migration is more favorable than a [1,5] benzyl migration, as the relative amounts of **370** and **371** confirm.



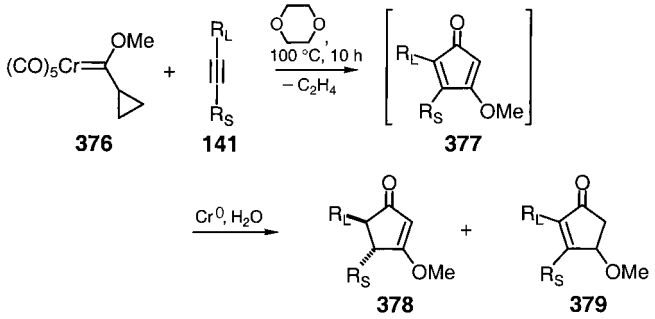
The (1-aziridinylethylidene)chromium complex **372** shows a different reaction behavior. Initially, a chromapyrroline **373** is formed by a thermally induced sigmatropic rearrangement, and this is probably followed by double alkyne insertion into the metal–carbene carbon bond and subsequent CO insertion with formation of a 10-membered ring intermediate **374**, from



which the indolizidinonechromium complex **375** is produced by electrocyclization and final reductive elimination.[173]

The chemistry of the cyclopropylcarbenechromium complexes has been described in an independent review,[174] however, the reactions of these homologues of vinylcarbene complexes with alkynes should also be mentioned briefly here.

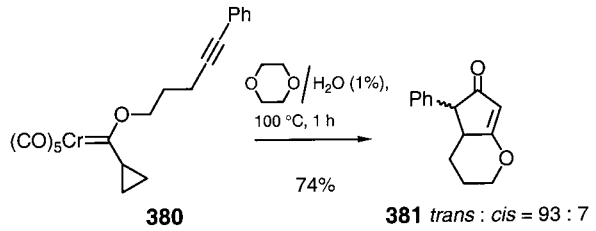
The simple cyclopropyl(methoxy)carbenechromium complex **376** reacts with alkynes **141** with release of ethene to form the intermediate cyclopentadienone **377**,[175] which in the presence of residual amounts of chromium(0) derivatives and water in the reaction mixture reacts to form the same cyclopentenones[174, 176] (Scheme 33) as the alkylmethoxycarbene complexes **357** (see Scheme 32).



	R_L	R_S	**378** [%]	**379** [%]
a	Ph	Ph	79	4
b	Ph	H	62	0
c	Ph	Me	73	12
d	*n*Pr	*n*Pr	55	0
e	*n*Pr	H	68	0
f	$(CH_2)_4OH$	H	54	0

Scheme 33. Reactions of cyclopropyl(methoxy)carbenechromium complex **376** with a variety of alkynes.

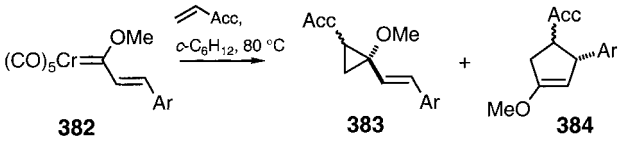
An intramolecular variant of this cyclopentenone synthesis has been realized. On heating complex **380**, with a phenylpentynyl moiety connected through the alkoxy substituent, in aqueous dioxan intramolecular insertion and cyclization takes place with high diastereoselectivity to furnish the phenyl-substituted ring-annelated cyclopentenone **381**.[174, 177]



5. Reactions of Alkenylcarbene Complexes with Alkenes and Butadienes

Fischer carbene complexes react mainly with acceptor-substituted alkenes, preferentially in a formal [2+1] cycloaddition reaction, to afford cyclopropane derivatives.[2g, 178]

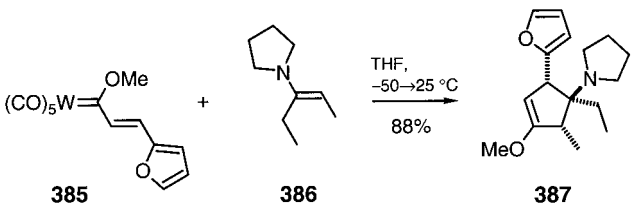
Two particularly impressive applications of this type of reaction in domino reactions have been described by Harvey et al.[162, 164] and Katz and Yang[163] (see **342** + **351** → **352** and Scheme 31). As Reissig and co-workers have found, alkenylcarbene complexes react principally in the same way, but the alkenylcyclopropanes **383** thus formed can rearrange to the cyclopentenes **384** (Scheme 34).[179] Clearly, this occurs particularly readily with the alkenylcyclopropane **383 f** formed from the 2-pyrryl-substituted complex **382 f** and methyl acrylate, for in this case only the cyclopentene derivative **384 f** was found by Reissig and co-workers.[179]



	Ar	Acc	**383** [%]	**384** [%]
a	Ph	CO_2Me	81	–
b	Ph	$CONMe_2$	45	–
c	Ph	CN	59	–
d	Ph	$PO(OMe)_2$	73	–
e		CO_2Me	40	19
f		CO_2Me	–	67

Scheme 34. Rearrangement of alkenylcyclopropanes **383** to the cyclopentenes **384**.

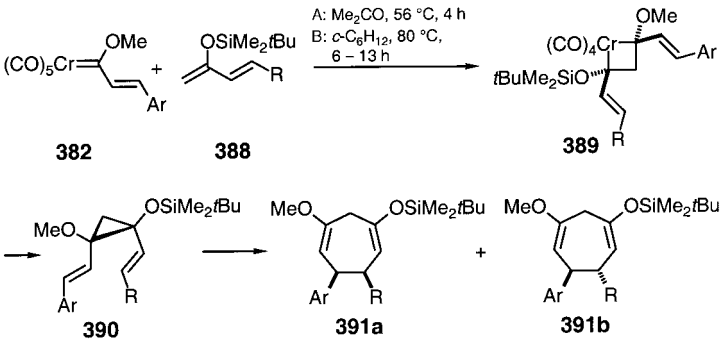
The 2-furyl-substituted (alkenylcarbene)tungsten complex **385** similarly reacts diastereoselectively with 2-pyrrolidino-2-pentene (**386**), even at relatively low temperatures, to afford the correspondingly highly substituted cyclopentene **387**.[180]



Electron-rich dienes of the type **388** (R = OMe, Ph) also react with alkenylcarbene complexes in a formal [2+1] cycloaddition. The *cis*-dialkenylcyclopropane **390** formed by a formal carbene transfer from **382** to the dienes **388**—by [2+2] cycloaddition of the Cr=C bond to the most electron-rich double bond in **388** with subsequent reductive elimination—give, however, cycloheptadienes of type **391** through immediately succeeding [3,3] sigmatropic rearrangements (Scheme 35).

Of note here is the high stereoselectivity of the formal [2+1] cycloaddition; normally such cyclopropanations with Fischer carbene complexes occur with only low diastereoselectivity.[178, 179, 181]

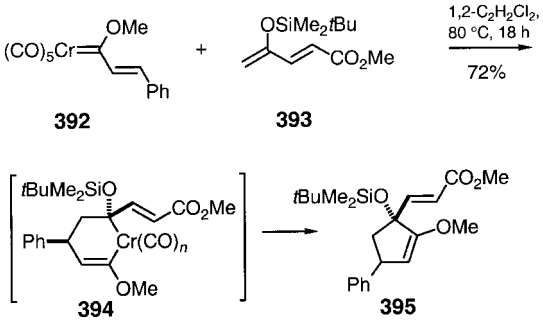
Dienes with a donor–acceptor substitution pattern, such as **393**, cocyclize with alkenylcarbene complexes to produce



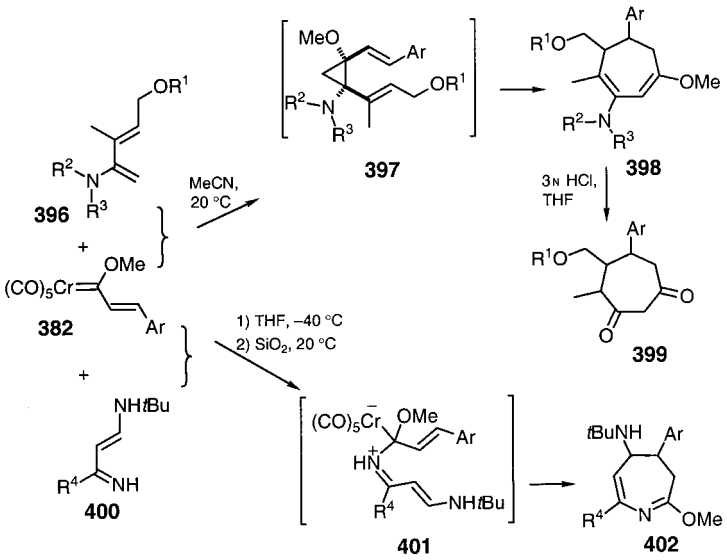
Ar	R	Conditions	**391a** [%]	**391b** [%]
Ph	OMe	A	49	2
Ph	Ph	A	28	–
	Ph	B	38	–
	Ph	B	9[a]	–
	OMe	B	25[b]	–

Scheme 35. [a] 1% of an alkenylcyclopentene was isolated. [b] 16% of an alkenylcyclopentene was isolated.

cyclopentenes. This transformation probably begins with a [4+2] cycloaddition of the electron-poor 1-chroma-1,3-butadiene **392** to the more electron-rich double bond—in a hetero-Diels–Alder reaction with inverse electron demand—to form the chromacyclohexene **394**, which affords the cyclopentene **395** by reductive elimination of the metal complex fragment.[181]



The reactions of $\alpha\beta$-unsaturated Fischer carbene complexes with aminobutadienes and aza-1,3-dienes represent a special situation. Barluenga and co-workers[182] have shown that aminobutadienes **396** and azadienes **400** react with the alkenylcarbene complexes **382** mainly to form the aminocycloheptadienes **398** (which are then hydrolyzed to the cycloheptanediones **399**) and the 2-azacyclohepta-1,3-dienes **402**, respectively (Scheme 36 and Table 11). The formations of these seven-membered ring derivatives probably each begin with a [2+1] cycloaddition to a dialkenylcyclopropane **397** or stabilized ylid **401**. A [3,3] sigmatropic rearrangement and



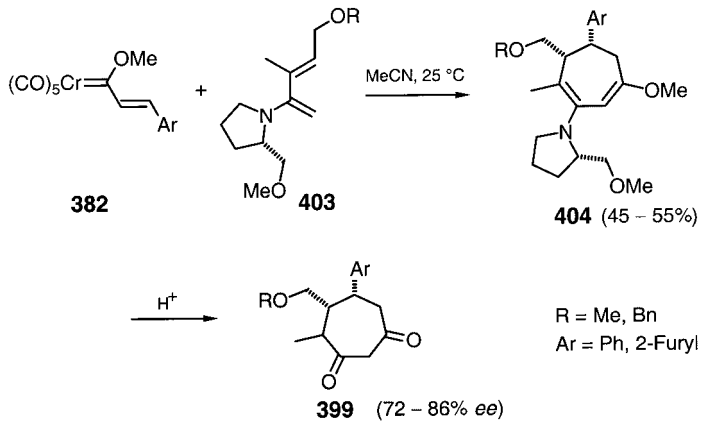
Scheme 36. For details see Table 11

Table 11. Carbo- and heterocyclic seven-ring derivates from α,β-unsaturated Fischer carbene complexes **382** and 2-dialkylaminobuta-1,3-dienes **396** or 1-aza-1,3-butadienes **400**.

	Ar	R^1	R^2	R^3	R^4	**399** [%]	**402** [%]
a	2-Furyl	Me	Me	Ph	–	82	
b	2-Furyl	Me	$(CH_2)_2$-O-$(CH_2)_2$		–	58	
c	Ph	Me	Me	Ph	–	71	
d	2-Furyl	Bn	Me	Ph	–	78	
e	Ph	Bn	Me	Ph	–	76	
f	Ph	–	–	–	*c*Pr	–	90
g	2-Furyl	–	–	–	*c*Pr	–	80
h	Ph	–	–	–	Et	–	91
i	2-Furyl	–	–	–	4-MeC_6H_4	–	62
j	Ph	–	–	–	Ph	–	70
k	Ph	–	–	–	4-ClC_6H_4	–	52

subsequent [1,3] proton shift then give in each case the respective cycloheptadiene **398**[182b,e] or dihydroazepine **402**.[182f,g]

These formal [3+4] cycloadditions occur even at relatively low temperatures. It has also been shown convincingly that this synthesis is suitable for the stereoselective construction of highly substituted cycloheptanediones of type **399**.[182b,e]



6. Summary and Outlook

The results summarized here show clearly that since their pioneering days of almost three decades ago, α,β-unsaturated Fischer carbene complexes have secured a permanent place in organic synthesis. Thanks to the unbelievable reaction versatility with which these metal-stabilized carbenes are endowed, a plethora of synthetically interesting carbo- and heterocyclic compounds are readily available in convincing yields. The selectivity with which these products are formed, can be excellently controlled by targeted fine tuning of all the factors which influence the reactions. The proper combination of cycloadditions such as Diels – Alder reactions and 6π-electrocyclization leads to domino reactions with which several new bonds can be connected selectively at the same time in a single operational step. The increase in molecular complexity, which is used as a suitable measure of the efficiency of a synthetic step, is particularly great in such reactions.

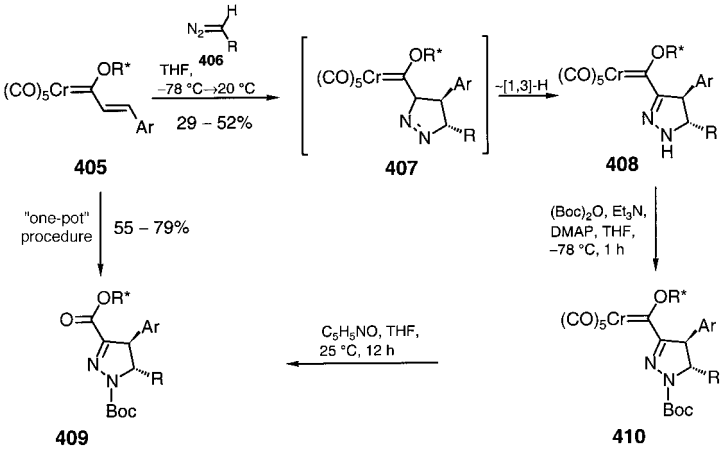
Even if concrete ideas on the mechanism of formation have in the meantime been deduced for most of the numerous cycloaddition and cocyclization products of α,β-unsaturated Fischer carbene complexes, the study of the bonding relationships in these organometallic reagents and their chemistry must be pushed forward continuously to further pave the way for their use in key steps of demanding syntheses.

In spite of the widespread repertoire of cycloadditions and cocyclizations no end is yet in sight for the discovery of new reactions of these complexes. The numerous possibilities of the domino-like coupling of carbene complex cocyclizations with other processes are far from exhausted, in spite of the many successes, and the imagination of chemists will not quickly reach the limits of this area. Even though positive beginnings have already been made in some areas, for example in asymmetric synthesis, a huge potential still lies slumbering. The ever increasing interest in the chemical industry for new lead structures for highly active pharmaceuticals or plant protection agents could secure new possibilities for the use of Fischer carbene complexes. It remains to be seen whether the high expectations can be justified in all these points.

Addendum

Since the preparation of the final version of this review further publications have appeared which will have an impact to further establish the reactions of α,β-unsaturated carbenepentacarbonylmetal complexes in organic synthesis.

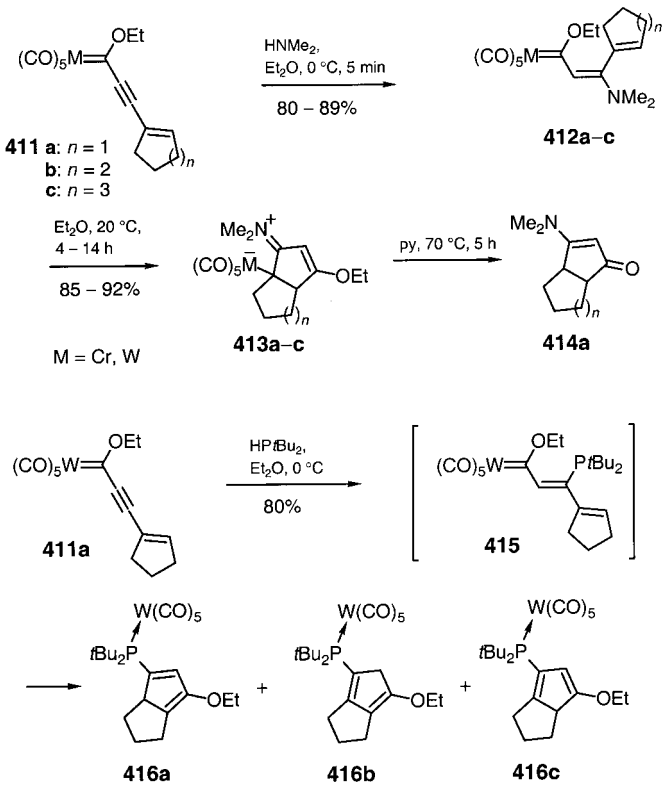
Thus, Barluenga et al. have reported recently on [3+2] cycloadditions of alkenylcarbenechromium complexes with 1,3-dipoles.[183] In analogy to the highly reactive alkynylcarbenechromium complexes (see Section 2.2) alkenylcarbenechromium complexes also react with diazoalkanes in [3+2] cycloadditions, as was demonstrated impressively in an enantioselective synthesis of esters of 1*H*-pyrazolin-3-carboxylic acids **409** from (−)-8-phenylmenthol or (±)-menthol-substituted (1-alkenyl-1-oxycarbene)pentacarbonylchromium complexes **405** (Scheme 37). Regio- and diastereoselective addi-



Scheme 37. Ar = Ph, 2-furyl; R* = (±)-menthyl, (−)-8-phenylmenthyl; R = Ph, $SiMe_3$, CH_2=CH; DMAP = 4-dimethylaminopyridine.

tion of the diazomethane derivative **406** to the complexes **405** and a subsequent [1,3] hydrogen shift led to the (4,5-dihydro-1*H*-pyrazolyl)carbenechromium complexes **408**. Protection of the secondary nitrogen with a *tert*-butoxycarbonyl (Boc) group and oxidation with pyridine-*N*-oxide gave the final products **409**. When all three steps were carried out in a single operational step without isolation of the intermediates **408** and **410** the yields of **409** were increased significantly.[183]

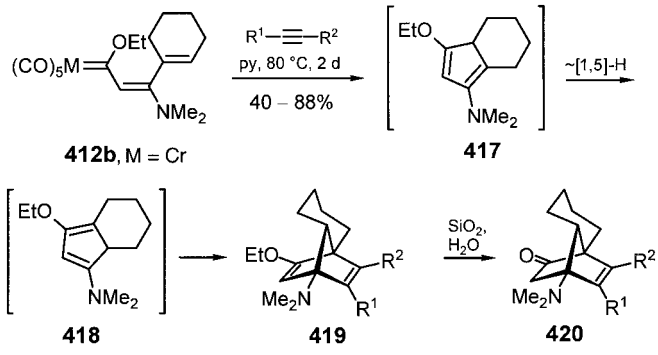
A new five-membered-ring formation which must involve intramolecular insertion of a cycloalkene double bond into the metal–carbon double bond of the 1-metalla-1,3,5-hexatriene **412**, prepared from the corresponding alkenynylcarbene complex **411** by 1,4-addition of a secondary amine, has been reported by Aumann et al.[184] The complexes **412** cyclize on standing in diethyl ether even at room temperature within 4–14 h to give the zwitterionic η^1-cyclopentenyl complexes **413** from which the carbonylchromium fragment is eliminated by treatment with pyridine. Subsequent hydrolysis of the enol ether function then gives the bicyclo[3.3.0]octenones **414** in excellent yields. The addition of di-*tert*-butylphosphane to the (cyclopentenylpropynylidene)tungsten complex **411a** affords directly a mixture of the three isomeric phosphanylcyclopentadiene complexes **416a–c**.[184]



Although β-cycloalkenyl-β-dimethylamino-substituted ethenylcarbene complexes of the type **412** undergo further intramolecular reactions even at room temperature,[184] the cyclohexenyl-substituted complex **412b** (M = Cr) could be isolated in 94% yield from hexacarbonylchromium and 1-ethynylcyclohexene by working in THF and applying the one-pot process.[2l, 123, 185] In pyridine at 80 °C complex **412b** reacted with a series of alkenyl- and arylsubstituted terminal alkynes to afford the tricyclic dienes **419**, which were hydrolyzed to the ketones **420**, by traces of water during chromatographic purification.[185]

The formation of **419** most probably begins with the rapid cyclization of **412b** (M = Cr) as already observed by Aumann et al.[184] which in pyridine, however, would directly lead to the metal free six-ring annelated cyclopentadiene derivative **417**. By [1,5] hydride shift this may yield **418**, which reacts with the added alkyne in a [4 + 2] cycloaddition to give the tricyclic compound **419**. It is remarkable though, that even donor-substituted arylethynes apparently are sufficiently reactive dienophiles for the substrate **418** (Scheme 38).

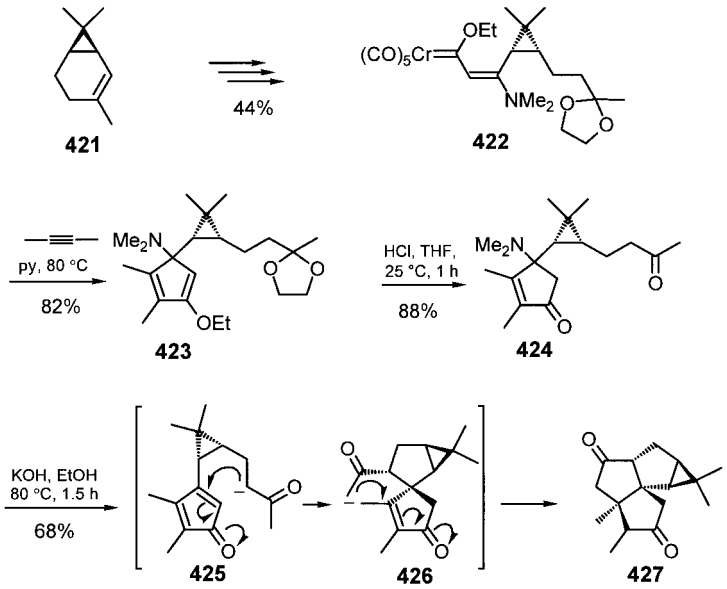
A new use of the alkoxycyclopentadienes,[123] readily prepared from (β-aminoalkenyl)carbenechromium complexes and alkynes in pyridine by the method of de Meijere et al., convincingly demonstrates the synthetic potential of this class of compounds. Starting from (+)-2-carene **421**, a



	R^1	R^2	**420** [%]
a		H	73
b		H	40
c	C_6H_5	H	88
d	4-$OEtC_6H_4$	H	87
e	4-$nPrC_6H_4$	H	50
f		Ph	60

Scheme 38. Norbornadiene production from the reactions of complex **412b** (M = Cr) with a variety of alkynes.

terpene from the "chiral pool", the enantiomerically pure alkenylcarbenechromium complex **422** was prepared in four steps in an overall yield of 44%. The formal [3+2] cycloaddition of **422** to 2-butyne afforded the corresponding



ethoxycyclopentadiene **423** (82%) which was hydrolyzed to the cyclopentenone **424** under acidic conditions. Treatment of the diketone **424** with ethanolic potassium hydroxide apparently leads to elimination of dimethylamine to give the cyclopentadienone **425**, which reacts immediately in a cascade of two sequential Michael additions to form the angular triquinane **427**.[186] This almost totally diastereoselective sequence of elimination and twofold Michael addition in which four new stereocenters are formed affords the highly substituted, enantiomerically pure angular triquinane **427** in an overall yield of 26% from (+)-2-carene **421**.

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