Diene, Alkyne, Alkene, and Alkyl Complexes of Early Transition Metals: Structures and Synthetic Applications in Organic and Polymer Chemistry

By Hajime Yasuda* and Akira Nakamura*

An unprecedented series of highly reactive alkene- and diene-complexes of the early transition metals (Groups 3A-5A of the periodic system) have been isolated recently. Diene complexes of this sort (M = Ti, Zr, Hf, Nb, Ta) prefer, besides the (η^4-s-*cis*-diene)metal structure, either a novel bent η^4-metallacyclo-3-pentene structure or the unique (η^4-s-*trans*-diene)metal structure. In bis(diene)metal complexes of Nb and Ta the η^4-s-*cis*-dienes assume an unusual *exo-endo* (*supine-prone*) geometry. The M-C bonds in these diene-metal complexes generally exhibit highly polarized σ-bonding along with π-bonding character. The complexes therefore undergo a variety of regio- and stereoselective carbometalations with substrates containing C-C, C-O, or C-N multiple bonds. Examples of the products that can be obtained include ketones, vinyl ketones, unsaturated primary, secondary, and tertiary alcohols, as well as diols and unsaturated acids. Mechanistic studies on the stoichiometric and catalytic conversions of unsaturated hydrocarbons provides, inter alia, some insights into the course of polymerization reactions.

1. Introduction

Organic compounds of the early transition metals (groups 3A-5A of the periodic system) are currently attracting considerable attention because of their fascinating structural features, their mode of M-C bonding, and their unusually high selectivity in carbometalations; all these features distinguish them from the conventional middle and late transition metal complexes. The recent accelerated development of alkene-metal chemistry in this area is largely a consequence of the successful isolation of highly reactive novel species with suitable auxiliary ligands, especially cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) ligands. The first part of this article is concerned with new aspects of the structural chemistry of diene-, alkene-, and alkyne- as well as allyl- and pentadienyl-metal complexes of the early transition metals, while the second part deals with the unusual C-C coupling reactions that have been accomplished with these complexes. For an overview of the organometallic chemistry of the early transition metals in its entirety, the reader should consult some of the excellent monographs[1] and reviews on alkylmetal compounds,[2] carbene-complexes,[3] and metallacycles[4] that are available.

2. Remarkable Structural Features of Diene, Alkene, and Alkyne Complexes of the Early Transition Metals

2.1. Structures of η^4-Metallacyclo-3-pentene- and η^4-s-*trans*-Diene-Metal Complexes

Conjugated dienes, typified by 1,3-butadiene, may coordinate to a metal in several ways. The relative contribution of each of the limiting structures **1**-**6** would appear to depend upon the ligands of the metal and the substituents of the diene. The vast majority of middle and late transition metal-diene complexes assume the conventional (η^4-s-*cis*-1,3-diene) structure **1** or the (1,2-η^2-s-*trans*-1,3-diene) structure **6**, where the diene interacts with Fe, Ru, Rh, Mo, Mn etc. via alkene π-orbitals.[5] It is now apparent from X-ray and NMR data that the diene complexes of early transition metals of groups 4A (Ti,[6] Zr,[7-9] Hf[10]) and 5A (Nb,[11] Ta[12]), like those of group 3A (U,[13] Th[13,14]), prefer the bent (σ^2,π-bonded)η^4-metallacyclo-3-pentene structure **2**, the planar (σ^2-bonded)η^2-metallacyclo-3-pentene structure **3** or the novel (η^4-s-*trans*-diene)metal structure **4**. Unequivocal evidence for the structure of type **5** is still lacking. Differentiation of the η^2-structure **6** from its σ-bonded counterpart (2-vinylmetallacyclopropane) seems improbable on the basis of the prediction made by *Dewar* et al.,[15] although the latter geometry is well known in 2-vinylphosphiranes.[16] Typical synthetic routes to these diene complexes involve the use of dienemagnesium reagents[7] or of pentadienyl anions,[17] the chemical or photochemical reduction of the corresponding precursor complex in the presence of the diene,[8,9] metal atom vapor techniques,[18] rearrangements of transitory divinyl complexes,[19] or β-hydride elimination from allylmetal compounds or metallacycles.[20] As typical example of such a

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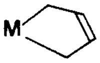

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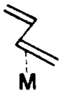

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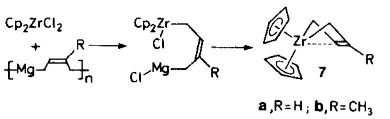
synthesis, a route leading to the isoprenezirconium complex **7b** in high yields from dienemagnesium adducts[21] is outlined. This type of reaction finds universal application in preparative chemistry.



a, R = H; **b**, R = CH_3

The complexes **7** kinetically favor the η^4-s-*trans*-coordination **4** but thermodynamically they favor the s-*cis* metallacyclic structure **2**. Thus, the η^4-s-*trans*-butadiene complex of zirconocene can be converted by heating in solution, into the s-*cis*-complex, which, in turn, can be converted by irradiation with UV light into the η^4-s-*trans*-isomer.[9b] Alkyl or aryl substitution of the butadiene ligand in position 2 or positions 2 and 3 always leads to zirconacyclo-3-pentene complexes such as **7**. The strong steric repulsion between the C_5H_5 ligands (Cp) and the substituents (see, e.g., R) should be the crucial factor forcing this type of coordination instead of the η^4-s-*trans*-coordination. Substitution at C-1 or C-1 and C-4, on the other hand, induces preferential formation of the η^4-s-*trans*-diene complexes by conjugation or hyperconjugation.[22]

This situation changes drastically upon replacing Zr by Ti, Ta or Nb. The relative ratios of the s-*cis* and s-*trans* isomers of the complexes are listed in Table 1. Typical examples for the molecular structures of the s-*cis* (type **2**) and s-*trans*-diene complexes (type **4**) are shown in Figures 1[6d] and 2,[7d] respectively.

Table 1. Proportion of s-*cis*-isomers of type **2** in

$[ML_2(R^1CH{=}CR^2{-}CR^3{=}CHR^4)]$, M = Ti, Zr, Hf, and
$[ML(R^1CH{=}CR^2{-}CR^3{=}CHR^4)_2]$, M = Nb, Ta.

$Cp = C_5H_5$, $Cp^* = C_5(CH_3)_5$.

M	L	R^1	R^2	R^3	R^4	s-*cis* [%] [a]
Zr	Cp	H	H	H	H	0–100 [b]
		CH_3	H	H	CH_3	36
		CH_3	H	H	H	39
		Ph	H	H	Ph	2
		H	CH_3	H	H	100
		H	CH_3	CH_3	H	100
		CH_3	CH_3	H	H	100
Zr	Cp*	H	H	H	H	0
		H	CH_3	H	H	100
Hf	Cp	H	H	H	H	0–100 [b]
		H	CH_3	H	H	100
Ti	Cp* Cl, Br, I [c]	H	H	H	H	100
		H	CH_3	H	H	100
		Ph	H	H	Ph	100
Nb	Cp*	H	H	H	H	100
		H	CH_3	H	H	100
Nb	Cp	H	CH_3	CH_3	H	100
Ta	Cp	H	H	H	H	100
	Cp*	H	H	H	H	100

[a] The other component is the s-*trans*-isomer (Type **4**). [b] The proportion of s-*cis*-isomer varies, depending upon the method of preparation and the temperature of measurement. [c] Formulas of the Ti compounds: $[TiCp^*Cl(R^1CH{=}CR^2{-}CR^3{=}CHR^4)]$ and bromo and iodo analogues.

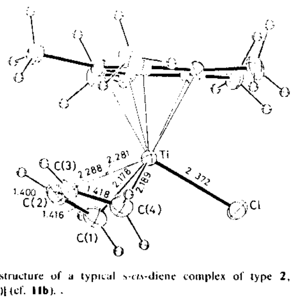


Fig. 1. Molecular structure of a typical s-*cis*-diene complex of type **2**, [TiCp*Cl(butadiene)] (cf. **11b**).

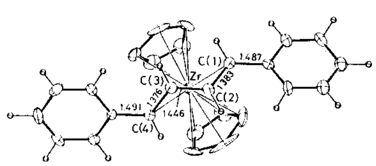
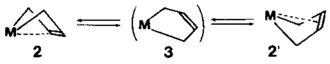


Fig. 2. Molecular structure of a typical s-*trans*-diene complex of type **4**, $[ZrCp_2(1,4\text{-diphenylbutadiene})]$.

The η^4-metallacyclo-3-pentene complexes **2** of elements of groups 3A-5A generally exhibit fluxional behavior, which may be attributed, on the basis of variable temperature ^{1}H-NMR studies, to rapid ring inversion (flipping) via a transitory planar metallacyclopentene species **3**. From the shape of the signal pattern, a simple rotational mechanism can be ruled out. More exact direct evidence for ring inversion has recently been provided by a sterochemical labeling experiment with a [CoCp(1,3-diene)] complex whose 1,3-diene ligand was deuteriated in positions 1 and 4.[23] The typical free energy of activation, ΔG^{+} (at the coalescence temperature), for the ring inversion in zirconacyclo-3-pentenes such as **7** varies in the range 6.5–17 kcal/mol.[9]



Very unusual is the large value (>25 kcal/mol) for $[MCl_2Cp^*(s\text{-}cis\text{-butadiene})]$, M = Ta, Nb; $Cp^* = C_5Me_5$.[24] Such a fluxional behavior could arise from the strong σ-bonding character of the M–C bonds at the diene termini. The ^{13}C-^1H coupling constant clearly confirms the enhanced sp^3 character of C-1 and C-4.[25] The value of n for sp^n hybridization of the carbon is in the range 2.0–2.2 in the case of conventional diene complexes of the late transition metals (Fe, Rh, etc.), but it reaches 2.7–3.0 in the case of $[MCp_2(2,3\text{-dimethylbutadiene})]$, M = Zr, Hf, and $[ZrCp^*_2(\text{isoprene})]$, which remain fluxional even at 90 °C.

The fluxional structure is also apparent in crystallographic data and it is reflected in the dihedral angle (θ) subtended by the C1–M–C4 and C1–C2–C3–C4 planes and the difference in the M–C bond distances (Δ*d*), defined by

$$\Delta d = [d(M{-}C1) + d(M{-}C4)]/2 - [d(M{-}C2) + d(M{-}C3)]/2$$

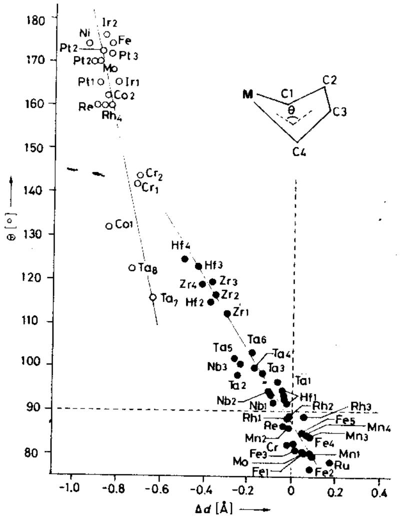
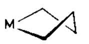


Fig. 3. Correlation plots between dihedral angle (θ) and difference in metal carbon distances (Δ*d*) in dienemetal complexes of type **1** or **2** (●) and metallacyclopentanes of type **8** (○). Data are selected from Cambridge Crystallographic Database (see ref. [26] for the structural details). The numbers next to the element symbols identify the complexes used.

As shown in the correlation plots (Fig. 3), the dihedral angles for s-*cis*-diene complexes (type **1**) of the late transition metals fall in the narrow range of 75–90°, and Δ*d* lies between −0.1 and 0.1 Å, i.e. the M–C1 and M–C4 bonds are nearly equal or slightly longer than the M–C2 or M–C3 bond.[12,26] On the other hand, the corresponding dihedral angles for the complexes of the early transition metals always exceed 90°, with a corresponding change in Δ*d* of −0.4 to 0 Å. Thus, the dihedral angles increase with decreasing Δ*d*. The dihedral angle of the metallacyclopentanes (type **8**), where no interaction takes place between the metal and the inner carbon atoms, is in the range 140–175° for late transition metals, since the four carbon atoms are not coplanar, as in **8b** (the angle given refers to "best planes").[26] In the case of tantala- or cobaltacyclopentanes (type **8a**), θ lies in the range 115–130°; this is nearly the same range as for $[MCp_2(s\text{-}cis\text{-butadiene})]$, M = Zr, Hf. We can conclude, therefore, that the diene complexes of metals of group 4A exhibit rather weak interaction between the metal atom and the inner carbon atoms, consistent with their high fluxional properties, whereas the diene complexes of metals of group 5A exhibit a rigid structure because of the strong π-interaction between the inner carbon atoms and the metal atom. There is also an approximate linear correlation between the dihedral angle (θ) and the difference in the C–C bond lengths (Δ*l*), defined by

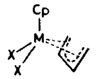
8a



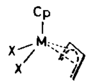
8b

$$\Delta l = [l(C1{-}C2) + l(C3{-}C4)]/2 - l(C2{-}C3)$$

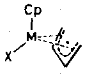
In the case of diene complexes of the late transition metals, Δ*l* lies between −0.1 and 0.0 Å, while in those of the early transition metals it falls in the range 0.0–0.2 Å. Thus, the dihedral angle increases with increasing Δ*l*.[12,26] A fairly good linear correlation is also observed between the values of n for sp^n hybridization of the diene terminal carbons and Δ*d* and Δ*l*.



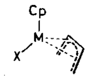
9 *supine (exo)*



10 *prone (endo)*

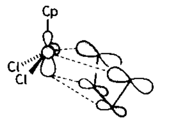


11a *supine*



11b *prone*

The diene complexes of metals of group 5A always have the metallacyclo-3-pentene structure **2**. Two orientations are possible for $[MCl_2Cp(diene)]$, M = Ta, Nb: *supine* and *prone* (we propose this nomenclature because the classical *exo* and *endo* nomenclature does not adequately characterize this type of conformation). A comparison of the total energy of $[TaCl_2Cp(butadiene)]$ for the *supine* (*exo*)-type **9** and *prone* (*endo*)-type **10** on the basis of an EHMO calculation revealed that the former is more stable than the latter by 15.7 kcal/mol due to the large overlap integrals $S(2a''\text{-}\pi_3^*)$ of **9a** and $S(1a'\text{-}\pi_3^*)$ of **9b** respectively.[12]



9a $S(2a''\text{-}\pi_3^*)$

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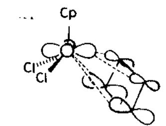
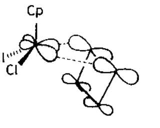


10a $S(1a''\text{-}\pi_2)$



9b $S(1a'\text{-}\pi_3^*)$

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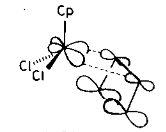
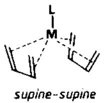
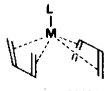


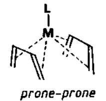
10b $S(1a''\text{-}\pi_2)$

The dimeric niobium complex $[NbClCp^*(butadiene)]_2$,[11] $[TiClCp^*(diene)]$, diene = isoprene, 2,3-dimethylbutadiene,[6a] as well as $[HfClCp^*(2,3\text{-dimethylbutadiene})]$,[6b] and the molybdenum complex $[MoCp(CO)_2$(butadiene, 1,4-diphenylbutadiene) exhibit a unique *prone* to $[TaCl_2Cp(C_4H_6)]$[12] as a result of steric repulsion between Cp* or Cp and the methyl groups of the diene ligands, while $[TiClCp^*(diene)]$ complexes (diene = butadiene, 1,4-diphenylbutadiene) exhibit a unique *prone* (*endo*) orientation **11b** (cf Fig. 4).

When a metal complex contains more than one diene, there are many possibilities for its coordination geometry. Thus, the complexes $[LM(diene)_2]$ may assume square-pyramidal or trigonal-bipyramidal structures if the diene ligand is assumed to occupy two coordination sites via its terminal carbon atoms. The bis(diene)metal complexes reported so far all prefer the square-pyramidal structure: the two diene ligands orient themselves in a parallel *supine-supine*(or *exo-exo*) fashion (**12**) with nearly C_{2v} symmetry, while L occupies the apical position. The novel *supine-prone* (*exo-endo*) orientation (**13**), observed for the first time in $[Ta(C_5R_5)(diene)_2]$ (R = H, Me; diene = butadiene, isoprene, 2,3-dimethylbutadiene),[12] has recently also been found in the analogous niobium complexes.[11] A similar *supine-prone* orientation is also found in the mixed-ligand zirconiumcomplex$[ZrCp^*(\eta^4\text{-butadiene})(\eta^3\text{-allyl})]$.[9f]


supine-supine
(*exo-exo*)
12


supine-prone
(*exo-endo*)
13


prone-prone
(*endo-endo*)
14

$[Hf(diene)_2(dmpe)]$, an unusual complex with the formula $[L_2M(diene)_2]$, prefers octahedral geometry[8] (dmpe = 1,2-bis(dimethylphosphino)ethane is a bidentate ligand). Bis(diene)metal complexes with a *prone-prone* (*endo-endo*) orientation (**14**) or a trigonal-bipyramidal conformation are still unknown. The relative stabilities of the conformations estimated from EHMO calculations for $[TaCp(butadiene)_2]$ indicate that the *supine-prone* conformation is more stable than the *prone-prone* or *supine-supine* conformation by 23.3 and 28.2 kcal/mol, respectively, whereas for $[RhCl(butadiene)_2]$, the *supine-supine* conformation is more stable than the *prone-prone* or *prone-supine* conformation by 25.8 and 27.2 kcal/mol, respectively.[7c] The calculated overlap population indicates that $[TaCp(butadiene)_2]$ favors the bent η^4-metallacyclo-3-pentene structure of type **2**, while $[RhCl(butadiene)_2]$ prefers the conventional η^4-s-*cis*-diene coordination of type **1**, in agreement with the crystallographic data. An unusual mixed diene complex, $[TaCp^*$(butadiene)(2,3-dimethylbutadiene)], also assumes the *prone-supine* structure, as shown in Figure 4.[28]

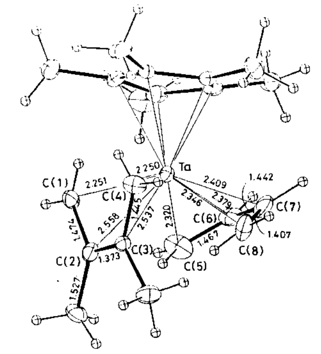
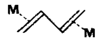


Fig. 4. Molecular Structure of a bis(diene) complex of type **13**, $[TaCp^*$(butadiene)(2,3-dimethylbutadiene)].

The s-*trans*-diene coordination to mononuclear species (type **4**), first found in complexes of the early transition metals in the case of $[ZrCp_2$(1,4-diphenyl-1,3-butadiene)][7d] and $[ZrCp_2(butadiene)]$,[9b] has recently also been found in $[HfCp_2(butadiene)]$[29] and $[MoCp(NO)$(2,4-dimethyl-2,4-hexadiene];[30] a bridging s-*trans*-diene coordination, on the other hand, had already been reported for several binuclear and trinuclear metal complexes. $[Mn_2Cp_2(CO)_4(butadiene)]$[31] and $[(Pt_2Cl_6)_2(butadiene)]^{2\ominus}$[32] are typical examples for complexes of type **15**, while $[Mn_2(CO)_8(butadiene)]$[33] and $[Os_3(CO)_{10}(butadiene)]$[34] represent complexes of the type **16**. (The third Os atom does not participate in the coordination.) The s-*trans*-diene molecule coordinated to $ZrCp_2$ or MoCp(NO) has a non-planar arrangement with torsional angles of ca. 124–126° (cf. Fig. 2). As a consequence, the bond lengths of M–C1 and M–C4 are very similar to those of M–C2 and M–C3. In sharp contrast to the behavior of the $[ZrCp_2(diene)]$ complexes, [MoCp(NO)(diene)] thermodynamically favors the s-*trans* coordination rather than s-*cis* coordination (in agreement with Fenske-Hall MO calculations).[30a] The HOMO energy of the former is ca. 0.9 eV lower than that of the latter. The asymmetry of the *trans*-diene ligand enables stabilization of the high-lying occupied orbitals of the MoCp(NO) fragment. The discovery of s-*trans*-diene coordination to mononuclear complexes of the early transition metals is of special importance, since it provides a new aspect of the reaction mechanism of the titanium- or zirconium-assisted oligomerization and polymerization of dienes (see Sections 5.3 and 6.1).



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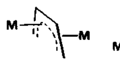

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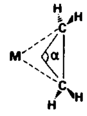
A novel type of binuclear metal complex containing a *cis*-coordinated diene (**17**), $[Rh_2(iPr_2PCH_2CH_2CH_2PiPr_2)_2(butadiene)]$, has appeared recently.[35] The butadiene unit is sandwiched between the two rhodium centers; the metal atoms interact with the twisted s-*cis*-butadiene (torsion angle of 45.0°) in an η^3-fashion. Coordination of a bridging s-*cis*-diene to M–M bonded binuclear complexes (**18**), e.g. $[Co_2Cp_2(CO)(butadiene)]$,[36] has also been reported.

The collection of structural details on s-*cis*- and s-*trans*-diene complexes and mononuclear and dinuclear metal species has thus only recently been completed. This information is indispensable for gaining an insight into the reaction mechanism of the oligomerization, polymerization and carbometalation of dienes by early transition metals.

2.2. Characteristic Properties of the M–C Bonding of Alkenemetal- and Alkynemetal-Complexes, and Related Complexes

Several reactive alkene complexes of the early transition metals (M = Ti,[37,38] Ta,[39] Nb[40,41]) have become available in recent years, while a number of alkene complexes of the late transition metals, represented by Zeise's salt, are already well documented. Table 2 lists the structural data for selected ethylene complexes together with the values for the chemical shift in the ¹H-NMR spectrum; α is the angle between the normals of the H–C–H planes shown in **19**. It is clear from the data in Table 2 that electron-rich ethylenemetal complexes exhibit relatively large α values and significant lengthening of the ethylene C–C bond; this confirms the enhanced sp^3 character of the carbon atoms. In general, the α value increases with increasing C–C bond length. The δ values—apart from in the case of the Ti complex **43**—are also consistent with the structural data. (In **43** the downfield shift could be explained in terms of the deshielding effect of the Cp* ring.) The enhanced carbon sp^3 hybridization must arise from substantial electron back-donation from the metal.



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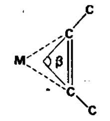

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Table 2. C-C bond distances, dihedral angle α (see **19**) and ¹H-NMR data (δ-values) for ethylene-transition metal complexes.

	C-C [Å]	α [°]	δ
$CH_2{=}CH_2$	1.337	0	123
$[Ni(dmpe)_2PPh_3(C_2H_4)]$ [a]	1.320	3.3	—
$[IrCl(PPh_3)_2(C_2H_4)]$	1.376	24.2	—
$[RuCl_2(CO)(PMe_2Ph)_2(C_2H_4)]$	1.376	24.2	58.6
$[Mo(PMe_3)_4(CO)(C_2H_4)]$	1.403	59.07	—
$[NbCpC_2H_5(C_2H_4)]$	1.407	52.5	29.4
$[TiCp^*_2(C_2H_4)]$ **43**	1.408	70	105.1
$[TaCp^*(CHCMe_3)(PMe_3)(C_2H_4)]$	1.477	68.5	—
Cyclopropane	1.510	—	−3.5

[a] dmpe = 1,3-bis(dimethylphosphino)propane.

Alkynemetal complexes show a similar trend with respect to the metal–carbon bonding. In the case of the electron-rich metal complexes there is usually a considerable lengthening of the acetylenic C–C bonds; however, the bite angle β (angle between the two C–C bonds in **20**) is hardly influenced by the metal and ligands.[26,42]

Let us now turn to the allylmetal complexes! For allylmetal complexes, primarily two limiting structures, **21** and **22**, are possible (see also Ref. [43a] for classification of the allylmetal complexes). The mode of M–C bonding varies depending upon the valence state of the metal and the hapticity of the ligand. Formally, the Zr^{IV} complexes $[ZrCp_2(CH_2CH{=}CHCH_3)_2]$ and $[ZrCp_2Cl(CH_2CH{=}CHCH_3)]$ exist in a σ-2-butenylmetal form (**21**) at low temperatures.[43b,c] However, low valent allylmetal species, for example $[TiCp_2[CH_2C(CH_3){=}CHCH_3]]$, exist in a η^3-*syn* form (**22**).[44] In general, in the compounds of the early transition metals and some nickel compounds,[45] the bond distances between metal and η^3-allyl terminal carbons are nearly equal to or a little shorter than that between the metal and the central carbon atom, while this trend is reversed in the compounds of the electrophilic late transition metals.[26]

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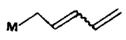
When the conjugation is extended further to pentadienyl systems, the ligand should be capable of binding to a metal in σ-, η^3-, and η^5 modes. The structural preference depends on the valence state of the metal and the π-acceptor properties of the ligands. Thus, the ligand in $[ZrCp_2$(2,4-pentadienyl)$_2]$ and its alkyl-substituted derivatives always prefer the terminally σ-bonded zigzag-like (*E*)-geometry (**23**),[17] while $[M(2,4\text{-dimethylpentadienyl})_2]$, M = V, Cr, Fe, Ti, and $[M(PR_3)(2,4\text{-dimethylpentadienyl})]$, M = Zr, Nb, prefer the U-shaped (**25**) or S-shaped (**26**) η^5-bonded structure, because this type of coordination is effective in stabilizing the naked or highly coordinatively unsaturated metal species.[46] Note that $[Ti(\eta^5\text{-pentadienyl})_2]$ derivatives are isolable, while $[Ti(\eta^5\text{-cyclopentadienyl})_2]$ is thermally unstable. Transition metal complexes of type **24**, which contain *syn*- or *anti*-η^3-pentadienyl ligands, include $[Fe(PMe_3)_2(C_5H_7)_2]$,[47] $[Co(PMe_3)_3(C_7H_{11})]$,[48] $[Co(CO)_2(PPh_3)(C_5H_7)]$,[49] and $[Mn(CO)_3(PMe_3)(C_5H_7)]$.[50] The manganese complex is converted into the η^5-coordinated isomer upon heating in solution, while the thermodynamic stability is reversed in the case of the cobalt complex. The corresponding change in hapticity for Cp ligands has not yet been well established, except for $[(\eta^3\text{-}Cp)(\eta^5\text{-}Cp)W(CO)_2]$,[51a] $[MCp_4]$, M = Ti, Zr, Hf,[51b] and some indenyl complexes.[51c-d]



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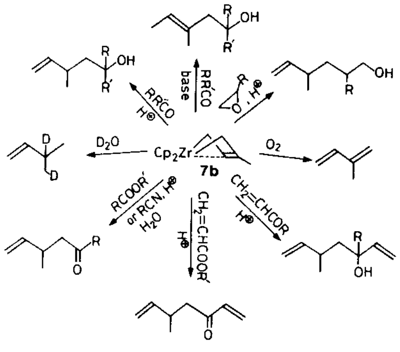
3. Selective Carbometalation of Organic Substrates Containing C–O and C–N Multiple Bonds with Organic Compounds of the Early Transition Metals

3.1. Regio- and Stereoselective Addition of Diene Complexes to Carbonyl Compounds, Nitriles, and Oxiranes

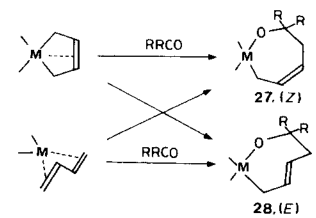
Carbometalation with organic compounds of metals of groups 3A–5A is one of the more important strategies in modern organic synthesis. The metal–carbon bond in these compounds is generally polarized as $M^{\oplus}$–$C^{\ominus}$ and hence renders the carbon site susceptible to electrophilic attack. Dienezirconium complexes, especially those with an unsymmetrical diene, e.g. isoprene, may serve as models for demonstrating the unique chemical behavior of complexes of the early transition metals, for they can readily rearrange into various geometrical isomers (see **1**–**6**) depending on the reaction conditions, and can afford a variety of products upon reaction with numerous unsaturated organic and inorganic molecules. As typical examples of such reactions, the carbometalation of oxygen-containing compounds with [ZrCp$_2$(isoprene)] **7b** and related reactions are illustrated in Scheme 1.[7a] The most striking feature is the exceptionally high regioselectivity (>95%) in the reactions with saturated and unsaturated aldehydes, ketones, and nitriles. The yields exceed 90% in all reactions. The reaction proceeds irreversibly at the sterically more congested 1-position of the isoprene rather than at the sterically favorable 4-position. Subsequent acid cleavage of the product of aldehyde or ketone insertion furnishes 3-methyl-4-penten-1-ol derivatives selectively (>90%), while base-catalyzed cleavage with secondary amines (e.g. pyrrolidine, piperidine) leads to 3-methyl-3-penten-1-ol derivatives.[52a] Esters and nitriles also react at C-1 of the isoprene and afford acylated compounds upon hydrolysis of the adduct.[52b] The mode of this reaction markedly differs from that of the well documented Grignard reaction or the reaction of [ZrCp$_2$(2-butenyl)$_2$] with esters, which leads to tertiary alcohols by double allylation. Some of the alkyllanthanoids react analogously with esters, with monoalkylation to give products which can be hydrolyzed to acylates.[53] Especially noteworthy is the highly selective 1,2-addition (>95%) observed in the reaction of dienezirconium complexes with α,β-unsaturated ketones and esters. The regiochemical selectivity may be ascribed to the high ionicity of the Zr–C bond and the high oxophilicity of the zirconium metal together with the rigid tetrahedral geometry of the complexes, since simple [RTiCl$_3$][54] and alkyllanthanoids[55] are also able to promote the selective 1,2-addition to enones. The carbometalation of oxiranes (R = aryl or vinyl) with the isoprenezirconium complex **7b** leads, with 99% regioselectivity, to C–C bond formation between C-1 of the isoprene and C-2 of the oxirane.[56] Thus, the subtle electronic and steric difference existing between C-1 and C-4 of isoprene could be clearly enhanced by complexation to zirconium. Analogous diene complexes, for example [TiCp*Cl(diene)], [HfCp$_2$(diene)], [TaCl$_2$Cp(diene)], [TaCp(diene)$_2$], and [NbCp(diene)$_2$], also promote the selective carbometalation, although diene complexes of metals of group 5A generally show relatively low reactivity toward these electrophiles.[57] The selective carbometalation with [M(OR)$_2$(diene)], M = Ti, Zr, generated in situ from M(OR)$_4$ or M(OR)$_2$Cl$_2$ and dienemagnesium, could be useful for large-scale organic syntheses.



Scheme 1. Nucleophilic addition of [ZrCp$_2$(isoprene)] **7b** to oxygenated or nitrogenated unsaturated compounds.

Two reaction pathways seem conceivable: insertion into the *cis*-dienemetal species (Type **2**), and insertion into the s-*trans*-isomer (type **4**). In order to obtain information on the reaction pathways, the reactions of the analogues of **7**, [ZrCp$^*_2$(isoprene)] (100% *cis*) and [ZrCp$^*_2$(butadiene)] (100% s-*trans*), with 2,4-dimethyl-3-pentanone were examined.[25] Both diene complexes are thermally stable even at 90°C but readily react with the ketone at 30°C. If the reactions proceed straightforwardly with retention of configuration, each of the stereoisomers might give rise to (*Z*)- and (*E*)-oxazirconacycloheptenes, **27** and **28** respectively. The X-ray analyses of the above two insertion products clearly confirm that both compounds have essentially the same configuration at the double bond, namely a (*Z*)-configuration as in **27** (Fig. 5). Hence, the s-*trans*-diene complex undergoes reaction with change of configuration, while the *cis* isomer retains its geometry. A similar (*Z*)-oxazirconacycloheptene structure is also found in a diphenyl ketone adduct of [ZrCp$_2$(butadiene)] **7a**.[58] However, we cannot immediately conclude that the (*Z*)-form of the isoprene adduct is a direct consequence of the *cis*-structure of the precursor, since an isomerization via **27b** is probable (*vide infra*).

In sharp contrast to the thermally induced reactions, a photoinduced reaction occurs preferentially (78%) at the sterically less crowded 4-position at −70°C. At this temperature the thermal reaction is completely suppressed.[59] The s-*trans* isomer of the isoprene complex (generated photochemically) also furnishes predominantly the same regioisomer **32b**, even in the absence of light. Thus, the geometry of the coordinated dienes is the crucial factor in determining the regiochemistry. A [2+2]-type oxidative coupling process has been proposed for both the photochemically- and the thermally-induced addition of the s-*trans*-diene complexes, since the regiochemistry is consistent with that found in the addition of the diene complex to unsaturated hydrocarbons (see Section 4). The insertion should proceed via **31**. A competition experiment with a mixture of s-*trans*- and *cis*-butadiene complexes confirmed the higher reactivity of the s-*trans* isomer.[58] On the basis of these findings, a four-centered insertion mechanism or a dipolar mechanism has been proposed for the thermally induced addition reaction of the *cis*-diene complexes. The coupling of a planar zirconacyclo-3-pentene species of type **3** with a carbonyl group via the four-centered transition state **29a** and further reaction via **29b** seems most likely. The C–C bond formation occurs at C-1 with cyclization to give **30**, since substantial negative charge accumulates on the C-1 atom rather than the C-4 atom by the inductive effect of the methyl group. Since the LUMO of [Cp$_2$Zr(s-*cis*-butadiene)] **7a** has a similar shape as 1a$_1$ of the "Cp$_2$Zr" fragment,[60] the carbonyl group can approach the metal only in the C1–Zr–C4 plane, as shown in **29a**. Actually, such a planar arrangement of the three M–X' bonds is commonly seen in pentacoordinated zirconocene derivatives.[61] The attack of allylic carbon atoms (C-2 or C-3) via the usual nonplanar six-membered transition state is forbidden because of this orbital symmetry requirement.



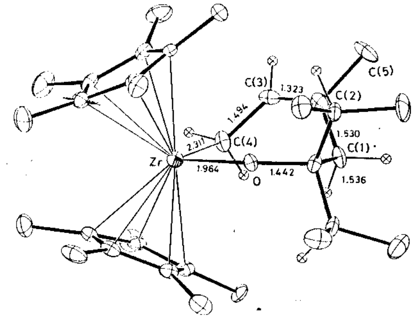
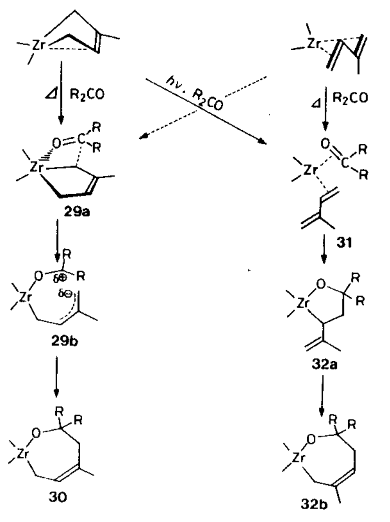
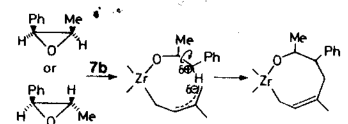


Fig. 5. Molecular structure of a (*Z*)-configurated complex of type **27**, [Cp$^*_2$ZrOC(*i*Pr)$_2$CH$_2$C(CH$_3$)=CHCH$_2$]. The complex is formed by ketone insertion.

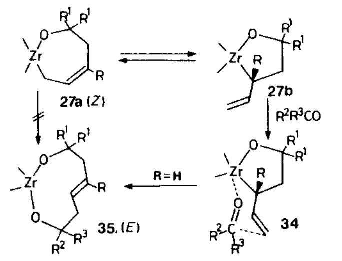


The result of the carbometalation of *cis*- and *trans*-2-methyl-3-phenyloxirane with the isoprene complex **7b** may support the above dipolar insertion mechanism.[56b] The insertion to give **33b** occurs with excellent regioselectivity (100%), but the configuration at C-2 and C-3 of the oxirane is destroyed during the reaction. To explain the free rotation around the oxirane C–C bond prior to the coupling, which leads to a mixture of the diastereoisomers (1 : 2 ratio), a transition state **33a** has been proposed.



33a 33b

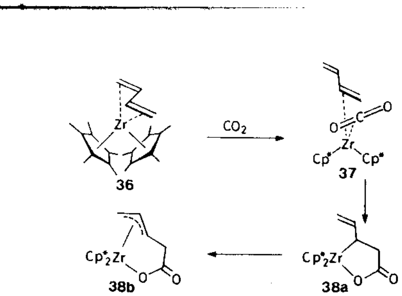
Isoprene-, 2,3-dimethylbutadiene-, and 3-methyl-1,3-pentadienezirconium complexes (with s-*cis* geometry) undergo only the 1:1 addition reaction of carbonyl compounds, even when the reaction is carried out at higher temperatures (≈100°C) in the presence of excess carbonyl compound, whereas s-*cis*-butadiene-, pentadiene-, and 2,4-hexadiene-complexes (ca. 1 : 1 mixture of the s-*cis* and s-*trans* isomers) readily add two equivalents of butanal or 3-pentanone in high yields (95%) at lower temperature (30°C).[17] Especially noteworthy is that the s-*cis*-butadiene complex predominantly forms an (*E*)-dioxazirconacyclo-4-nonene (**35**) as a result of double insertion; upon hydrolysis, **35** selectively affords (*E*)-3-hexene-1,6-diol derivatives. If the second incoming carbonyl compound directly attacks the (*Z*)-oxazirconacycloheptene **27a**, the (*Z*)-analogue of **35** ought to be formed. This controversy can be resolved by assuming an insertion process via a six-membered transition state in a chair form (**34**). The mode of this reaction is, in principle, the same as that postulated for the *threo*-selective incorporation of aldehydes and ketones into zirconium-[43b,62a] or titaniumallyl compounds[62b,c] such as [ZrCp$_2$(2-butenyl)$_2$], [ZrCp$_2$Cl(2-butenyl)], and [TiCp$_2$(2-butenyl)]. In the case of ketone or aldehyde adducts of isoprene- and 2,3-dimethylbutadiene-complexes, the equilibrium between **27a** and **27b** may be shifted to the



thermodynamically more favored species **27a**, because the steric repulsion between Cp and tertiary α-carbon interferes with the generation of 3-vinyl-1,2-oxazirconacyclopentanes (**27b**, R = Me). In fact, five- and six-membered 1,2-oxazirconacycloalkenes, Cp$_2$ZrO(CH$_2$)$_n$ (n = 3, 4, 5) without vinyl component,[63] are completely inert to carbonyl compounds under normal reaction conditions. Despite the presence of a methyl group at C-2, s-*cis*-2-methyl- and s-*cis*-2,4-dimethyl-1,3-pentadienezirconium complexes can promote double insertion, since the carbonyl compound is first attacked predominantly at C-4, affording an intermediate with a conformation similar to **34** (R = H).[64] As an extension of this reaction, the successive insertion of two kinds of electrophiles, e.g., isobutanal/3-pentanone, ethyl acetate/isobutanal, and 3-pentanone/acetonitrile, into both ends of the butadiene molecule to give **35** has been realized by treating [ZrCp$_2$(s-*cis*-butadiene)] with a carbonyl compound at 0°C in hexane and then with the other electrophile in THF at 60°C. However, attempts to carry out addition of the electrophiles in the reverse order, e.g. isobutanal/ethyl acetate or acetonitrile/3-pentanone, met without success.[64]

3.2. Addition of Diene Complexes to CO$_2$ and Heterocumulenes

Alkenyl- and aryltitanium compounds readily react with CO$_2$, thus reflecting their high oxophilicity, while alkylzirconium derivatives are not reactive enough for practical purposes.[65] Dienezirconium complexes undergo a variety of reactions, resulting in 1:1, 1:2 or 2:1 addition depending on the bulkiness of the Cp ligand, the geometry of the coordinated diene, and the nature of the alkyl substituents on the diene. [ZrCp$^*_2$(butadiene)] (**36**), containing a bulky pentamethylcyclopentadienyl group together with an s-*trans*-diene ligand, undergoes the 1:1 addition reaction, even when excess CO$_2$ is introduced at elevated temperatures. The reaction should proceed via **37** by oxidative [2+2]-coupling or directly with generation of a 3-vinyl-1,2-oxazirconacyclopentan-5-one (**38a**), which immediately



rearranges into the more stable complex **38b**. The C=O group in **38b** is bent away from the metal, as confirmed by the X-ray structure analysis (Fig. 6).[66] A similar metal–

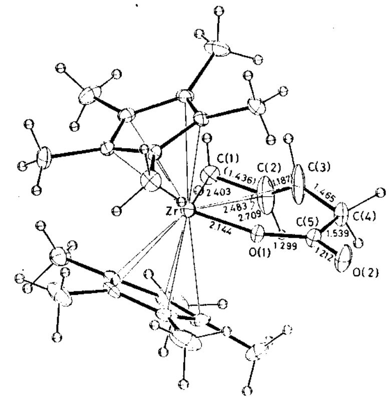
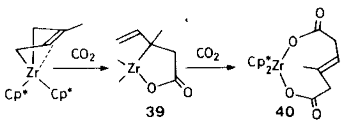
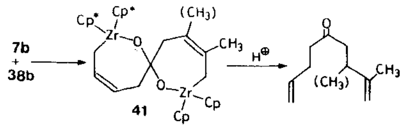


Fig. 6. Molecular structure of the complex [Cp$^*_2$ZrOCOCH$_2$CH=CH–CH$_2$] **38** formed by CO$_2$ insertion.

carbon linkage is also found in the product of the stoichiometric reaction between [MCp$_2$(butadiene)], M = Zr,[67] Th,[14] and [M(CO)$_6$], M = Cr, Mo, W. In sharp contrast to the above reaction, a double insertion of CO$_2$ yielding **40** occurs at the diene termini when [ZrCp$^*_2$(s-*cis*-isoprene)] or [ZrCp$^*_2$(s-*cis*-2,3-dimethylbutadiene)] is used. This drastic difference may be attributed to the conformational instability of the transient 1:1 adduct **39** (i.e. the steric repulsion between the methyl group at the α-carbon atom and the Cp* ligand cannot stabilize the conformation **39** and hence forces a further reaction.[68]

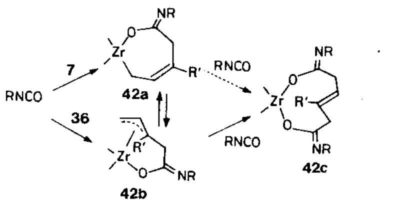
When the Cp* ligand is replaced by a less bulky Cp li-





gand, all the [ZrCp$_2$(s-*cis*-diene)] complexes examined undergo the 2:1 addition reaction leading to dioxadizirconaspiroalkadienes. An example is complex **41**. A reaction pathway for this insertion has been proposed which is based on the stoichiometric reaction between **38b** and **7b**. This sequence affords the expected spiro compound **41**, which yields a mixture of butenyl 2-methylbutenyl ketone and butenyl 3-methylbutenyl ketone in ca. 5:3 ratio on hydrolysis. Thus, a delicate balance of the electronic and steric effects determine the reaction course.

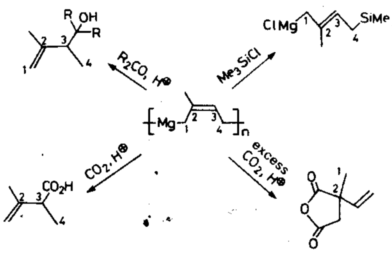
A heterocumulene, RN=C=O (R = Me, *t*Bu, Ph), readily reacts with both [ZrCp$_2$(s-*cis*-butadiene)] **7a** and [ZrCp$^*_2$(s-*trans*-butadiene)] **36** to give *syn*-allyl compounds of type **42b**, while reaction of [ZrL$_2$(isoprene)], L = Cp, Cp*, with *t*BuNCO gives oxazirconacycles **42a** with (*Z*)-geometry. When **7a**, **7b**, **36**, or **42b** was treated with an excess of reactive PhNCO the 1:2 adduct **42c**, R = Ph, with (*E*)-geometry was obtained in high yield. These results indicate that the conformational stability of the adducts, and not the configuration of the precursor dienemetal complexes, is the crucial factor in determining the geometry [(*E*) or (*Z*)] of the products.[69] The direct transformation of **42a** into **42c** seems very unlikely on steric grounds.



R' = H, Me.

3.3. Regiochemistry of the Reactions of Allylmetal Compounds

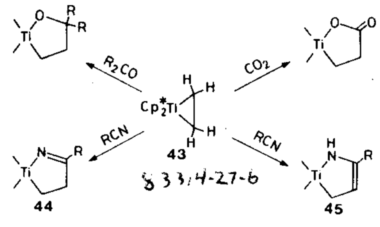
The chemistry of the allylzirconium and -titanium compounds is of fundamental importance for demonstrating the characteristic properties of the complexes of group 4A metals and for unfolding the origin of the fascinating regiochemistry observed in reactions with dienezirconium complexes, since the metal–carbon linkage of metallacyclo-3-pentenes can be regarded as representing a special case of the bis(2-butenyl)metal complexes. [ZrCp$_2$CH$_3$(3-methyl-2-butenyl)], [ZrCp$_2$CH$_3$(2-methyl-2-butenyl)], and [ZrCp$_2$(2-butenyl)$_2$], containing σ-bonded allyl groups, react, like the corresponding η^1-2-butenyltitanium(III) compounds, with acetone or ethanal exclusively at C-3 of the 2-butenyl group. High regio- and *threo*-selectivity (85–100%) are observed in reactions with aldehydes.[43b,62] A six-membered chair-like transition state has been proposed for these reactions. The corresponding allylic compounds of main group metals likewise react at C-3, but show almost no *threo*-selectivity.[70] Nine-membered metallacycles, [ZrCp$_2$(C$_{10}$H$_{16}$)] and [ZrCp$_2$(C$_8$H$_{12}$)], containing a 4-4 bonded dimeric isoprene or a 1-1 bonded dimeric butadiene unit (see Section 4.2), however, react with isobutanal or 3-pentanone at the 3-position of these ligands, and not at the terminal carbon atoms. Thus, the five-membered ring is crucial for the selective insertion at the terminals of the diene. The 1:1 magnesium–isoprene adduct, (polymeric 2-methyl-2-butenediylmagnesium) exhibits a completely different chemical behavior, as shown in Scheme 2. All of the electrophiles react selectively at C-3 (γ-position), presumably via a conventional six-membered transition state; the transmetalation with trimethylsilyl chloride occurs exclusively at C-4, thus lending support to the reaction pathway leading to **7** (Section 2.1). σ-Pentadienylzirconium compounds of type **23**, higher homologues of allylzirconium compounds, behave similarly, and add aldehydes and ketones selectively at C-3 (γ-position).[17a]



Scheme 2. Mode of reaction between magnesium–isoprene (1:1) adduct with electrophiles.

3.4. Nucleophilic Addition of Alkenemetal and Alkynemetal Complexes

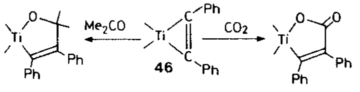
Alkene complexes of group 4A metals readily react with electrophiles in essentially the same manner as described for the diene complexes of these metals, whereas the coordinated olefin in the compounds [MCpH(CH$_2$=CHR)], M = Ta, Nb, is completely inert. The ethylene complex [TiCp$^*_2$(C$_2$H$_4$)] (**43**), undergoes a variety of nucleophilic



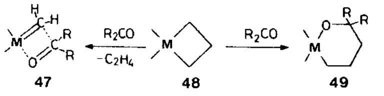
Scheme 3. Addition reaction of [TiCp$^*_2$(C$_2$H$_4$)] **43** to electrophiles.

additions, affording oxa- or azametallacycles (Scheme 3).[71] Reactions with ketones and esters are rather complex. *tert*-Butyl and *p*-tolyl cyanide (RCN with bulky R group) undergo direct addition to give **44**, whereas alkyl cyanides with less bulky groups (CH_3, C_2H_5) favor formation of the metallacycloenamine tautomer **45**.

The chemical reactivity of alkyne complexes of Ti and Zr toward electrophiles resembles that of the alkene complexes.[72] The addition of acetone or CO_2 to the 1,2-diphenylacetylene complex **46** led to oxametallacycles. Such a nucleophilicity has never been demonstrated for the corresponding alkyne complexes of group 5A metals (Ta, Nb) or late transition metals.

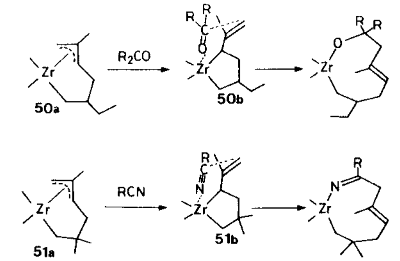


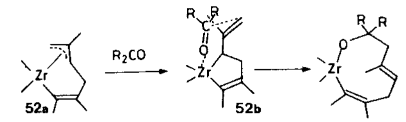
With regard to the alkene complexes, there exist four-membered metallacyclobutanes of type **48** containing W,[73] Ta[74] or Ti[75] which function as alkene-metathesis catalysts or active species for the polymerization or oligomerization of olefins. Stoichiometric reactions of these compounds with electrophiles should provide valuable information about the characteristic properties of their M–C bond, since the complexes are in equilibrium with a methylenemetal ethylene species. We can observe the enhanced carbene-complex property of **48**, $>M = Cp^*_2Ti$, in the reaction with carbonyl compounds, which is essentially a condensation reaction of the Wittig type (cf. **47**).[75b] Wittig-type reactions are also known for $>M = Cp^*Cl_2Ta$,[74b] 1,3-dititanacyclobutane derivatives[76] and $[Cp_2TiCHR \cdot AlMe_2Cl]$ species.[77] However, such a metal-carbene character is virtually lacking in the case of $>M = Cp_2Hf$, i.e., this complex undergoes only normal carbometalation, leading to an oxahafnacyclohexane derivative of type **49**.[78] A related carbenezirconium complex, $[Cp_2Zr{=}CHCH_2R]$, has recently been isolated by stabilizing it with a trialkylphosphane.[79] Metallacyclopentanes with M = Ti, Zr, Hf (cf. **8**) are less reactive than metallacyclobutanes toward electrophiles and behave similarly to dialkylmetal compounds.



3.5. Metal-Assisted Selective Three-Component Addition

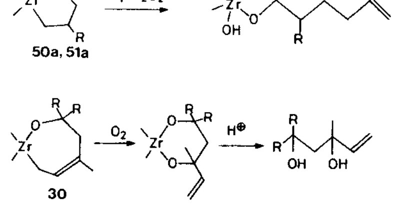
A stepwise three-component addition reaction has been realized by taking advantage of the highly regioselective reaction between dienezirconium complexes and alkenes, dienes or alkynes (see Sections 4.1 and 4.2). The allylic moiety of the resulting complexes **50a** and **51a** selectively inserts a variety of aldehydes, ketones, esters, and nitriles.[70] Thus successive diene–alkene–aldehyde, diene–alkene–ketone or diene–alkene–nitrile additions take place in the reaction sphere of $ZrCp_2$ species with excellent regioselectivity (>95%) in ca. 90% yield. Similarly, successive three-component addition of diene–alkyne–aldehyde and diene–alkyne–nitrile has been achieved via the isoprenezirconium complex **52a** with inserted 2-butyne. These processes should have potential utility in organic synthesis, since a variety of combinations can be chosen. It should be noted that these compounds react in a completely different fashion to the conventional allylzirconium compounds. In **50a**, **51a**, and **52a** the C–C bond formation occurs at the α-position, thus suggesting involvement of the intermediates **50b**, **51b**, and **52b**. In the case of normal allylmetal compounds bond formation takes place at the sterically more crowded γ-position (see, e.g., Scheme 2).





3.6. Oxidation of Complexes of the Early Transition Metals with Hydrogen Peroxide or Air

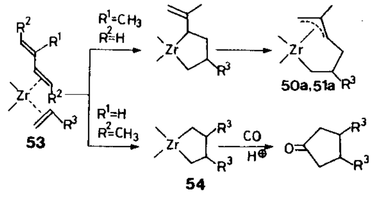
Generally, oxidation of organozirconium complexes is effected by the addition of aqueous H_2O_2 (30%), *t*BuOOH, *m*-$ClC_6H_4CO_3H$ or even air in some cases. Transformation of an alkylzirconium complex into a zirconium alkoxide, e.g. $[ZrCp_2Me_2]$ into $[ZrCp_2(OMe)_2]$, has already been achieved with these oxidizing agents.[80] However, such protic oxidizing agents are not suitable for the oxidation of allylzirconium, allyltitanium, or dienezirconium complexes, because a protonolysis takes place prior to the oxidation. Therefore, only the alkylmetal part of σ,η³-allyl compounds (**50a**, **51a**) is oxidized with aqueous H_2O_2, whereby monoalcohols are formed in good yield.[81] Oxazirconacycles **30** are however readily oxidized by aqueous H_2O_2 or by air, whereupon 1,3-diols are formed in high yield (80%) with high selectivity (96%). The diene ligands in $[ZrCp_2(diene)]$, $[TaCl_2Cp(diene)]$, and $[NbCp(diene)_2]$ are readily removed quantitatively in solution by passage of air.



4. Oxidative Coupling of 1,3-Dienes and Alkenes with Unsaturated Hydrocarbons in the "MCp₂" Sphere

4.1. Regioselective Addition of Dienemetal Complexes to Alkenes

Most of the simple alkenes (ethylene, 1-butene, 2-butene, isobutene etc.) rapidly react with both $ZrCp_2$(s-*cis*-diene)] and $[ZrCp_2$(s-*trans*-diene)] complexes (diene = butadiene, isoprene) at ambient temperatures with formation of 1:1 adducts of the type **50a** and **51a**.[82] In the case of the s-*cis*-isoprene complex, the C–C bond formation takes place quantitatively at the sterically less crowded C-4 atom of the isoprene with >98% regioselectivity. The regiochemistry contrasts sharply with that of the additions to compounds with C–O and C–N multiple bonds. In the case of s-*cis*- and s-*trans*-butadiene complexes the C–C bond formation presumably takes place via the same transition state **53**, $R^1 = R^2 = H$, since the products have the same structure in both cases. Alkenes with internal double bonds (e.g. 2-pentene, 2-hexene) undergo migratory insertion into the isoprene complex **7b** at elevated temperature (>60°C) to give the same compounds as are obtained from alkenes with terminal double bonds (e.g. 1-pentene, 1-hexene). $[Cp_2Zr$(1,4-diphenylbutadiene)], however, is completely inert to these alkenes because of its strong M–C bonding.



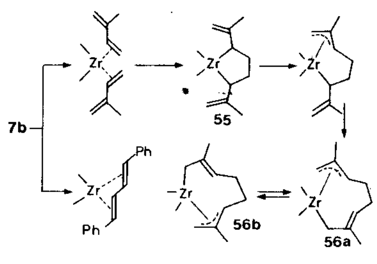
As confirmed by ligand exchange experiments, the relative strength of the diene zirconium bond is found to decrease in the following order:[83]

1,4-diphenylbutadiene > 2,3-dimethylbutadiene > butadiene > isoprene > 1,3-pentadiene > 1,3-hexadiene > 2,4-hexadiene

The order approximately parallels the π-acidity of the dienes. 2,4-Hexadiene counts among the most weakly bound ligands, so it is very easily displaced by 1-butene or 1-hexene.[17] At the same time, 3,4-dialkylzirconacyclopentanes (**54**) are generated by oxidative coupling between the two 1-alkene molecules in the $ZrCp_2$ sphere. Direct reduction of $[ZrCl_2Cp_2]$ with $NaC_{10}H_8$ or RMgX in the presence of 1-alkenes provides a more convenient route to the compounds **54**.[84] The subsequent carbonylation with CO under atmospheric pressure affords an enolate, which upon hydrolysis furnishes a 3,4-dialkylcyclopentanone in 70–80% yield. The synthesis of cyclopentanones by carbonylation of metallacycles is already well known.[85] The 1,4-diphenylbutadiene and 2,3-dimethylbutadiene ligands are bound to the metal very tightly, and hence they are completely inert toward almost all alkenes. Thus, zirconium complexes of butadiene and isoprene (dienes with a moderate π-acidity) can promote the stoichiometric carbometalation of alkenes.

4.2. Diene–Diene Coupling in the "ZrCp₂" Sphere

Conjugated dienes show fairly good reactivity toward $[ZrCp_2(diene)]$ complexes. Depending upon the π-acidity of the dienes, either a ligand exchange reaction or a 1:1 coupling reaction takes place.[86] Addition of one equivalent of (*E*,*E*)-1,4-diphenyl-1,3-butadiene to butadiene-, isoprene-, and hexadienezirconium complexes results in the quantitative displacement of the coordinated dienes, with concomitant formation of $[ZrCp_2$(s-*trans*-1,4-diphenylbutadiene)]. Addition of one equivalent of isoprene to the isoprene complex **7b** at 20°C, on the other hand, promotes 1:1 coupling with formation of the equilibrium mixture **55** ⇌ **56**, (4–4 bonded) together with **75** (3,4-bonded, cf. Section 5.3) in a 76:24 ratio. According to the NMR spectrum, the 4–4 bonded compound assumes the thermodynamically more favored structure **56**. The complex **56** could be prepared in a high state of purity by treating $[ZrCl_2Cp_2]$ with a 4–4 bonded isoprene dimer/Mg adduct,

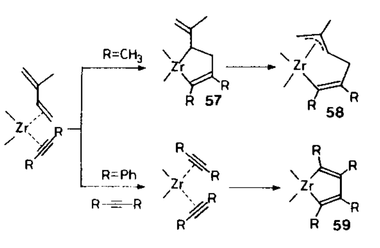


$[MgC_{10}H_{10}]_n$, at −20°C. The corresponding butadiene dimer complex, $[ZrCp_2(C_8H_{12})]$, is accessible by 1:1 reaction of $[ZrCp_2(butadiene)]$ with butadiene or by reaction of $[ZrCl_2Cp_2]$ with $[MgC_8H_{12}]_n$. The resulting 18e complexes have a fluctional structure: σ-π rearrangement occurs rapidly between **56a** and **56b** even at −70°C. The bis(η^3-allyl) structure is favored when these ligands are bound to coordinatively unsaturated species such as Zr(cyclooctatetraene),[87] CpV,[88] etc.

Group 5A metal-diene complexes of the type $[MCl_2(C_5R_5)(diene)]$ and $[M(C_5R_5)(diene)_2]$ (M = Ta, Nb; R = H, Me), are, with exception of $[NbClCp(butadiene)]_2$, generally inert to alkenes and dienes.[89] This is due to the enhanced stabilization of the M-C bonding by strong π-electron donation from internal carbon atoms to vacant metal d-orbitals together with back donation from filled metal orbitals to π* orbitals of the diene C–C bonds. The very strong M-C bonding in these complexes may be the major reason why organic compounds of group 5A metals generally do not catalyze diene oligomerization and polymerization.

4.3. Selective Coupling of Dienes with Alkynes

A series of alkynes readily react with zirconium-diene complexes by way of either a 1:1 addition reaction or a ligand exchange reaction, depending upon the nature of the alkynes.[82-90] Most 1- or 2-alkynes bearing one or more alkyl groups (e.g., 1-butyne, 2-hexyne etc.) react with $[ZrCp_2(s\text{-}cis\text{-}isoprene)]$ irreversibly at ambient temperature to give 1:1 addition compounds, where the alkyne binds selectively to the C-4 atom of isoprene. The whole geometry of the resulting σ,η^3-*syn*-allyl compounds **58** (cf. **52a**) is very similar to that of the compounds **50a** and **51a** with inserted alkene. The molecular structure of the complex with inserted 2-butyne is representative of this type of complexation (Fig. 7). Alkynes with aromatic substituents, however, favor the ligand exchange reaction. A typical example is seen in the stoichiometric reaction between $[ZrCp_2(isoprene)]$ and diphenylacetylene leading to 2,3,4,5-tetraphenylzirconacyclo-2,4-pentadiene (**59**). Analogous zircona- or titanacyclo-2,4-pentadiene derivatives are also accessible by reduction of $[MCl_2Cp_2]$ in the presence of alkynes.[91] Recently, the isolation of alkynezirconium and alkyneytterbium complexes has been reported.



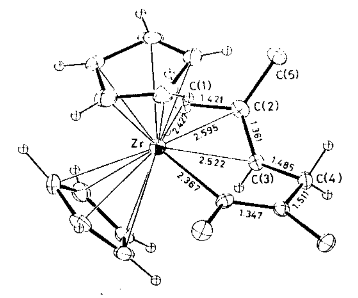


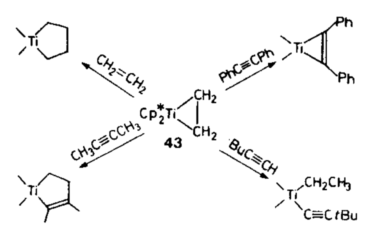
Fig. 7. Molecular structure of a 2-butyne inserted complex of type **58**, $[Cp_2ZrC(CH_3){=}C(CH_3)CH_2CH{-}C(CH_3){-}CH_2]$.

From competition experiments, it can be concluded that the relative reactivity of aliphatic substrates toward $[ZrCp_2(diene)]$ decreases in the following order:

aldehydes > ketones ≈ nitriles ≈ isocyanates > CO_2 > oxiranes ≈ esters ≈ alkynes > dienes > alkenes

4.4. Reactions of Alkenemetal Complexes with Unsaturated Hydrocarbons

$[TiCp^*_2(CH_2{=}CH_2)]$ (**43**) is a typical alkene complex of an early transition metal which undergoes facile reactions with a variety of unsaturated hydrocarbons.[71] Ethylene reacts reversibly with **43** to yield an equilibrium mixture containing a titanacyclopentane; higher alkenes (propene, butene, etc.), however, are generally inert to **43**, presumably because of the unfavorable steric interaction between the bulky Cp* ligand and the alkyl substituents. Alkynes are more reactive toward **43**; their modes of reaction can be classified into three types (Scheme 4). Alkynes with internal double bonds, whose π-acceptor property is less pronounced, are incorporated into the Ti-C bond to give metallacyclo-2-pentene derivatives, while alkynes which are good π-acceptor ligands exclusively undergo ligand exchange to give, for example, a diphenylacetylene complex, preventing the formation of 2,3-diphenyltitanacyclo-2-pentene. Terminal alkynes, typically *t*BuC≡CH, react with **43** to yield alkynyl(ethyl)titanium compounds. Alkene complexes of Ta and Nb, e.g. $[TaCp_2H(RCH{=}CH_2)]$ and $[NbCp_2H(RCH{=}CH_2)]$, generally do not form metallacycles like the corresponding titanium complexes, but they can undergo ligand exchange reactions with other alkenes and alkynes.[92c]



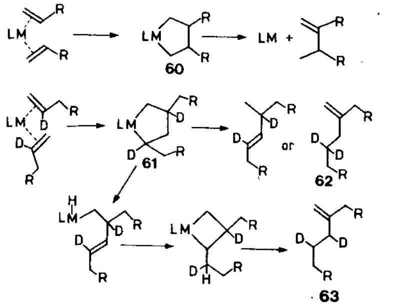
Scheme 4. Coupling reaction between $[TiCp^*_2(C_2H_4)]$ **43** and unsaturated hydrocarbons.

5. New Aspects of the Catalytic Conversion of Hydrocarbons

5.1. Regioselective Dimerization of 1-Alkenes

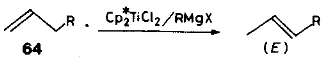
The metal-assisted selective linear or cyclic oligomerization of 1-alkenes has recently become a subject of intensive study.[93] Although various homogeneous catalyst systems involving low-valent organonickel[94] and organopalladium species[95] are known to effect the linear dimerization of 1-alkenes, highly regioselective dimerization leading to an isomerically pure head-to-head, head-to-tail or tail-to-tail dimer has been achieved in only a few cases.[96] Recently, selective coupling of propylene has been achieved with $[TaCp^*Cl_2(propylene)]$;[97] the catalytic dimerization leads, with high regioselectivity (95%), to formation of 2,3-dimethyl-1-butene (head-to-head dimer).

A reaction path via a metallacyclization to give a 3,4-dimethyltantalacyclopentane (**60**) followed by β-hydride elimination has been proposed for the tantalum mediated dimerization.[98] This type of β-elimination has already been confirmed by thermal degradation of titana-[99] and zirconacyclopentanes[100] bearing two Cp ligands. In the case of dimethyl substituted titanacyclopentanes, the formation of 2,4-dimethyltitanacyclopentane is electronically more favorable than that of the 3,4- and 2,5-isomers; according to MO calculations, however, 3,4-dimethyltitanacyclopentane is sterically the more stable.[101] As found in the dimerization of 3,3-dimethyl-1-butene or 1-hexene, when bulky 1-alkenes are employed in the tantalum-mediated dimerization, head-to-tail dimerization predominates over head-to-head dimerization.[98] A novel reaction pathway has been proposed for this reaction based on a labeling experiment using [2-D]-1-hexene. If the head-to-tail dimerization were to arise directly from the β-elimination of the resulting 2,4-dialkylmetallacyclopentane **61**, it should lead to a 4,4-dideuterated 1-alkene derivative (**62**); in practice, however, the two deuterium atoms in **63** are found exclusively at the 3- and 4-positions, thus indicating that the reaction proceeds via a ring closure. A similar ring closure is reported for metallacyclopentanes containing Pt,[102a] Rh,[102b] and Re[102c] atoms. However, an alternative mechanism via an intermolecular ring opening process must be taken into consideration, as has been reported recently for platinacyclopentanes.[102d]



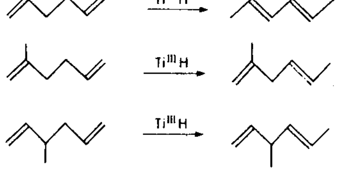
5.2. Selective Migration of the Double Bond of 1-Alkenes

Transition-metal-catalyzed isomerization of 1-alkenes has been extensively studied with soluble metal hydrides[103] or carbonyl metal compounds[104a] and, more frequently, with heterogeneous catalysts.[104b-d] These catalysts generally require a relatively high temperature (>70°C) for initiation of the reaction, and consequently a mixture of isomeric alkenes is formed as a result of the thermodynamic equilibrium. It therefore appears necessary to conduct the catalytic reaction at lower temperatures in order to freeze out the equilibrium. Recently, a catalytic system prepared by reduction of $[TiCl_2Cp^*_2]$ with $NaC_{10}H_8$, *i*PrMgBr, BuLi or $LiAlH_4$ was found to effect a highly stereoselective isomerization of 1-alkenes **64** to (*E*)-2-alkenes



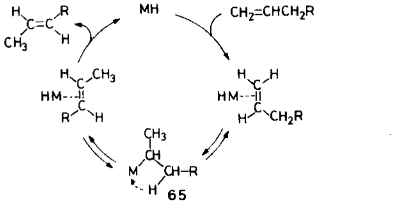
64

(R = CH_3, C_2H_5, C_6H_5, NEt_2, etc.).[105] The reaction proceeds quantitatively and with extremely high selectivity (>98%) within a few minutes. The maximized turnover is ca. 130 mol/(mol·min) in the case of 1-hexene. 1,5-Hexadiene and 1,7-octadiene are similarly converted into (*E*,*E*)-2,4-hexadiene and (*E*,*E*)-2,6-octadiene, respectively, with 99% selectivity. However, this catalyst proved to be inert in attempts to isomerize 2-methyl- and 3-methyl-1-alkenes. Exploiting this property, 2-methyl- and 3-methyl-1,5-hexadiene could be isomerized successfully to pure (*E*)-2- and (*E*)-3-methyl-1,4-hexadiene, respectively, in quantitative



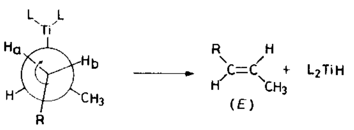
yields. The $[TiCl_2Cp_2]/iPrMgBr$ and $[TiCl_2Cp_2]/NaC_{10}H_8$ systems containing less bulky auxiliary ligands exhibit similar or higher activity, but the stereoselectivity is much lower (50–75%).[105, 106] The [ZrCl$_2$Cp$_2$]/*i*PrMgBr system also promotes selective isomerization (95–99%), but the rate of reaction is less than 1/10 of that observed for the [TiCl$_2$Cp$^*_2$]/*i*PrMgBr system.

Two major mechanisms have been proposed for the double bond migration: addition-elimination[103–107] and 1,3-hydrogen shift.[108a] These two mechanisms are usually differentiated by a deuterium labeling experiment. Since a hydrogen/deuterium scrambling occurs in the closely related reaction between [TiCp$^*_2$(CH$_2$=CH$_2$)] (**43**) and a mixture of CH$_3$CH=CH$_2$ and CD$_3$CD=CD$_2$, which presumably proceeds via a hydride species, [Cp*(C$_5$Me$_4$-μ-CH$_2$)TiH(CH$_2$=CH$_2$)],[71] the addition-elimination mechanism seems the most likely one for these isomerizations



Scheme 5. Proposed mechanism for the selective isomerization of 1-alkenes to (*E*)-2-alkenes.

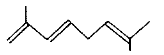
(Scheme 5). A metal hydride reacts reversibly with a 1-alkene to give an alkylmetal derivative (**65**), and then the alkyl group undergoes β-hydride elimination to give either the original 1-alkene or a 2-alkene. The factor which determines the configuration is almost certainly the conformation of the complex **65**, M = Cp$^*_2$Ti, with inserted 1-alkene. Informative is the view along the C2–C3 bond. The preferential formation of the (*E*)-isomer will arise from steric re-



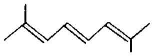
pulsion between R and Cp* or TiCp* as well as between CH$_3$ and R groups. The RCH$_2$ group should rotate clockwise for steric reasons to place the Ti and H$_a$ in elipsed position. The subsequent *cis*-elimination yields an (*E*)-2-alkene. For the isomerization of allyl ethers and allylamines, Ir$^{\text{I}}$[108b] and Rh$^{\text{I}}$[108c] organometallic catalysts were recently found to be more effective than catalysts containing group 3A–5A metals.

5.3. Regioselective Dimerization of Conjugated Dienes

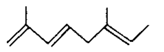
[ZrCp$_2$(s-*cis*-isoprene)] (**7b**) has been found to be a relatively good catalyst for the dimerization of isoprene to 4–4



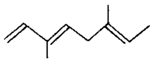
66 (tail/tail)



67 (tail/tail)

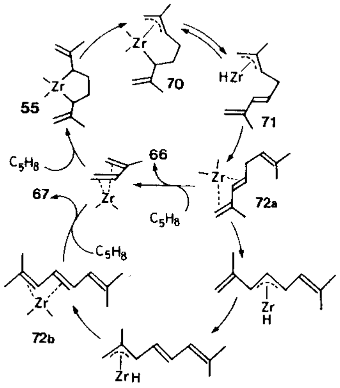


68 (tail/head)



69 (head/head)

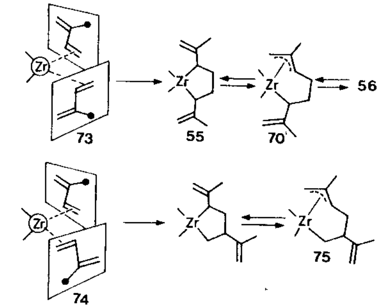
bonded (*E*)-2,7-dimethyl-1,3,6-octatriene (**66**) at 30°C and (*E*)-2,7-dimethyl-2,4,6-octatriene (**67**) at 60°C. An excellent regioselectivity (99%) and ca. 70% conversion was achieved when five equivalents of isoprene were added to the catalyst.[82] A catalytic cycle (Scheme 6) involving a single or double β-elimination sequence has been proposed on the basis of the following findings: 1) The stoichiometric reaction between [ZrCp$_2$(s-*cis*-isoprene)] and isoprene at 10°C affords **56** (see Section 4.2) or **70** in equilibrium with **56**. 2) The complex **70** is immediately isomerized via **71** to **72a** and **72b** upon warming in benzene to 40°C without further addition of isoprene. This transformation is confirmed by a chemical trapping experiment with molecular oxygen: a 3:2 mixture of **66** and **67** is obtained at the initial stage, but the ratio is reversed (2:5) when the solution is kept at 30°C for prolonged periods of time before treatment with O$_2$. 3) Addition of 1,4-diphenylbutadiene to **56** leads to a ligand exchange reaction. The 1,4-diphenylbutadiene complex is formed, and **66** and **67** (2:5) are liberated. [HfCp$_2$(isoprene)] also catalyzes the corresponding dimerization at elevated temperatures (80°C), but the catalytic activity is much lower than that of [ZrCp$_2$(isoprene)], presumably due to the predominant formation of catalytically inactive metal species of the type **75**.

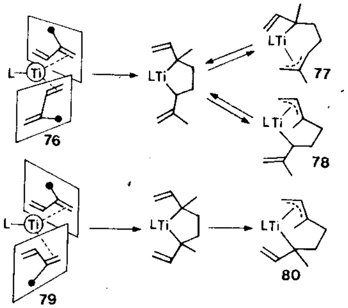


Scheme 6. Proposed mechanism for the selective dimerization of isoprene.

The mode of reaction changes drastically when diene-titanium complexes are used as catalysts. The complexes are generated in situ by treating [TiCl$_3$Cp], [TiCl$_2$Cp] or [TiCl$_2$Cp$_2$] with isoprene Mg adducts or RMgX in the presence of isoprene. These catalysts effect the tail-to-head (**68**) and/or sterically unfavorable head-to-head (**69**) dimerization of isoprene in ca. 3:2 ratio, with complete suppression of the tail-to-tail dimerization.[86] The use of bulky auxiliary ligands is highly effective for improving the selectivity. Thus, the sole isomer with tail-to-head bonding was prepared for the first time using [TiCl$_3$Cp*]/BuMgBr as catalyst. It seems reasonable to postulate that the active species is the isoprene complex of Ti$^{\text{III}}$, not of Ti$^{\text{IV}}$, as can be concluded from the following observations: 1) A Ti$^{\text{III}}$ species was detected by EPR spectroscopy. 2) Ti$^{\text{IV}}$ compounds are generally easily reduced to Ti$^{\text{III}}$ species by treating them with RMgX, Mg etc., while the reduction of Zr$^{\text{IV}}$ to Zr$^{\text{III}}$ species is quite difficult. 3) The shape and the orientation of the vacant d-orbitals of "TiCp$_2$", as well as the whole geometry, are quite similar to those for "ZrCp$_2$", as predicted from EHMO calculations. This indicates that Ti$^{\text{IV}}$ species should, contrary to the observations, produce a tail-to-tail dimer. 4) Isolated [TiClCp*(diene)] complexes of Ti$^{\text{IV}}$ (diene = butadiene, isoprene, 2,3-dimethylbutadiene) exhibit very weak or practically no catalytic activity, but the reduction of these complexes with RMgX or Mg leads to excellent catalysis with tail-to-head dimerization.[6]

On the basis of these findings, we can postulate the coordination geometry of the transient bis(diene) complexes. According to molecular models the coordination of two isoprene molecules with geometries **73** and **74** are sterically most favorable for the zirconocene species. The 4–4 bonding of isoprene should occur via **73**; subsequent β-elimination from **70** then leads to **72a**. Scheme 6 shows this further reaction to **66** and **67**. If the β-hydrogen elimination proceeds at the metallacycle **55** and the subsequent hydrometalation occurs at the γ-position (referred to **71**), then 1,3,7-octatriene derivatives should be formed instead of the 1,3,6-octatriene derivative **66**. Actually, such a catalytic reaction to produce 1,3,7-octatriene derivatives via an intermediate of type **55** takes place in the Pd-mediated dimerization of 1,3-conjugated dienes.[109a, b] The molecular structure of platinacycles of the type **55** has indeed been confirmed crystallographically.[109c] Unlike **73**, the intermediate **74** will lead to a catalytically inactive complex **75**. The complexes **50a**–**52a**, which are related to **75**, also exhibit no catalytic activity in the dimerization. These results indicate that the methyne group at the β-position is highly resistant to hydrogen elimination. The reaction pathway discussed here is essentially the same as that predicted for the metallacyclization starting from [Cp$_2$Ti(ethylene)$_2$].[60, 110]

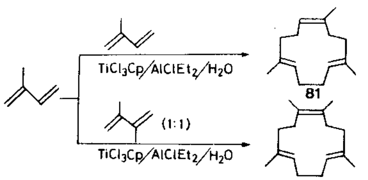




From experimental results, two types of intermediates (**76**, **79**) are conceivable for the titanium-catalyzed dimerization. In the species **76**, two isoprene molecules coordinate in the anti-parallel orientation to avoid the steric repulsion between the two methyl groups. The resulting coordinatively unsaturated 2,5-disubstituted titanacyclopentane should be rapidly transformed into either **77** or **78**. β-Hydrogen elimination from **78** dominates over the elimination from **77**, since the latter has a sterically less favorable conformation. Zr(OR)$_4$/AlR$_3$ catalysts also promote tail-to-head dimerization.[109d, e] The head-to-head coupling of isoprene most likely proceeds via the intermediate **80**. The coordinatively unsaturated Ti$^{\text{III}}$ species has an enhanced σ-acceptor capability and free space around the metal; hence, when the acceptor orbital is suitably positioned, an isoprene molecule can coordinate to a metal at the C1–C2 bond, rather than the C3–C4 bond. This reflects the higher electron density of the Ti$^{\text{III}}$ species.

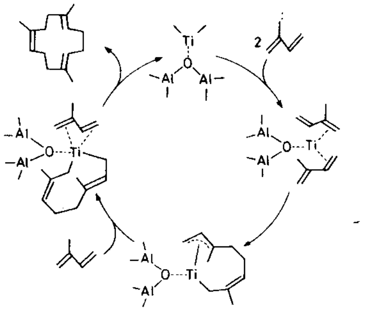
5.4. Highly Selective Cyclotrimerization of Conjugated 1,3-Dienes

Regio- and stereo-controlled catalytic cyclotrimerization of monoalkyl substituted dienes has not yet been accomplished despite concerted efforts by many workers, although several nickel, titanium, and chromium catalyst systems are already known to promote the cyclotrimerization of isoprene and pentadiene, albeit with insufficient regioselectivity.[26, 109f, g] Recently, a novel catalyst system, [TiCl$_3$Cp]/[AlClEt$_2$]/H$_2$O, was found to be capable of converting isoprene into a single isomer, (*Z*,*E*,*E*)-1,5,10-trimethyl-1,5,9-cyclododecatriene (**81**), with exceptionally high



selectivity (86%).[84] The contaminating product in this system is exclusively 2,4-dimethyl-4-vinylcyclohexene (14%), a compound easily separable by flash distillation. The addition of water is crucial to promote the cyclic trimerization; in the absence of water the reaction furnishes only 2,4-dimethyl-4-vinylcyclohexene in low yield. Both yield and selectivity can be optimized by addition of [$TiCl_3Cp$]/[$AlClEt_2$]/H_2O in the ratio 1:3:1. A catalyst prepared by addition of water to a 1:3 mixture of [$TiCl_3Cp$]/[$AlClEt_2$] at 20°C exhibits almost the same catalytic activity as that prepared from the product of the reaction of $AlClEt_2$-H_2O (3:1) and [$TiCl_3Cp$] at 20°C. The addition of products from $AlEt_3$-H_2O and $Al\textit{i}Bu_3$-H_2O (3:1) also leads to good catalytic activity but insufficient regioselectivity. Use of alcohols (BuOH etc.) or secondary amines (Bu_2NH etc.) instead of water led to inactivation of the catalysts.

The addition of one to two equivalents of electron donors (NEt_3, pyridine, PBu_3) to the [$TiCl_3Cp$]/[$AlClEt_2$]/H_2O system causes a drastic change in the distribution of the products, i.e., a mixture of tail-to-head and head-to-head linear isoprene dimers (cf. **68** and **69**, respectively) was obtained in place of **81**. The association of the EtClAl-O-AlClEt and Ti^{III} species is apparently disrupted by the coordination of donor ligands. This behavior would indicate that the diene ligands in the intermediate of the cyclic trimerization have the same coordination geometry as in the intermediate of the linear dimerization. If this assumption is correct, the principle of the catalytic cycle may be represented as in Scheme 7. The present catalytic system is also effective for cyclic homo- and cotrimerization of other dienes. Butadiene is converted with 87% selectivity (90% yield) into (*E,E,E*)-1,5,9-cyclododecatriene, while a 1:1 mixture of isoprene and 2,3-dimethylbutadiene is converted with 85% selectivity into (*E,E,Z*)-1,6,9,10-tetramethyl-1,5,9-cyclododecatriene (**82**) (30% conversion). The polymerization of ethylene and propylene catalyzed by [MCl_2Cp_2]/$AlMe_3$/H_2O (M = Ti, Zr) is also accelerated by addition of water.[111] These systems, however, require a large excess of $AlMe_3$/H_2O (1:0.9) component (see Section 6.2).



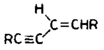
Scheme 7. Proposed mechanism for the selective cyclotrimerization of isoprene.

5.5. Regioselective Linear Dimerization of 1-Alkynes

Three different structures are conceivable for the linear dimers of 1-alkynes when steric interference is taken into consideration. A dimer of the type **83** has been prepared in good yield with [$RuH_2(CO)(PPh_3)_3$][112] and a dimer of the type **84** with [$RhCl(PPh_3)_3$][113] or [$Cr(O\textit{t}Bu)_4$]/$ZnEt_2$.[114] The [$TiCl_2Cp^*_2$]/[$AlEt_2Cl$] (1:3) system exhibits an excellent catalytic activity and effects the highly regioselective (>99%) dimerization of $RC{\equiv}CH$ to 1-buten-3-yne derivatives **85**, R = C_2H_5, C_3H_7, C_6H_{11}, C_6H_5, Me_3Si, Me_3SiCH_2, etc., in quantitative yield.[115] The use of a bulky ligand such as Cp* is essential for achieving this type of selective dimerization. When Cp* is replaced by the less bulky Cp ligand only a mixture of cyclic trimers, i.e. 1,3,5- and 1,2,4-trisubstituted benzene is obtained. By exploiting the excellent catalytic activity of [$TiCl_2Cp^*_2$]/[$AlClEt_2$], highly selective codimerization of two alkynes has been realized for the first time. A combination of acidic 1-alkynes and less acidic 1-alkynes provides the best result concerning both selectivity and yield. For example, highly stereo- and regioselective codimerization occurred in quantitative yield when a 1:1 mixture of $PhC{\equiv}CD$ (acidic alkyne) and $BuC{\equiv}CH$ (less acidic alkyne) or of $PhC{\equiv}CH$ and $BuC{\equiv}CD$ was used. The (*Z*)- and (*E*)-dimers, respectively, were formed in 98% yield. The reaction completely suppresses the homodimerization of each alkyne. A proposed mechanism for the formation of the (*Z*)-isomer is illustrated in Scheme 8. The active species should be the complex [$Cp^*_2TiC{\equiv}CPh$], generated by reaction of [$Cp^*_2Ti^{III}R$] or [$Cp^*Ti^{III}H$] with $PhC{\equiv}CD$, isolation of which is quite difficult.[116] The thermally more stable [$Cp_2M(C{\equiv}CPh)_2$] species, M = Ti^{IV}, Zr^{IV}, are almost catalytically inactive. Insertion of $BuC{\equiv}CH$ into the $TiC{\equiv}CPh$ bond followed by Ti-C bond cleavage by $PhC{\equiv}CD$ leads to regeneration of the [$Cp^*_2TiC{\equiv}CPh$] species.

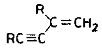
$RCH{=}C{=}C{=}CHR$

83



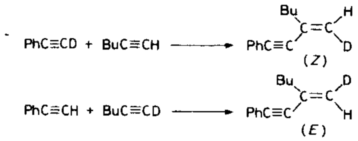
$RC{\equiv}C{-}C(H){=}CHR$

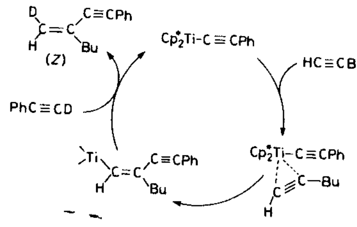
84



$RC{\equiv}C{-}C(R){=}CH_2$

85

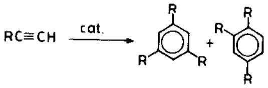




Scheme 8. Proposed mechanism for the selective linear codimerization of 1-alkynes.

5.6. Cyelic Trimerization of Alkynes

The selective cyclization of 1-alkynes is of special interest, since the products are of potential commercial utility. Various transition-metal complexes in both high and low oxidation states are known to catalyze the cyclotrimerization of 1-alkynes; however, an efficient regiocontrol has not yet been achieved.[117] $TaCl_5$ and $NbCl_5$ exhibit relatively high selectivity (ca. 90%) in the conversion of 1-butyne into 1,2,4-triethylbenzene, while the closely related compounds [$TaCl_4Cp$], [$NbCl_4Cp$], [$TiCl_3Cp$], and [$TiCl_4$] are practically inactive. A binuclear low valent niobium complex, [$NbClCp(butadiene)$]$_2$, and the [$NbCl_4Cp$]/[$AlClEt_2$] system show a similar selectivity in the cyclization of 1-butyne to 1,2,4-triethylbenzene.[117d] Several mechanisms have been proposed for the alkyne cyclization, but the issue is still controversial. The most commonly accepted mechanism involves a metallacyclopentadiene with low valent metal as intermediate which can undergo reductive elimination by the attack of a third alkyne molecule.[118a,b] However, the π-complex multicenter mechanism, in which alkyne molecules are assembled into a ring on one or more metals cannot, as yet, be ruled out.[118c]



6. Stereocontrolled Polymerization of Dienes, Alkenes, and Alkynes

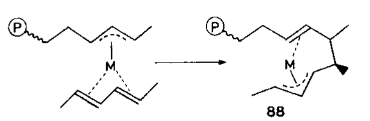
6.1. Stereoselective Polymerization of Conjugated Dienes

Several mechanisms have been proposed for the stereoselective polymerization of conjugated dienes. The η^4-s-*cis*-coordination (type **1**) of dienes to the metal was postulated to be the determining factor for formation of the *cis*-1,4-polymer[119] and the η^2-s-*trans* coordination (type **6**) for formation of the *trans*-1,4-polymer.[120] In the meantime it has been shown (see Section 2.1) that early transition metals (Zr, Hf, Mo) occasionally prefer the η^4-s-*trans*- (type **4**) rather than the η^2-s-*trans*- (type **6**) or η^4-s-*cis*-butadiene coordination (type **1**). In agreement with this trend, butadiene forms a *trans*-1,4-polymer with $TiCl_4$/$AlEt_3$,[121a] $TiCl_3$/$AlEt_3$,[121b] and VCl_3/$AlEt_3$ catalyst systems.[122] EHMO calculations on the s-*cis*- and s-*trans*-butadiene complexes of [$ZrCl_4$]$^{n-}$ (n = 0, 1, 2) with C_{2v} symmetry have revealed that the total energy for the s-*trans* complex is similar to or slightly smaller (1.0–2.0 kcal/mol) than that for the s-*cis* complex but significantly smaller than that for the η^2-s-*trans*-butadiene complex [1.8 for Zr^{IV} (n = 0), 9.9 for Zr^{III} (n = 1), and 18.4 kcal/mol for Zr^{II} (n = 2)].[7c] Therefore, the η^4-s-*trans*-diene coordination of type **4**, as in **86**, is regarded as an important factor in the *trans*-polymerization of butadiene (Ⓟ signifies polymer). The s-*trans*-diene ligand is smoothly transformed into a *syn*-η^3-allyl complex by insertion into the polymer end. Very high thermal instability and chemical reactivity preclude isolation of the active species. For the *cis*-1,4-polymerization, the reaction pathway via **87** has been proposed. [$ZrCp(\eta^3$-butenyl)(s-*cis*-butadiene)], a Zr^{IV} species, has a structure very similar to that of the intermediate **87**,[9f,123] but shows no catalytic activity in the polymerization. A more electron-deficient low-valent allyl(diene)metal species should, on the other hand, be catalytically active.

86

87

A terminally disubstituted butadiene, e.g. (*E,E*)-2,4-hexadiene, has been polymerized to a stereoregular polymer with an *erythro-trans*-1,4-diisotactic structure by catalysis with [$Ti(acac)_3$]/[$AlEt_2Cl$] or [$Co(acac)_2$]/[$AlEt_2Cl$].[124] 2,4-Hexadiene, however, favors the s-*trans* coordination to $ZrCp_2$ species.[17] Furthermore, it is reported that the (*E,E*)-isomer of $ZrCp_2$(2,4-hexadiene) is thermally more stable than the (*E,Z*)- or (*Z,Z*)-isomer.[125] The good correlation between the preferred geometry of the complex and the s-*trans* structure of the polymer suggests that the titanium-catalyzed 2,4-hexadiene polymerization may proceed via an intermediate of type **86**. The diene should be coordinated to the metal in an η^4-s-*trans*-(*E,E*)-fashion and



88

eventually transformed into the *syn*-allyl species **88** during the insertion into the polymer end. The *trans*-1,4-polymerization of 1,3-pentadiene catalyzed by $VCl_3/AlEt_3$[126] or $[VO(acac)_2]/[AlEt_2Cl]$[127] may be rationalized in essentially the same way as the alternating copolymerization of butadiene and propylene.[128]

6.2. Novel Catalytic Systems for Alkene- and Alkyne-Polymerization

Notable topics in this area involve the discovery of highly reactive systems for homogeneous catalysis (Kaminsky catalysts) having the composition $[MCp_2R_2]/AlMe_3$-H_2O (M = Ti, Zr; R = CH_3, Cl)[111] and a novel reaction mechanism proposed for the polymerization of alkenes[102b, 129a] or alkynes[130] via metallacyclic species. The Kaminsky catalyst is prepared from a large excess of aluminoxane and a metallocene compound (Al : M = 1000 : 1). Its activity in ethylene polymerization is 1000 times higher per Ti atom than that of a typical Ziegler catalyst system, $TiCl_4/AlEt_3$. Isotactic propylene polymerization in homogeneous solution has been realized for the first time with this system, but the exact reaction mechanism still a matter for debate.

In place of the well known Cossee's mechanism, an alternative mechanism via metallacycles has been proposed for the transition-metal-catalyzed alkene polymerization.[131] The reaction pathway via titanacyclobutane species well accounts for the kinetic studies on ring opening polymerization of norbornene and cyclopentene,[129a] but is untenable for the polymerization of linear alkenes.[129b,c] A similar metallacycle-mechanism via tungstenacyclo-1,3-butadiene has also been proposed for the alkyne polymerization with olefin metathesis catalysts.[102b, 130]

7. Conclusion

The chemistry of complexes of the early transition metals is now in a state of rapid development. A variety of highly regio- and stereoselective stoichiometric as well as catalytic reactions has already been realized using specifically designed complexes of the type mentioned in this article. Continued efforts in the preparation and characterization of coordinatively more unsaturated organometallics (e.g., with Ti^{III}, Zr^{III}, Ta^{IV}, Ta^{III}) surely promises further development in this field.

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