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Bis(cyclopentadienyl)zirconium(IV) or -hafnium(IV) Compounds with Si-, Ge-, Sn-, N-, P-, As-, Sb-, O-, S-, Se-, Te-, or Transition Metal-Centered Anionic Ligands

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Contents

I. Scope of the Review

This review covers the literature from roughly 1981 to 1992 with reference being made to earlier publications in this area where necessary. Neutral bis(cyclopentadienyl)zirconium(IV) and -hafnium(IV) complexes, which are referred to here as metallocene(IV) complexes, are treated exclusively. Thus, cationic metallocene(IV) complexes with heteroelement-centered anionic ligands are not considered. Titanocene(IV) complexes have also been omitted since their chemistry often differs considerably from that of zirconocene(IV) and hafnocene(IV) complexes. For extensive coverage of the literature before 1981 see ref 1.

II. Metallocene(IV) Complexes with Silyl, Germyl, or Stannyl Ligands

A. Synthesis

Up to 1980 only six complexes were known that contain a metallocene–group 14 element bond: [MCl(ER$_3$)Cp$_2$] (M = Zr, ER$_3$ = SiPh$_3$, GePh$_3$, SnMe$_3$, GeEt$_3$; M = Hf, ER$_3$ = SiPh$_3$, GePh$_3$), which were obtained by reaction of [MCl$_2$Cp$_2$] with LiER$_3$, NaER$_3$, or [Cd(GeEt$_3$)$_2$].[2–4] It was only in 1985 that studies of these complexes were resumed. Some results are summarized in a recent review article.[5] Similarly, the bulky E(SiMe$_3$)$_3$ ligand was introduced by the reaction of [MCl$_2$Cp(η-C$_5$R$_5$)] with [Li(THF)$_3$E(SiMe$_3$)$_3$] to give [MCl{E(SiMe$_3$)$_3$}Cp(η-C$_5$R$_5$)] (62–71% yield,

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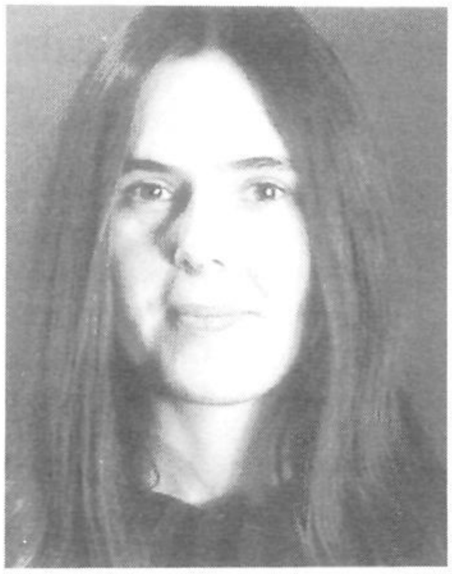


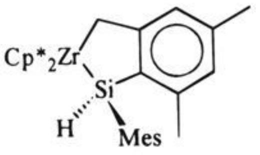
Evamarie Hey-Hawkins was born in Scherfede, Germany, in 1957. She received her Diplom and Dr. rer. nat. degrees in chemistry with Professor Dr. K. Dehnicke from the University of Marburg, Germany. She was a Visiting Scientist at the University of Sussex (1984–1985), the University of Western Australia (1985), and the Australian National University (1985–1986), during which time she carried out research toward her habilitation thesis on P-functionalized phosphido ligands. This work was funded by the Fonds der Chemischen Industrie (Liebig grant) and the Deutsche Forschungsgemeinschaft (habilitation grant). In 1988 she was awarded the title Privatdozentin at the University of Marburg, Germany. From 1988 to 1990 she carried out research in Professor Dr. H. G. von Schnering's group at the Max-Planck-Institute of solid-state research in Stuttgart, Germany. From 1990 to 1993 she was a Visiting Scientist at the University of Karlsruhe, funded by a Heisenberg grant from the Deutsche Forschungsgemeinschaft. In 1993 she accepted a chair in inorganic chemistry at the University of Leipzig. Her research interests include synthetic inorganic/organometallic chemistry of transition metal complexes with functionalized ligands of the elements of groups 13 and 15 as well as their spectroscopic and structural studies.

M = Zr, Hf, R = H, E = Si;[6] M = Zr, R = H, E = Ge;[7] M = Zr[8] or Hf,[9] R = Me, E = Si). Analogously, reaction of $[ZrCl(SiMe_3)Cp_2]$ or $[(ZrClCp_2)_2O]$ with $[Li(THF)_3Si(SiMe_3)_3]$ yielded $[Zr(SiMe_3)\{Si(SiMe_3)_3\}Cp_2]$ and $[Cp_2(Cl)Zr(\mu\text{-}O)Zr\{Si(SiMe_3)_3\}Cp_2]$, respectively.[6] Replacement of the second chloro ligand was not observed in the latter. Both chloro ligands of $[ZrCl_2Cp_2]$ are replaced on reaction with $[Li(SiPh_2)_5Li]$ in THF; the product $[\overline{Zr\{SiPh_2(SiPh_2)_3Si}Ph_2\}Cp_2]$ was obtained in 4% yield.[10]

The previously reported $[MCl(EPh_3)Cp_2]$ (M = Zr, Hf, E = Si, Ge, Sn) were described as being difficult to purify due to their instability in solution at room temperature.[2] However, the analogous complexes $[MCl(EPh_3)Cp^*(\eta\text{-}C_5R_5)]$ ($Cp^* = \eta\text{-}C_5Me_5$; M = Zr, Hf, E = Si, Ge, Sn, R = H; M = Zr, E = Si, Ge, Sn, R = Me; M = Hf, E = Si, R = Me) have been obtained as stable, hydrocarbon-soluble materials by reacting metallocene dichlorides with $LiEPh_3$ in THF or by σ-bond metathesis of $[ZrCl\{Si(SiMe_3)_3\}CpCp^*]$ or $[ZrCl(EPh_3)CpCp^*]$ (E = Si, Ge) with Ph_3SnH in 60–78% yield.[11] Reaction of $[ZrCl_2CpCp^*]$ with $LiSnPh_3$ yielded only the aryl complex $[ZrCl(Ph)CpCp^*]$.[11]

Silylation of $[MCl_2Cp_2]$ with $[Al(SiMe_3)_3(OEt_2)]$ gave $[MCl(SiMe_3)Cp_2]$ as red (M = Zr) or orange (M = Hf) solids in 72–80% yield;[12] $[ZrCl(X)CpCp^*]$ [X = Cl, $Si(SiMe_3)_3$] failed to react.[8] The reaction of $[ZrCl_2Cp_2]$ with $[Hg(SiMe_3)_2]$ in benzene was earlier reported to give white solids, formulated as $[Zr(SiMe_3)(X)Cp_2]$ (X = Cl, $SiMe_3$);[13] however, the product with X = Cl was later shown to be $[ZrCl(OSiMe_3)Cp_2]$,[12] which was obtained by reaction of $[ZrCl(SiMe_3)Cp_2]$ with dry oxygen.

Application of the above synthetic route to silyl complexes having Si–H bonds is limited by the scarcity of the corresponding lithium reagents. Thus, the only hydrogensilyl derivatives obtained by lithium halide elimination are $[ZrMe(SiHMes_2)Cp_2]$, which is unstable above 0 °C, and the thermally stable $[ZrMe(SiHMes_2)Cp^*_2]$.[14] An attempt to replace both chlorine atoms in $[ZrCl_2Cp^*_2]$ with $[Li(THF)_2SiHMes_2]$ yielded the metallacyclic dehydrohalogenation product **1** and Mes_2SiH_2.[14] **1** was also obtained from $[ZrCl(SiHMes_2)Cp^*_2]$ and $[Li(THF)_2SiHMes_2]$.[14] $[ZrMe(SiHMes_2)Cp^*_2]$ reacted rapidly with gaseous HCl in toluene at −78 °C to give methane and the chloro complex in 76% yield.[14]



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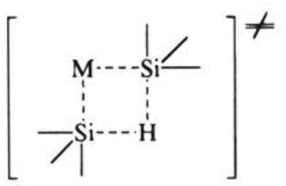
A more general route to hydrogensilyl complexes is the σ-bond metathesis of silyl or germyl complexes with primary or secondary silanes under fluorescent room light.[9,11,15] In contrast, the stannyl derivative $[HfCl(SnPh_3)CpCp^*]$ failed to react with $PhSiH_3$.[11] Unsymmetrically substituted secondary silanes yield both diastereomers.[9,15] Depending on the nature of the reactants, further dehydrocoupling reactions of the initial products may occur (eq 1).[15] In the dark,

$$
\begin{array}{l}
[ZrCl\{Si(SiMe_3)_3\}CpCp^*] + PhSiH_3 \\
\qquad\qquad\downarrow \\
[ZrCl(SiH_2Ph)CpCp^*] + HSi(SiMe_3)_3 \\
\qquad\qquad\downarrow \\
[ZrCl(H)CpCp^*] + (SiHPh)_n
\end{array}
\tag{1}
$$

the hydrogensilyl complex is formed initially, but with proceeding reaction decomposes to zirconocene hydride chloride and a mixture of polysilanes.[15] Under fluorescent room light, no decomposition is observed.

Small Lewis bases (e.g. py, PMe_2Ph), but not large ones (e.g. PCy_3), strongly inhibit the photochemical and thermal σ-bond metathesis reactions.[9] Clearly, this process requires an empty coordination site at the metal center. A four-center transition state (**2**) was proposed for the σ-bond metathesis mechanism.[9]



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$[MCl\{Si(SiMe_3)_3\}CpCp^*]$ (M = Zr or Hf) reacts with Ph_3SnH to give $(SiMe_3)_3SiH$ and the triphenylstannyl derivative.[11] Secondary silanes reacted slower than primary silanes, and tertiary silanes (Me_3SiH, Et_3SiH) either failed to react or reacted slowly with $[HfCl\{Si(SiMe_3)_3\}CpCp^*]$.[9] No reaction was observed between $[MCl(SiR_3)Cp^*(\eta\text{-}C_5R'_5)]$ (M = Zr, Hf, R = Me, $SiMe_3$, R′ = H, Me) and bulky silanes such as Me_3SiH, Et_3SiH, $Bu^t{}_2SiH_2$, or $CyMeSiH_2$.[15] Bulky cyclopentadienyl ligands also prevent the formation of isolable silyl derivatives. For example, $[MCl(SiPh_3)Cp^*_2]$ (M = Zr, Hf) reacted with phenylsilane to give the metallocene hydride chloride, triphenylsilane, and dehydrocoupling products.[11] Generally, hafnocene silyls undergo smooth σ-bond metathesis with primary or secondary silanes that introduce a smaller silyl ligand. An exception is the reaction of $[HfCl\{Si(SiMe_3)_3\}CpCp^*]$ with trichlorosilane, which yields only hafnocene dichloride together with unidentified silicon products.[15]

An attempt to introduce alkoxysilyl ligands by reaction of $[HfCl\{Si(SiMe_3)_3\}CpCp^*]$ with $MeSiH(OMe)_2$ gave the hydrogensilyl complex $[HfCl(SiH_2R)CpCp^*]$ (R = Me); with $SiH(OMe)_3$ the silyl complex (R = H) was formed in 60% yield, together with hafnocene dichloride and hafnocene methoxide chloride.[15]

The bimetallic silyl complex $[\{CpCp^*(Cl)Hf\}_2\{1,4\text{-}(SiH_2)_2C_6H_4\}]$ was obtained from the reaction of $[HfCl\{Si(SiMe_3)_3\}CpCp^*]$ with $1,4\text{-}(SiH_3)_2C_6H_4$ (2:1 reaction).[15] The 1:1 reaction allowed the observation by NMR of $[HfCl(SiH_2C_6H_4SiH_3)CpCp^*]$, the intermediate in the 1:2 reaction. The *trans* arrangement of the Hf—Cl bonds was deduced from NMR data.[15]

A number of Zr and Hf silyl complexes of the type $[MR(SiR'_3)(\eta\text{-}C_5R''_5)_2]$ (M = Zr, Hf, R = Cl, alkyl, silyl, R′ = Me, Ph, $SiMe_3$, R″ = H, Me) act as catalyst precursors for the dehydrogenative coupling reaction of silanes $RSiH_3$ to polysilanes $H(SiR'_2)_nH$ ($n = 10$–20).[16] Hydrogensilyl zirconocene complexes have been proposed as the reactive intermediates in the dehydrocoupling of secondary organosilanes catalyzed by metallocene alkyls. In some cases these complexes have been isolated from stoichiometric reactions. Thus, the reaction of $[ZrMe_2Cp_2]$ with phenyl-,[17] diphenyl-, phenylmethyl-, or butylmethylsilane yielded the hydrido-bridged dimeric complexes $[Cp_2RZr(\mu\text{-}H)_2ZrR'Cp_2]$ (**3**)[17,18] [(**3a**) R = $PhSiH_2$, R′ = MePhSiH;[17] (**3b**) R = MePhSiH, R′ = Me_2PhSi; (**3c**) R = Ph_2SiH, R′ = $MePh_2Si$; (**3d**) R = Me, R′ = Ph_2SiH; (**3e**) R = Me, R′ = $MePh_2Si$; (**3f**) R = R′ = BuMeSiH][18] in moderate to good yields (^1H NMR). Only compounds **3a**,**b**,**d** were isolated (21–58% yield).[18] A possible mechanism for the formation of **3** was discussed.[18] The σ-bond metathesis route was also employed in the synthesis of the five-coordinate $[ZrH(SiHPh_2)(PMe_3)Cp_2]$, which was obtained as two geometric isomers from the reaction of $[ZrH(SiPh_3)(PMe_3)Cp_2]$ with Ph_2SiH_2.[19]

$[ZrBu_2Cp_2]$ decomposes readily to give $[Zr(\eta^2\text{-}1\text{-}butene)Cp_2]$, which reacts with 2 equiv of Ph_2SiH_2 to give **3** (R = R′ = Ph_2SiH, 85% yield) and $BuPh_2SiH$.[20] The proposed intermediate in this reaction, $[ZrH(SiHPh_2)Cp_2]$, resulting from oxidative addition of Ph_2SiH_2 to zirconocene(II), was trapped as the phosphine adducts $[ZrH(SiHPh_2)(L)Cp_2]$ (L = PMe_3, $PMePh_2$) in 70–80% yield by carrying out the reaction at −78 °C in the presence of a slight excess of phosphine.[20] However, **3** (R = R′ = Ph_2SiH) did not react with PMe_3 to give a monomeric hydrogensilyl complex.[20] Oxidative addition of Ph_3SiH to the zirconocene(II) or hafnocene(II) complexes or of diphenylsilane to the zirconocene(II) complexes $[M(\eta^2\text{-}alkene)(PMe_3)Cp_2]$ (M = Zr, alkene = 1-butene; M = Hf, alkene = isobutylene), which were generated in situ in THF, also afforded $[MH(SiPh_3)(PMe_3)Cp_2]$ and $[ZrH(SiHPh_2)(PMe_3)Cp_2]$ in 40–60% yield. The hafnocene derivative is unstable in benzene solution. Of two plausible pathways for the addition of Ph_3SiH—loss of olefin, followed by oxidative addition, or addition of Si—H across the M—C bond followed by β-H elimination and loss of alkene—the latter was favored since the intermediate "$[Hf(CH_2CHMe_2)(SiPh_3)Cp_2]$" was observed by ^1H NMR.[19] $[ZrH(SiHPh_2)(PMe_3)Cp_2]$ was also shown by ^1H NMR to be formed in the σ-bond metathesis of $[ZrH(SiPh_3)(PMe_3)Cp_2]$ with Ph_2SiH_2.[19]

The black zirconocene, $[(ZrCp_2)_4]$, synthesized by reduction of zirconocene dihydride with red phosphorus, was reported to oxidatively add trimethylchlorosilane in refluxing toluene to give $[ZrCl(SiMe_3)Cp_2]$ as a pale yellow solid in 79% yield. The reaction with trimethyltin chloride afforded the pale-orange zirconocene(III) complex $[\{Zr(\mu\text{-}SnMe_3)Cp_2\}_2]$ as well as $[ZrCl_2Cp_2]$ and Me_6Sn_2. The products were characterized by elemental analysis, ^1H NMR and MS. The parent ion peaks showed the expected isotope pattern.[21] Decomposition of $[ZrBu_2(\eta\text{-}C_5H_4R)_2]$ (R = H, Me), generated in situ, in the presence of 2 equiv of $[Sn\{CH(SiMe_3)_2\}_2]$ yielded the red-purple zirconocene(II) complex $[Zr(Sn\{CH(SiMe_3)_2\})_2(\eta\text{-}C_5H_4R)_2]$, which was characterized by a crystal structure determination.[22]

The η^2-silanimine complex $[Zr(\eta^2\text{-}NBu^tSiMe_2)(PMe_3)Cp_2]$ has been prepared by the reaction of $[ZrI(NBu^tSiMe_2H)Cp_2]$ with $LiCH_2SiMe_3$ in the presence of PMe_3 (elimination of LiI, Me_4Si).[23]

B. Structural Data

Crystal structures of several four- and five-coordinate metallocene silyl complexes have been determined. No structural data for metallocene germyl complexes are available; in $[HfCl_2\{Ge(SiMe_3)_3\}Cp^*]$ the Hf—Ge bond length is 2.740(1) Å[7] and the only crystal structures reported for a metallocene compound with a metal—tin bond are those of $[Zr(Sn\{CH(SiMe_3)_2\})_2Cp_2]$ [Zr—Sn 2.8715(11) Å][22] and $[TiCl(SnPh_3)Cp_2]$ [Ti—Sn 2.843(1) Å].[24]

The sensitivity of the Hf—Si bond lengths toward steric factors is apparent from the structures of $[HfCl(SiH_2Ph)CpCp^*]$ and $[HfCl\{Si(SiMe_3)_3\}CpCp^*]$.[15] While the Hf—Si bond length of 2.729(3) Å in the former is comparable to that found in $[HfCl_2\{Si(SiMe_3)_3\}Cp^*]$ [2.748(4) Å],[7] the latter showed a considerably longer Hf—Si bond [2.881(4) and 2.888(4) Å; two independent molecules per unit cell] due to steric crowding. This is also expressed in compressed Si—Si—Si angles (average 101°).[15]

Attempts to solve the crystal structures of $[Cp_2(SiH_2Ph)Zr(\mu\text{-}H)_2Zr(SiHMePh)Cp_2]$[17,18] and $[Cp_2(SiHMePh)Zr(\mu\text{-}H)_2Zr(SiMe_2Ph)Cp_2]$[18] to complete crystallographic satisfaction failed due to a disorder problem resulting from an ordered superimposition of enantiomers. Due to the absence of a chiral silyl ligand in $[\{Zr(\mu\text{-}H)(SiHPh_2)Cp_2\}_2]$, no disorder problem arose and a satisfactory crystal structure determination was possible [Zr—Si 2.7590(8) Å].[20]

The five-coordinate zirconocene silyl complexes $[ZrH(SiPh_3)(PMe_3)Cp_2]$ [Zr—Si 2.721(2) Å, hydride

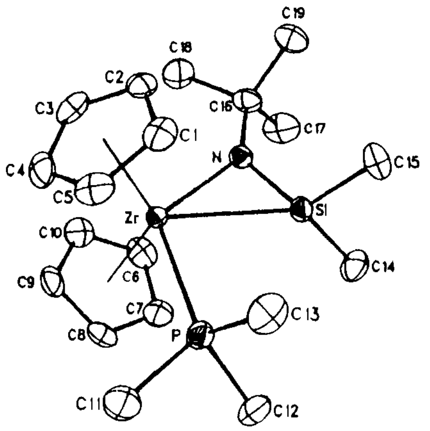
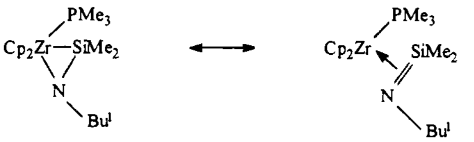


Figure 1. Molecular structure of $[Zr(\eta^2\text{-}NBu^tSiMe_2)(PMe_3)Cp_2]$. (Reprinted from ref 23. Copyright 1991 American Chemical Society.)

located by difference maps][19] and $[ZrH(SiHPh_2)(PMe_3)Cp_2]$ [Zr—Si 2.707(5) Å][20] exhibit shorter Zr—Si bonds than the previously characterized $[ZrCl(SiPh_3)Cp_2]$ [Zr—Si 2.813(2) Å].[25] The Zr—Si bond length of the latter is comparable to the value of 2.815(1) Å observed in $[Zr(\eta^2\text{-}S_2CNEt_2)(SiMe_3)Cp_2]$.[12]

The short Zr—Si bond [2.654(1) Å] and the long Si—N bond [1.687(3) Å] in $[Zr(\eta^2\text{-}NBu^tSiMe_2)(PMe_3)Cp_2]$ (Figure 1) suggest that the bonding between the metal and silanimine fragment is best described by a metallacyclic Zr(IV) resonance form (eq 2).[23]



(2)

C. Spectroscopic Properties

^1H, ^{13}C, and ^{29}Si NMR data are available for most complexes.

1. ^1H NMR

In the ^1H NMR $[MCl(EPh_3)Cp(\eta\text{-}C_5R_5)]$ (M = Zr, Hf, E = Si, Ge, Sn, R = H,[1,2] Me[11]) exhibit sharp resonances for the phenyl protons, while $[ZrCl(EPh_3)Cp^*_2]$ (E = Si, Ge) show broad signals due to restricted rotation about the E—C bond.[11] Sharp resonances were observed for the stannyl derivative (E = Sn).[11] This observation is consistent with the expected steric demand of the EPh_3 group ($SiPh_3 > GePh_3 > SnPh_3$). A $\Delta G^{\ddagger}$ (223 K) = 42.3 ± 0.9 kJ mol^{-1} was determined for the silyl derivative by variable-temperature ^1H NMR.

^1H NMR studies of $[Zr(SiHMes_2)(X)Cp^*_2]$ (X = Cl, Me) revealed significant steric interaction between the Mes and Cp* ligands, resulting in restricted rotation about both the Zr—Si and Si—C(Mes) bonds. From variable-temperature studies the barriers to rotation about the Si—C(Mes) (X = Me, $\Delta G^{\ddagger} = 43.5 \pm 0.9$ kJ mol^{-1}; X = Cl, $\Delta G^{\ddagger} = 53.6 \pm 0.9$ kJ mol^{-1}) and Zr—Si bonds (X = Me, $\Delta G^{\ddagger} = 49.4 \pm 0.9$ kJ mol^{-1}; X = Cl, $\Delta G^{\ddagger} = 56.1 \pm 2.0$ kJ mol^{-1}) were determined.[14] For $[ZrMe(SiHMes_2)Cp_2]$ unrestricted rotation was observed down to −85 °C.[14]

2. ^{29}Si NMR

^{29}Si NMR data have been reported for $[M\{Si(SiMe_3)_3\}(X)CpCp^*]$ (M = Zr, X = Me, −105.72;[8] M = Zr, X = Cl, −87.30;[8] M = Hf, X = Cl, −77.87 ppm[15]), $[ZrCl(SiH_2Ph)CpCp^*]$ (−14.33 ppm),[9,15] $[HfCl(SiH_2R)CpCp^*]$ (R = Ph,[9,15] p-Tol, $4\text{-}MeOC_6H_4$, $4\text{-}FC_6H_4$, Mes, Bz, Cy, $4\text{-}SiH_3C_6H_4$, 1.49−14.83 ppm;[15] R = Me, −7.36; R = H, −46.52 ppm[15]), $[HfBr\{SiH_2(p\text{-}Tol)\}CpCp^*]$ (7.74 ppm),[15] $[HfCl(SiH_2Cy)Cp_2]$ (11.07 ppm),[15] $[HfCl(SiHPh_2)Cp(\eta\text{-}C_5R_5)]$ (R = H, Me, ca. 32 ppm),[15] $[HfCl(SiHPhR)CpCp^*]$ [R = Me, 21.75, 25.10 (diastereomers); R = SiH_2Ph, −9.05, −9.86 ppm (diastereomers)],[15] $[MCl(SiPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (M = Zr, R = H, 42.42; M = Hf, R = H, 39.96 ppm; M = Zr, R = Me, 47.34; M = Hf, R = Me, 42.86 ppm).[11] Clearly, the substituents bound directly to silicon play a dominant role in determining the ^{29}Si chemical shift. For example, replacement of hydrogen atoms with phenyl ligands resulted in pronounced down-field shifts, while silyl substituents [i.e. $Si(SiMe_3)_3$ or $SiHPh(SiH_2Ph)$] lead to pronounced up-field shifts.[15] Significant steric interaction between the Cp* and the Mes ligands in $[ZrMe(SiHMes_2)Cp^*_2]$ led to an up-field shift (−21.94 ppm)[14] compared with other hydrogensilyl complexes, such as $[ZrMe(SiHMes_2)Cp_2]$ (−12.36 ppm) or the metallacyclic derivative 1 (−15.72 ppm). Zirconocene methyl derivatives exhibit a down-field shift compared with the corresponding chloro complexes. The five-coordinate complexes $[ZrH(SiPh_2R)(PMe_3)Cp_2]$ show ^{29}Si NMR resonances at 39.48 (R = Ph) and 50.46 ppm (R = H), respectively.[19] In general, the hydrogensilyl complexes show low ^1J(Si—H) coupling constants (140−160 Hz), which reflect the presence of an electropositive substituent on silicon.[15]

3. Infrared

IR spectra have been recorded for most compounds, but assignments for the ν(M—E) modes (M = Zr, Hf, E = Si, Ge, Sn) have not been made. The ν(Si—H) stretching frequencies of metallocene hydrogensilyl complexes are generally observed in the range 2020−2060 cm^{-1} and are shifted by ca. 100 cm^{-1} to lower wavenumbers relative to the corresponding hydrogensilanes [e.g. $[HfCl(SiH_2Ph)CpCp^*]$,[15] ν(Si—H) 2050 cm^{-1}; $PhSiH_3$, 2140 cm^{-1}).[9,14,15]

4. Electron-Impact Mass Spectroscopy

Electron-impact mass spectroscopic data have been reported only for $[ZrCl(SiMe_3)Cp_2]$ and the zirconocene(III) complex $[\{Zr(\mu\text{-}SnMe_3)Cp_2\}_2]$. The parent ion peaks showed the expected isotope pattern.[21]

5. Electronic Spectra

In general, zirconocene silyl complexes are dark-red to orange, and the hafnocene analogues yellow. The color is associated with the presence of a silyl ligand; related alkyl derivatives are colorless. In pentane, the zirconocene silyl complexes $[Zr\{Si(SiMe_3)_3\}(X)CpCp^*]$ exhibit low-intensity absorptions at 461 (X = Cl)[9,15] or 435 nm (X = Me).[15] The hafnocene analogues show transitions at higher energy: 405 (X = Cl)[9,15] or 398 nm (X = Me),[15] respectively. These absorptions were characterized as silyl-to-metal charge-transfer transitions and were shown to be associated with photochemical reactions of metallocene silyl complexes. For hafnocene hydrogensilyl complexes $[HfCl(SiH_2R)CpCp^*]$ (R = Ph, *p*-Tol, Cy) electronic absorptions in the range 380–390 nm were observed.[15]

D. Chemical Properties

The metallocene–group 14 element compounds are air and moisture sensitive. $[ZrCl(SiMe_3)Cp_2]$ reacted with water to give the known $[(ZrClCp_2)_2O]$; with oxygen the siloxide $[ZrCl(OSiMe_3)Cp_2]$ was formed.[12] The latter is possibly the product isolated from the reaction of $[ZrCl_2Cp_2]$ with $[Hg(SiMe_3)_2]$.[13]

As was observed earlier,[2] protic species (HCl or HBr) cleave the metal–group 14 element bond. Thus, $[ZrCl(EPh_3)Cp^*_2]$ (E = Si, Ge) reacted with HCl to give zirconocene dichloride and Ph_3EH; the stannyl analogue (E = Sn) afforded zirconocene dichloride, but no Ph_3SnH was observed due to cleavage of the Sn–C(Ph) bonds.[11] Treatment of $[ZrH(SiHPh_2)(PMe_3)Cp_2]$ with 3 N HCl gave Ph_2SiH_2,[20] while $[\{Zr(\mu\text{-H})(SiHPh_2)Cp_2\}_2]$ did not react under analogous conditions.[20] Silver triflate oxidatively cleaved the Zr–Si bond in $[ZrMe(SiHMes_2)Cp^*_2]$ with quantitative formation of pale-green $[ZrMe(OSO_2CF_3)Cp^*_2]$ and silanes.[14]

1. Thermolysis

The compounds are generally stable in the solid state, but slow decomposition in solution was observed for $[MCl(EPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (M = Zr, Hf, E = Si, Ge, Sn, R = H; M = Zr, Hf, E = Si, R = Me; M = Zr, E = Ge, Sn, R = Me) with elimination of Ph_3EH.[11] The decomposition is accelerated by light. The following trends in stability were found: $MCpCp^* > MCp^*_2$; Hf > Zr; Sn > Ge > Si.[11]

Thermolysis of $[MCl(SiMe_3)Cp_2]$ (M = Zr, Hf) in C_6D_6 (monitored by ^1H NMR) gave Me_3SiH and unidentified products after 2 (M = Zr) and 24 h (M = Hf).[12] Similarly, thermal or photochemical decomposition of $[ZrCl\{Si(SiMe_3)_3\}CpCp^*]$ gave $(SiMe_3)_3SiH$ after 2 h. The zirconium product was shown to be $[\{Zr(\mu\text{-Cl})Cp^*\}_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)]$.[15] The methyl derivatives $[MMe(SiPh_3)Cp^*_2]$ (M = Zr, Hf),[11] $[ZrMe\{Si(SiMe_3)_3\}CpCp^*]$,[8] and $[ZrMe(SiHMes_2)Cp_2]$[14] are thermally unstable in solution at room temperature, while $[ZrMe(SiHMes_2)Cp^*_2]$[14] decomposed on heating in C_6D_6 for 24 h with formation of Mes_2SiH_2. The hydrogensilyl complexes $[MCl(SiH_2Ph)CpCp^*]$ decomposed at room temperature (M = Zr) and 75 °C (M = Hf), with formation of metallocene hydride chloride and polysilanes, $(SiHPh)_n$.[9] The decomposition of the hafnocene complex was shown to be a second-order process.[9]

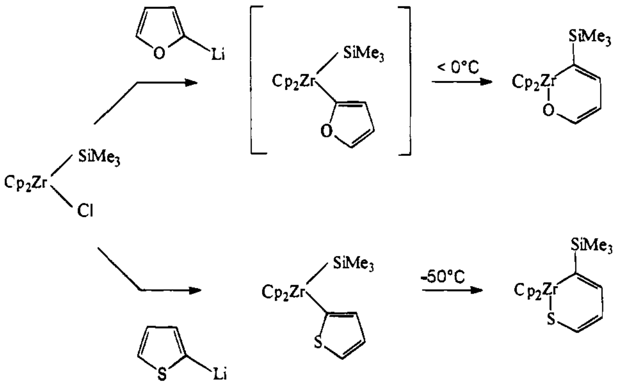
2. Hydrogenolysis

Hydrogenolysis of $[Zr(SiMe_3)(X)Cp_2]$ [X = Cl, $Si(SiMe_3)_3$][6] and $[MCl(SiPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (M = Zr, Hf, R = H, Me)[11] rapidly yielded zirconocene hydride chloride and the corresponding silanes. Reaction of $[ZrMe(SiHMes_2)Cp^*_2]$ with hydrogen showed that the Zr–Si bond is cleaved faster than the Zr–Me bond. After 10 min (NMR experiment) zirconocene methyl hydride and Mes_2SiH_2 had formed quantitatively.[14] The reaction of $[MMe(SiPh_3)Cp^*_2]$ with hydrogen gave zirconocene dihydride (M = Zr), while the less labile hafnocene silyl derivative (M = Hf) gave $[HfH(Me)Cp^*_2]$.[11] The germyl complexes $[ZrCl(GePh_3)Cp^*(\eta\text{-}C_5R_5)]$ (R = H, Me) react more slowly with hydrogen than the corresponding silyl complexes, yielding metallocene hydride chloride and triphenylgermane. The stannyl complexes $[MCl(SnPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (M = Hf, R = H; M = Zr, R = Me) failed to react.[11] Hydrogenolysis of $[Zr(\eta^2\text{-}NBu^tSiMe_2)(PMe_3)Cp_2]$ yields $[ZrH\{NBu^t(SiHMe_2)\}Cp_2]$.[23] General reactivity trends were established for hydrogenolysis: $MCp^*_2 > MCpCp^*$; $M\{Si(SiMe_3)_3\} > M(SiPh_3)$; $MMe(SiR_3) > MCl(SiR_3)$; M–Si > M–Ge ≫ M–Sn; Zr > Hf.

3. Salt Elimination

The halide in metallocene silyl complexes $[MCl(SiR_3)Cp_2]$ can be displaced by a salt elimination route via reaction with M′R′ (M′ = Li or Na; M = Zr, Hf, R = Me, R′ = S_2CNEt_2, BH_4, OBu^t; M = Zr, R = $SiMe_3$, R′ = BH_4).[6,12,26] The η^2-coordination of the dithiocarbamato ligand and the presence of a $M(\mu\text{-}H)_2BH_2$ unit were shown by IR spectroscopy[6,12] and crystal structure determination (R′ = S_2CNEt_2, M = Zr, R = Me).[12]

$[ZrCl(SiMe_3)Cp_2]$ reacted with 2-furyl- or 2-thienyllithium at −78 °C in Et_2O, as shown in eq 3. The substitution products underwent dyotropic rearrangement to give an oxa- or thiazirconacyclohexadiene complex.[26]



(3)

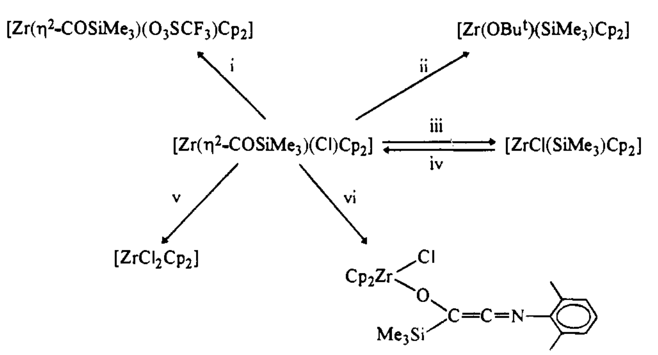
Reaction of $[MCl(SiR_3)(\eta\text{-}C_5R'_5)(\eta\text{-}C_5R''_5)]$ with MeMgBr in diethyl ether at −78 °C allowed the synthesis of the corresponding methyl silyl complexes in 62–82% yield (M = Zr, R = $SiMe_3$, R′ = R″ = H;[6] M = Zr, Hf, R = Ph, R′ = R″ = Me;[11] M = Zr, R = $SiMe_3$, R′ = H, R″ = Me[8]).

4. Insertion Reactions

Pioneering studies by Tilley[6,8,9,12,27] and by Harrod[16,17,28–30] have demonstrated that metallocene silyl complexes are reactive toward insertion of unsaturated substrates such as CO, isonitriles, etc.[6,8,12] and participate in silane polymerization[17,27–30] and σ-bond metathesis reactions.[9,16]

a. Carbon Monoxide. The reactivity of the metal–silicon bond can be influenced by changing the substituents on the metal or silicon atom. While $[ZrCl(SiMe_3)Cp_2]$ is readily carbonylated,[6,31] the $Si(SiMe_3)_3$ analogue is not.[6] The pink reaction product, $[Zr(\eta^2\text{-}COSiMe_3)(Cl)Cp_2]$, obtained in 90% yield, is a versatile starting material for further reactions (Scheme 1). The Ti analogue $[TiCl(SiMe_3)Cp_2]$ re-

Scheme 1[a]



[a] (i) $Me_3SiO_3SCF_3$, refs 6, 31; (ii) $LiOBu^t$, refs 6, 31; (iii) Δ, ref 31; (iv) 50–100 psi CO, refs 6, 31; (v) HCl, ref 6; (vi) CNR (R = 2,6-$Me_2C_6H_3$), ref 6.

acted with CO by an apparent ligand-induced reductive elimination to furnish $[Ti(CO)_2Cp_2]$ and Me_3SiCl.[6]

In the reaction of $[Zr(SiMe_3)\{Si(SiMe_3)_3\}Cp_2]$ or $[ZrMe\{Si(SiMe_3)_3\}Cp_2]$ with CO, insertion into the Zr—$SiMe_3$ or Zr—Me bond occurred exclusively,[6] with formation of the corresponding η^2-silaacyl or η^2-acyl complex. With benzoic acid, $[Zr(\eta^2\text{-}COSiMe_3)\{Si(SiMe_3)_3\}Cp_2]$ underwent substitution of the η^2-silaacyl ligand by an η^2-carboxylato ligand.[6] The presence of the bulkier Cp* ligand in $[ZrCl\{Si(SiMe_3)_3\}CpCp^*]$ results in higher reactivity of the metal—silicon bond due to increased steric interaction around the metal center. Thus, reaction with CO at 100 psi readily gave the pink silaacyl complex $[Zr\{\eta^2\text{-}COSi(SiMe_3)_3\}(Cl)CpCp^*]$ in 71% yield.[8,32] The same trend in reactivity is observed in the reaction of $[ZrCl(SiPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (R = H, Me) with CO. While the complex with R = H failed to give a pure product, the more crowded compound (R = Me) cleanly inserts CO to give dark purple $[Zr(\eta^2\text{-}COSiPh_3)(Cl)Cp^*_2]$.[11] On reaction with gaseous HCl these silaacyl complexes formed zirconocene dichloride and the first stable formylsilanes, $(Me_3Si)SiCHO$[32] and Ph_3SiCHO.[11] Like the chloro derivative, $[ZrMe\{Si(SiMe_3)_3\}CpCp^*]$ reacted with CO to give the pink intermediate $[Zr\{\eta^2\text{-}COSi(SiMe_3)_3\}(Me)CpCp^*]$, which rearranged in pentane solution during 1 h to the beige enolate hydride complex $[Zr\{OC(=CH_2)Si(SiMe_3)_3\}(H)CpCp^*]$.[8]

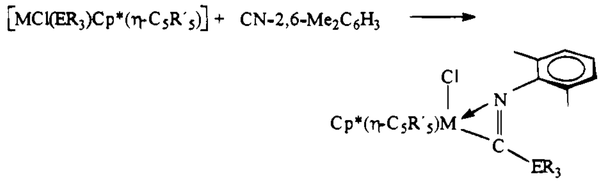
The influence of steric effects was also evident in the reaction of $[ZrMe(SiHMes_2)(\eta\text{-}C_5R_5)_2]$ (R = H, Me) with CO. While the Cp* complex yielded an η^2-silaacyl derivative (insertion into Zr—Si), the Cp complex formed an η^2-acyl derivative (insertion into Zr—Me).[14] The former isomerized slowly in benzene solution to give the enolate hydride complex $[Zr\{OC(=CH_2)SiHMes_2\}(H)Cp^*_2]$.[14] Due to the lower reactivity of Zr—Ge and Zr—Sn bonds compared to Zr—Si bonds, $[ZrCl(EPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (E = Ge, R = H; E = Ge, Sn, R = Me) failed to react with CO.[11]

b. Olefin Insertion. The enhanced reactivity of zirconocene silyl complexes with sterically demanding ligands is also demonstrated by the photochemically induced reaction of $[ZrCl(SiR_3)Cp_2]$ (R = Me, $SiMe_3$) or $[ZrCl\{Si(SiMe_3)_3\}CpCp^*]$ with ethylene. Whereas the former did not react,[6,31] the latter gave the yellow insertion product $[Zr\{CH_2CH_2Si(SiMe_3)_3\}(Cl)CpCp^*]$ in 50% yield.[33] The quantum yield for this reaction (λ = 380–470 nm) in the presence of excess ethylene is 2.5, suggesting a radical chain mechanism initiated by homoleptic Zr—Si cleavage.[33] No reaction with ethylene was observed for $[ZrCl(EPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (E = Si, Ge, R = H; E = Si, Ge, Sn, R = Me)[11] or $[ZrMe\{Si(SiMe_3)_3\}CpCp^*]$;[34] the latter also failed to react with styrene.[34] Reaction of $[ZrH(SiHPh_2)(L)Cp_2]$ (L = PMe_3, $PMePh_2$) with 1-octene gave the hydrosilylation product Oct^nPh_2SiH.[20] $[\{Zr(\mu\text{-}H)(SiHPh_2)Cp_2\}_2]$ did not react with 1-octene under analogous conditions.[20]

$[Zr(\eta^2\text{-}NBu^tSiMe_2)(PMe_3)Cp_2]$ reacts with ethylene or formaldehyde with insertion into the Zr—Si bond to yield the five-membered metallacycles $[Zr(CH_2CH_2SiMe_2NBu^t)Cp_2]$ or $[Zr(OCH_2SiMe_2NBu^t)Cp_2]$.[23]

c. Alkynes. To date insertion of alkynes into M—E bonds has not been observed. Attempted reactions include: $[ZrCl(SiR_3)Cp_2]$ (R = Me, $SiMe_3$) with phenylacetylene,[6] $[ZrCl(EPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (E = Si, Ge, R = H; E = Si, Ge, Sn, R = Me)[11] and $[ZrCl\{Si(SiMe_3)_3\}CpCp^*]$[8] with phenylacetylene or acetylene, and $[ZrMe\{Si(SiMe_3)_3\}CpCp^*]$ with acetylene.[34] $[ZrH(SiPh_3)(PMe_3)Cp_2]$ reacts with dimethylacetylene to give the metallacycle $[Zr(CMe{=}CMe{-}CMe{=}CMe)Cp_2]$ in 83% yield.[19]

d. Isonitriles. The metallocene silyl and germyl complexes shown in eq 4 cleanly inserted isonitriles to give η^2-iminosilaacyl or η^2-iminogermaacyl complexes (M = Hf, E = Si, R = Ph, R′ = H;[11] M = Zr, Hf, E = Si, R = Ph, R′ = Me, formation of products observed in solution by ¹H NMR;[11] M = Zr, E = Ge, R = Ph, R′ = H;[11] M = Zr, E = Si, R = Me or $SiMe_3$, R′ = H;[6] M = Zr, E = Si, R = $SiMe_3$, R′ = H[8]). The stannyl complexes $[MCl(SnPh_3)Cp^*(\eta\text{-}C_5R'_5)]$ (M = Hf, R′ = H; M = Zr, R′ = Me) did not react.[11] $[Zr\{\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3\}(Cl)CpCp^*]$ was structurally characterized.[8]



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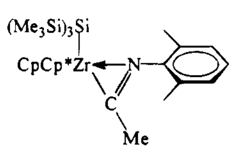
The methyl complex $[ZrMe\{Si(SiMe_3)_3\}CpCp^*]$ undergoes exclusively insertion of the isonitrile into the Zr—Me bond, forming **4**.[8] $[ZrH(SiPh_3)(PMe_3)Cp_2]$ underwent insertion of Bu^tNC into the Zr—H bond to give $[Zr\{\eta^2\text{-}C(H)NBu^t\}(SiPh_3)Cp_2]$.[19]



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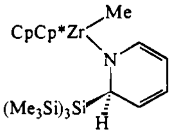
e. Nitriles, Pyridines. Insertion of nitriles (RCN, R = Me, CH=CH_2, Ph) into the Zr—Si bond of $[ZrMe\{Si(SiMe_3)_3\}CpCp^*]$ gave the orange to yellow azomethine derivatives $[ZrMe\{N{=}C(R)Si(SiMe_3)_3\}CpCp^*]$ in 60–78% yield.[34] Reaction with pyridine gave deep-red **5** in 75% yield, which results from 1,2-addition of the Zr—Si bond to pyridine.[34] Only one diastereomer of **5** was formed. The silyl complex was much less reactive toward substituted pyridines. No reaction was observed with 2- and 3-picoline, bipyridine, 1,10-phenanthroline, and pyrazine.[34] Slow insertion of 4-picoline and 4-(dimethylamino)pyridine was observed by ^{1}H NMR.[34] The related complexes $[Zr\{Si(SiMe_3)_3\}(X)Cp(\eta\text{-}C_5R_5)]$ (X = Me, R = H; X = Cl, R = Me) were much less reactive toward nitriles or pyridine.[34]



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No reaction was observed between $[ZrCl(SiR_3)Cp_2]$ (R = Me, $SiMe_3$) and benzonitrile (R = Me) or 4-methoxybenzonitrile (R = $SiMe_3$).[6] $[ZrCl\{Si(SiMe_3)_3\}CpCp^*]$ did not react with benzonitrile, but a reaction was observed with 4-methoxybenzonitrile or acetonitrile, a mixture of unidentified products being obtained.[8] $[ZrH(SiPh_3)(PMe_3)Cp_2]$ undergoes insertion of Bu^tCN into the Zr—H bond yielding $[Zr(\eta^1\text{-}N{=}CHBu^t)(SiPh_3)Cp_2]$ in 95% yield.[19]

f. Isocyanates. $[ZrCl\{Si(SiMe_3)_3\}Cp_2]$[6] and $[ZrCl(EPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (E = Si, Ge, R = H; E = Si, Ge, Sn, R = Me)[11] did not react with phenyl isocyanate.

$[Zr\{Si(SiMe_3)_3\}(X)CpCp^*]$ (X = Me) did not react with *p*-tolyl isocyanate,[34] but the chloro complex (X = Cl) reacted with phenyl isocyanate or isocyanide to give a mixture of unidentified products.[8]

g. Others. $[ZrH(SiPh_3)(PMe_3)Cp_2]$ underwent insertion of acetone into the Zr—H bond to give $[Zr(OCHMe_2)(SiPh_3)Cp_2]$.[19] No reaction of $[\{Zr(\mu\text{-}H)(SiHPh_2)Cp_2\}_2]$ with acetone was observed.[20]

No reaction occurred between $[ZrCl(SiMe_3)Cp_2]$[6,31] or $[ZrMe\{Si(SiMe_3)_3\}CpCp^*]$[34] and CO_2 or CS_2, nor between $[ZrCl(EPh_3)Cp^*(\eta\text{-}C_5R_5)]$ (E = Si, Ge, R = H; E = Si, Ge, Sn, R = Me) and CS_2.[11] $[ZrCl\{Si(SiMe_3)_3\}CpCp^*]$ reacted with CO_2 to give a mixture of unidentified products.[8]

No reaction of $[Zr\{Si(SiMe_3)_3\}(X)CpCp^*]$ with PMe_3 (X = Cl)[8] or trimethylsilyl azide (X = Me)[34] was observed.

As mentioned earlier σ-bond metathesis is a useful synthetic route to hydrogensilyl complexes. Activation of the Si—H bond in hydrogensilyl complexes ($M{-}SiHR_2$) to produce terminal silylene ($M{=}SiR_2$) or bridging silylene ($M{-}SiR_2{-}M$) complexes has not been observed up to now. However, as mentioned above, reaction of $[ZrI(NBu^tSiMe_2H)Cp_2]$ with $LiCH_2SiMe_3$ in the presence of PMe_3 leads to deprotonation of the silyl group, elimination of LiI, and formation of the η^2-silanimine complex $[Zr(\eta^2\text{-}NBu^tSiMe_2)(PMe_3)Cp_2]$.[23] The phosphine ligand is displaced by CO to give the corresponding carbonyl complex $[Zr(\eta^2\text{-}NBu^tSiMe_2)(CO)Cp_2]$.[23]

III. Metallocene(IV) Complexes with N-Centered Anionic Ligands

A. Metallocene(IV) Amides

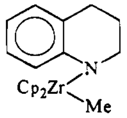
1. Synthesis and Spectroscopic Properties

A general synthetic approach to metallocene bisamido complexes which was also employed earlier[35,36] is the reaction of metallocene dichlorides with alkali metal amides M′NRR′ (M′ = Li or Na) to give $[M(NRR')_2Cp_2]$ (M = Zr, NRR′ = pyrrolyl;[37] M = Zr, NRR′ = 2,5-dimethylpyrrolyl;[38] M = Zr, R = R′ = $SiMe_3$;[39] M = Zr, Hf, R = H, R′ = Mes;[40] M = Zr, R = H, R′ = 2,6-$Me_2C_6H_3$, 4-$Bu^tC_6H_4$, *o*-Tol;[41] M = Zr, R = H, R′ = Ph[42]). $[Zr\{N(SiMe_3)_2\}_2Cp_2]$ exhibits one ^{1}H NMR signal for the equivalent Cp ligands, and two for the inequivalent $SiMe_3$ groups. A variable-temperature study gave a rotation barrier of $\Delta G^\ddagger$ (357 K) = 75.3 kJ mol^{-1}.[39]

Reaction of zirconocene hydride chloride with $LiN(SiMe_3)_2$ gives the metallacycle $[\overline{M\{CH_2SiMe_2N}(SiMe_3)\}Cp_2]$ (**6**) (M = Zr), formed via a facile γ-hydrogen elimination. Interestingly, $[TiCl_2Cp_2]$ reacts with the lithium amide with formation of (**6**) (M = Ti) exclusively, independent of the stoichiometry employed.[39]

The metallocene dichlorides of Ti, Zr, and Hf react with equivalent amounts of the dilithium salts of 2-aminobenzenethiol or *o*-phenylenediamine to give the colored complexes $[M(1\text{-}NH\text{-}2\text{-}X\text{-}C_6H_4)Cp_2]$ (X = S, NH) in 33–79% yield.[43] Variable-temperature ^{1}H NMR studies suggest a folding of the five-membered MNC_2S metallacycles along the S···N axis (cf. section VI.A.2).[43] While the hafnocene derivative (X = S) shows two signals for the Cp ligands below −17 °C ($\Delta G^\ddagger$ = 58 kJ mol^{-1}), no fluxionality is observed for the Ti and Zr complexes. All three *o*-phenylenediamido complexes gave one signal for the Cp protons, suggesting rapid ring inversion.[43] In the mass spectra the parent ion peak is observed for all complexes. The fragment $M^+ - Cp$ had the highest signal intensity.[43]

Alkyl amides $[Zr(NHR')(R)Cp_2]$ (R = Me, R′ = 2,6-$Me_2C_6H_3$, 4-$Bu^tC_6H_4$, Bu^t;[41,44] R = $CH_2CH_2Bu^t$, R′ = *o*-Tol, $SiMe_2Bu^t$[41]) are accessible by the salt elimination route from $[ZrCl(R)Cp_2]$ and LiNHR′. The methyl zirconocene amides (R = Me) react with a further equivalent of amine to give bisamido zirconocene complexes $[Zr(NHR')_2Cp_2]$ (R′ = 2,6-$Me_2C_6H_3$, 4-$Bu^tC_6H_4$, Bu^t).[41] Alternatively, $[ZrMe_2Cp_2]$ reacted with 4-*tert*-butylaniline in benzene at 85 °C with loss of 1 equiv of methane and generation of the corresponding amido complex.[44] Methane elimination was also exploited in the synthesis of bisamido zirconocene complexes $[Zr(NHR)_2Cp_2]$ (R = 2,6-$Me_2C_6H_3$, 4-$Bu^tC_6H_4$, Bu^t, $SiMe_2Bu^t$) from dimethyl zirconocene and excess amine.[41] Compound **7** was prepared via salt elimination (R = Me) and used as a starting material for the synthesis of alkylated tetrahydroquinolines.[45]



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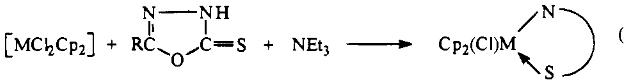
Mixed zirconocene alkoxide amides [Zr(NMe$_2$)(OR′)Cp$_2$] are obtained by reaction of [Zr(NMe$_2$)$_2$Cp$_2$] with R′OH (R′ = 2,6-Bu^t$_2$C$_6$H$_3$, 2,6-Bu^t$_2$-4-MeC$_6$H$_2$, 2,4,6-Bu^t$_3$C$_6$H$_2$) in benzene.[46] However, the zirconocene alkoxide chloride [ZrCl(OR′)Cp$_2$] did not react with LiNMe$_2$ (R′ = 2,6-Bu^t$_2$-4-MeC$_6$H$_2$).[46]

Zr—N or Hf—N σ-bonds are accessible by the reaction of [MCl$_2$Cp$_2$] (M = Zr, Hf) with amines in the presence of base. Thus, the heterocyclic thiones, i.e. oxadiazole thione and thiohydantoin derivatives, shown in eqs 5 (M = Zr, Hf, R = Ph, 3- or 4-NO$_2$C$_6$H$_4$, 2-ClC$_6$H$_4$) and 6 (M = Zr, Hf, R = Ph, *p*-Tol, Bz, 2- or 4-MeOC$_6$H$_4$, nap) were prepared in 52–60 (M = Zr)[47] and 40–70% yield (M = Hf).[48] If an excess of reagent is used, trisubstituted monocyclopentadienyl complexes of Zr or Hf are obtained (cf. dithiocarbamato complexes, section VI.E.1).[47,48] Mono- and disubstituted zirconocene complexes of 3-substituted 2-mercaptoquinazol-4-ones were also prepared.[49]



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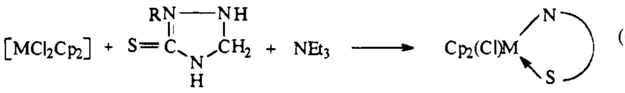
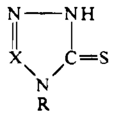


(6)

With [HfCl$_2$Cp$_2$], derivatives of 3-substituted 4-amino-*S*-triazole-5-thione (**8**) (R = NH$_2$, X = CMe, CEt, CPr;[48] R = NH$_2$, X = CCF$_3$[50]), 1-substituted tetrazoline-5-thione (**8**) (R = Ph, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$, *p*-Tol, X = N),[48] and the triazoline thione derivatives (**8**) (R = benzylidene, furylidene, salicylidene, X = CCF$_3$)[50] were prepared. Derivatives of the latter were also prepared from zirconocene and titanocene dichloride.[51] The ligands act as N,S-bidentate chelating agents. The complexes are gray, yellow, or brown, moisture sensitive, and decompose on heating. They are diamagnetic nonelectrolytes (in nitrobenzene). The electronic spectra show a single band in the range 431–444 nm (M = Zr)[47] and 403–431 nm (M = Hf),[48] which was assigned to a charge-transfer band. In the IR spectrum new bands at ca. 460–480 cm^{-1} and 440–480 cm^{-1} were assigned to the ν(Zr—N) and ν(Hf—N) mode, respectively. The ^{1}H NMR resonance of the Cp protons was observed at 6.5–6.8 ppm.[47,48]



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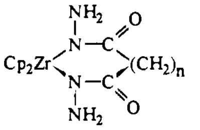
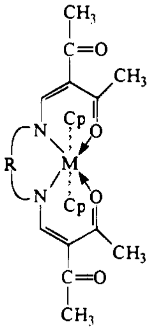
The synthetic approach of eqs 5 and 6 was used for the synthesis of **9** (*n* = 0, 2, 4) from [ZrCl$_2$Cp$_2$], base (NEt$_3$), and aliphatic acid dihydrazides.[52] Again, excess of reagent in the presence of BuNH$_2$ gave monocyclopentadienyl complexes. The products are yellow to brown, monomeric nonelectrolytes, and were characterized spectroscopically.[52] The reaction of **9** with β-diketones has been studied.[52] Derivatives of 6-aminopenicillinic acid were obtained in the same way and characterized spectroscopically.[53]



9

The reaction of [MCl$_2$Cp$_2$] (M = Zr, Ti) with Jäger-type ligands in refluxing THF for 10–38 h yields the corresponding amido complexes **10** (M = Ti, Zr, R = —CH$_2$CH$_2$—, *o*-phenylene, 4-Me-*o*-phenylene) as yellow to brown precipitates in 25 to 80% yield.[54] The products **10** are diamagnetic nonelectrolytes and show a single charge-transfer band in the range 408–426 nm. In the IR the ν(M—N) band appears at 410–430 cm^{-1} and ν(M—O) at 475–490 cm^{-1}.[54] Reaction of **10** (R = *o*-phenylene) with *o*-phenylenediamine gives the macrocyclic complex **11**.[54]



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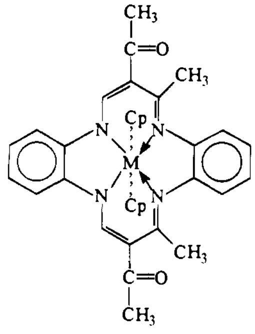


11

Reaction of hafnocene or zirconocene dihydride with excess NH$_3$[55] or of hafnocene dihydride with excess MeNH$_2$[56] gave the colorless complexes [MH(NH$_2$)Cp*$_2$] (M = Zr, Hf) (84–97% yield)[55] and [HfH(NHMe)Cp*$_2$] (52% yield).[56] The Zr complex is also obtained from the oxidative addition of ammonia to [{Zr(N$_2$)Cp*$_2$}$_2$(N$_2$)] (40–50% yield).[55] In the ^{1}H NMR spectrum the C$_5$(C*H*$_3$)$_5$ protons appear as a singlet (δ = 2.03 ppm), the N*H*Me proton as a broad resonance at 4.25 ppm, and the hydride at 9.1 ppm. The latter is comparable to the value observed for [HfH(NH$_2$)Cp*$_2$] (δ Hf—*H* 9.3 ppm).[55] It was concluded on the basis of the up-field chemical shifts of the hydride resonance in [HfH(NHR)Cp*$_2$] (R = Me,[56] H[55]) with respect to comparable azo derivatives that the amido ligands NHR are small enough to adopt a structure that allows effective d$_\pi$–p$_\pi$ interaction, leading to a Hf—N bond order > 1.[56] A crystal structure of the amido complex R = Me confirmed this assumption (see section III.A.2). However, in this case inequivalent Cp* ligands should be observed in the ^{1}H NMR. The equivalence of the Cp* ligands at room temperature can be explained by a simple oscillation about the Hf—N bond (eq 7).[56] Variable-temperature ^{1}H NMR experiments gave an upper limit of the activation barrier for this oscillation of $\Delta G^\ddagger \cong 41.9$ kJ mol^{-1}.[56]

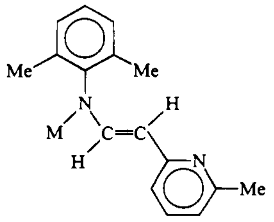
(7)

For $[HfH(NMe_2)Cp^*_2]$ the down-field shift of the hydride resonance (δ = 11.2 ppm) suggests little Hf—N π-back-bonding. Clearly, steric interaction between the NMe_2 ligand and the Cp* ligands prevents the former from adopting the necessary orientation for π-back-bonding.[55,56] Thus, in the complexes $[HfH(NRR')Cp^*_2]$ Hf ← N π-back-bonding increases in the order $NMe_2 < NHMe \approx NH_2$, while δ Hf—H decreases in the same order ($11.2 > 9.1 \approx 9.2$ ppm).[56]

Hafnocene hydride amides $[HfH(NHR)Cp^*_2]$ (R = Ph, p-Tol) are also accessible by the reaction of hafnocene dihydride with primary amines (elimination of H_2) or thermolysis of the corresponding triazenido complexes $[HfH(NHNNR)Cp^*_2]$ at 80 °C (elimination of N_2).[57] The latter were prepared from hafnocene dihydride and aryl azides (cf. section VIII.A).[57] Alternatively, the bisamido complexes $[Hf(NHR)_2Cp^*_2]$ (R = Ph, p-Tol) were obtained by reacting hafnocene dihydride, the corresponding monoamido complex, or the hafnocene triazenido complex with excess aryl azide, RN_3 (R = Ph, p-Tol).[57] The same product is obtained from the hafnocene monoamido complex and primary amine at 80 °C.[57]

Zirconocene dihydride complexes react with isonitriles to give formimidoyl complexes. Subsequent reaction with hydrogen or thermolysis yields methylamido zirconocene complexes (Scheme 2).[58] Alternatively, zirconocene hydride chloride or dimethylzirconocene react with benzylisonitrile to give imidoyl complexes $[Zr(CR{=}NBz)(X)Cp_2]$ (X = Cl, R = H; X = R = Me). Subsequent reaction with a zirconocene hydride derivative yields zirconocene monoamido complexes.[59]

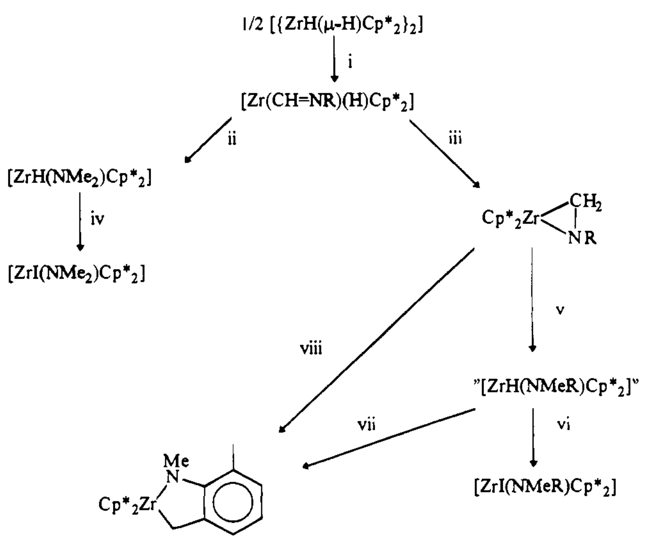
The dialkyl complexes $[MR_2Cp_2]$ (M = Zr, Hf; R = (6-methylpyridyl)methyl) undergo insertion of 2,6-dimethylphenyl isocyanide into the M—C bond, with formation of the vinylamido complexes $[M(NRR')(R)Cp_2]$ (M—NRR' = **12**).[60,61] Insertion of a second isocyanide molecule yields $[M(NRR')_2Cp_2]$. Both products are formed by a facile 1,2-hydrogen shift in intermediate η^2-iminoacyl complexes.[60,61]



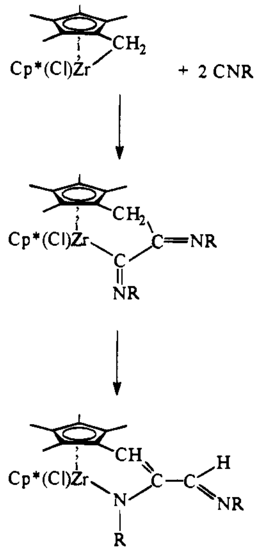
12

In a comparable reaction (eq 8; R = $2,6\text{-}Me_2C_6H_3$) insertion of isonitrile into the Zr—C bond is initially observed; at 140 °C the resulting imidoyl complex undergoes thermal rearrangement to an amido complex in 54% yield.[62] The product is formed via a 1,3-hydrogen shift from the original fulvene methylene group to a C atom of the second inserted isonitrile with concurrent formation of a Zr—N σ bond.[62]

Scheme 2[a]



[a] (i) RNC (R = Me, $2,6\text{-}Me_2C_6H_3$); (ii) H_2 (R = Me); (iii) 25 °C (R = $2,6\text{-}Me_2C_6H_3$); (iv) +MeI, −MeH; (v) H_2; (vi) +MeI, −MeH; (vii) 25 °C, $-H_2$; (viii) 65 °C.

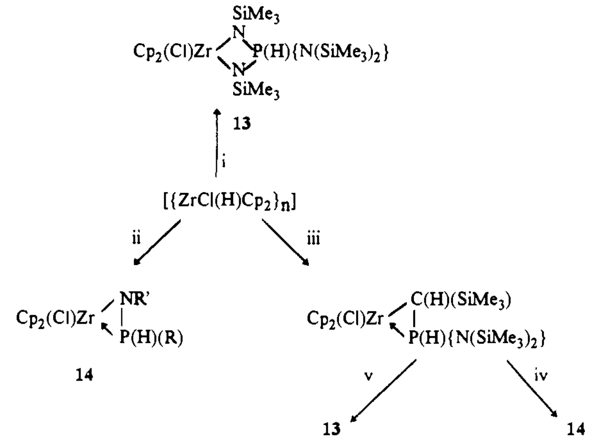


(8)

Schiff bases RR'C=NR″ react with zirconocene hydride chloride with hydrozirconation and formation of $[ZrCl\{N(R'')CHRR'\}Cp_2]$ (R, R', R″ = alkyl or aryl).[63] The reaction of these amido complexes, which were not isolated or characterized, with acetyl chloride or methyl oxalyl chloride gives enamides, imides or amides as products.[63]

Hydrozirconation of phosphaimines RP=NR' (R = $N(SiMe_3)_2$, R' = $SiMe_3$;[64,65] R = $N(SiMe_3)Bu^t$, R' = Bu^t; R = tetramethylpiperidino, R' = $SiMe_3$[64]), the phosphaalkene $(SiMe_3)_2NP{=}C(H)SiMe_3$,[64,66] or the bis(imino)phosphorane $(SiMe_3)_2NP({=}NSiMe_3)_2$[64,66] with zirconocene hydride chloride gives the three- or four-membered metallacycles shown in Scheme 3. Ligand exchange occurred when the zirconaphosphirane was treated with phosphinimine or the bis(imino)phosphorane (Scheme 3). No cyclization was observed in the reaction of zirconocene dihydride with $(SiMe_3)_2NP{=}N(SiMe_3)$, which gives $[ZrH\{N(SiMe_3)P(H)N(SiMe_3)_2\}Cp_2]$, while $[ZrMe_2Cp_2]$ gave the metalla-

Scheme 3[a]



[a] (i) $(SiMe_3)_2NP(=NSiMe_3)_2$; (ii) $RP{=}NR'$ [R = $N(SiMe_3)_2$ or tetramethylpiperidino, R′ = $SiMe_3$; R = $N(SiMe_3)Bu^t$, R′ = Bu^t]; (iii) $(SiMe_3)_2NP{=}C(H)SiMe_3$; (iv) $RP{=}NR'$ [R = $N(SiMe_3)_2$, R′ = $SiMe_3$]; (v) $(SiMe_3)_2NP(=NSiMe_3)_2$.

cycle $[Zr\{N(SiMe_3)P(Me)N(SiMe_3)_2\}(Me)Cp_2]$.[64] Hydrozirconation of the bis(imino)phosphorane was also observed with zirconocene dihydride, but the spectroscopic data did not distinguish between a cyclic $[[Zr\{NRP(H)(NR_2)NR\}(H)Cp_2]$, R = $SiMe_3$] or linear structure $[[Zr(H)\{NRP(=NR)(H)NR_2\}Cp_2]$, R = $SiMe_3$] of the product.[64]

The colorless metallacycles show parent ion peaks in the mass spectrum. ^{31}P NMR chemical shifts are −12 to 34 [J(PH) = 307−334 Hz] for Zr−N−P, 2.8 [J(PH) = 517 Hz] for Zr−N−P−N, and 42.6 ppm [J(PH) = 346 Hz] for Zr−C−P.[64]

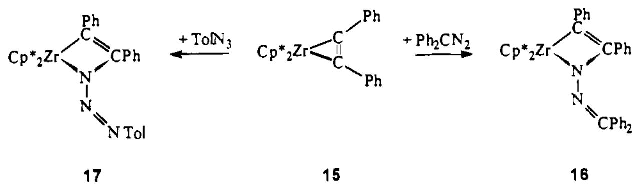
Ring opening of the zirconaazaphosphiranes $[Zr(NR'PRH)(Cl)Cp_2]$ [R = $N(SiMe_3)_2$, R′ = $SiMe_3$; R = $N(SiMe_3)Bu^t$, R′ = Bu^t] is observed on reaction with $Fe_2(CO)_9$, S_8, or Se.[64,65] However, in all cases only the hydrolysis products $HR'N{-}PHRX$ (X = $Fe(CO)_4$, =S, =Se) and $[(ZrClCp_2)_2O]$ were isolated and characterized. The metallacyclic structure is retained on reaction of $[ZrCl\{N(SiMe_3)P(H)N(SiMe_3)_2\}Cp_2]$ with RSO_3CF_3 (R = $SiMe_3$, Me)[64,65] or $NaBPh_4/CH_3CN$[64] (Scheme 4). Similarly, **13** reacts with $(SiMe_3)SO_3CF_3$ with elimination of $SiMe_3Cl$ and formation of the triflate derivative, which dissolves in acetonitrile to give the ionic compound $[Zr\{N(SiMe_3)P(H)N(SiMe_3)_2N(SiMe_3)\}(N{\equiv}CMe)Cp_2]^+CF_3SO_3^-$.[64]

$[Zr(NBu^tBPhNBu^t)Cp_2]$, which contains a 1,3-diaza-2-bora-4-zirconacyclobutane ring, was prepared from $[ZrCl_2Cp_2]$ and $Li_2(NBu^tBPhNBu^t)$ in THF at −78 °C (8% yield).[67] The orange product shows a singlet (20.2 ppm) in the ^{11}B NMR spectrum.[67]

The η^2-silanimine complex $[Zr(\eta^2\text{-}NBu^tSiMe_2)(PMe_3)Cp_2]$ was prepared from $[ZrI(NBu^tSiMe_2H)Cp_2]$ and $LiCH_2SiMe_3$ (see section II.A).[23]

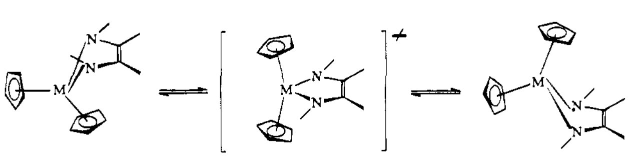
Insertion of isocyanate RNCO (R = Ph, nap) or p-tolylcarbodiimide into one Zr−C bond of $[ZrMe_2Cp_2]$ gives $[Zr(XCMeNR)(Me)Cp_2]$ (X = O, R = Ph or nap; X = NR, R = p-Tol).[68] The phenyl derivative (X = O) has been structurally characterized [Zr−N 2.297(4) Å].[68]

The alkyne complex **15** cleanly inserts Ph_2CN_2 or $TolN_3$ with formation of **16** and **17** (eq 9).[69]



(9)

Oxidative addition of diazadienes to in situ-generated zirconocene(II) yields the orange-red zirconocene(IV) enediamido complexes $[Zr\{NPhC(R){=}C(R)NPh\}Cp_2]$ (R = Ph, Me)[70] in 60−80% yield. The hafnocene analogues were not accessible by this route. The air- and moisture-sensitive products exhibit dynamic NMR spectra, indicating a rapid intramolecular migration of the bent Cp_2M fragment from one "face" of the reduced diazadiene to the other (eq 10). The activation barrier was determined from variable-temperature ^1H NMR data [$\Delta G^\ddagger$ = 56.7 (R = Ph) or 74.7 kJ mol^{-1} (R = Me)].[70]



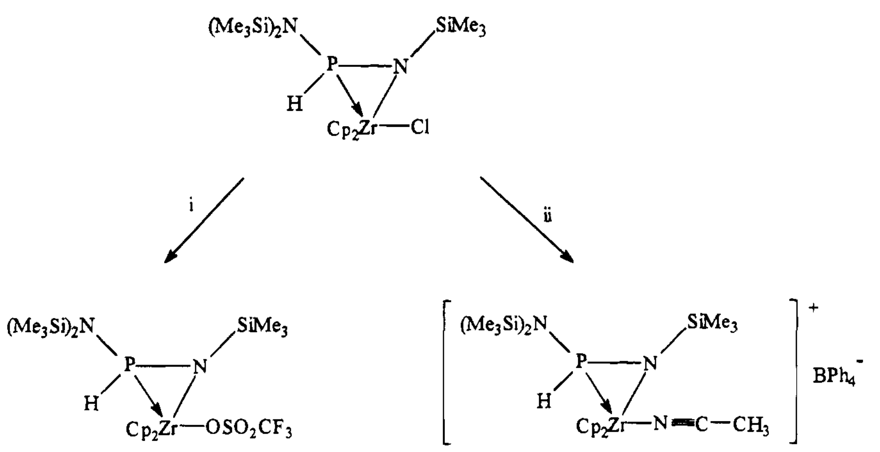
(10)

A comparable synthetic approach is the oxidative addition of 1-azadiene, $RN{=}CHCH{=}CHR'$, to zirconocene(II) via zirconocene butene, yielding 1-zircona-2-azacyclopent-3-enes $[Zr(NRCH{=}CHCHR')Cp_2]$ (R = Bz, Ph, CHMePh, NMe_2, R′ = Ph; R = Bz, Bu^t, R′ = Me) in 47−72% yield.[71] Variable-temperature NMR spectroscopy indicates a ring flipping ($\Delta G^\ddagger \cong$ 55 kJ mol^{-1}), analogous to that observed in zirconocene enediamido complexes.[71]

An alternative route to these complexes starts with allylic amides $LiN(R)(CH_2CHCH_2)$ (R = Ph, $SiMe_3$) and $[ZrCl(Me)Cp_2]$.[71] Loss of methane yields an intermediate η^2-imine complex, which rearranges to the 1-azadiene complex $[Zr(NRCH{=}CHCH_2)Cp_2]$ ($\Delta G^\ddagger$ = 46.8 kJ mol^{-1}, R = Ph, for ring flipping). Yields are 87−92%.[71]

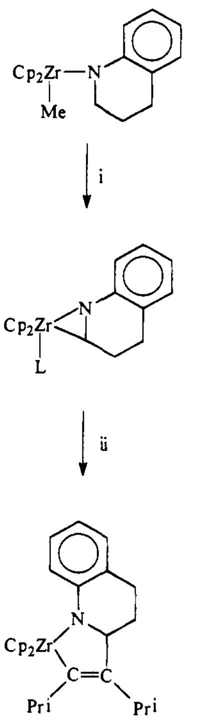
Similarly, the generation of transient acyclic zirconocene η^2-imine complexes and successive trapping with alkynes is a useful synthetic approach to 1-zircona-2-azacyclopentenes (Scheme 5[45] and 6). Products of Scheme 5 can be used for the synthesis of 1,2,3,4-tetrahydroquinolines,[45] while those of Scheme 6 are starting materials for the formation of substituted pyrroles[72] and geometrically pure allylic amines[73] (see section III.A.3). Isolable metallaaziridenes $[Zr(NRCHR')(L)Cp_2]$ (L = THF, R = $SiMe_3$, R′ = H, Pr, Ph; L = PMe_3, R = $SiMe_3$, R′ = Ph, 2-furyl, 2-thienyl; L = PMe_3, R = R′ = Ph) were obtained from methyl zirconocene chloride and $LiN(CH_2R')R$ (43−79% yield).[73]

Scheme 4[a]



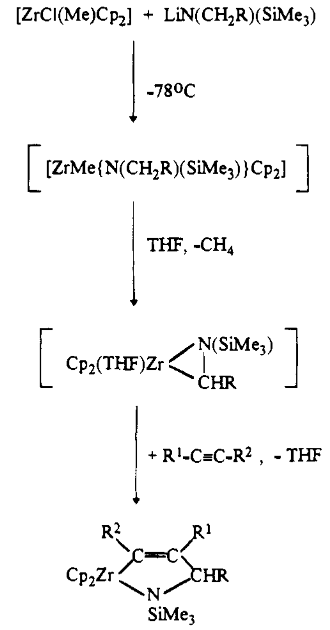
[a] (i) $+RSO_3CF_3$ (R = $SiMe_3$, Me), $-RCl$; (ii) $+NaBPh_4/CH_3CN$, $-NaCl$.

Scheme 5[a]



[a] (i) 60 °C, +L (L = THF, PMe_3), $-CH_4$; (ii) $Pr^iC{\equiv}CPr^i$.

Scheme 6[a]



[a] R = Ph, R^1 = H, R^2 = Ph, H, Pr, CH_2OSiBu_3, $SiMe_3$, $CH_2CH_2CH_2CN$; R = R^1 = Ph, R^2 = Ph; R = Ph, R^1 = R^2 = Me; R = H, R^1 = R^2 = Me; R = H, R^1 = n-C_8H_{17}, R^2 = H; R = n-C_5H_{11}, R^1 = Ph, H, R^2 = Ph; R = 2-thienyl, 5-methyl-2-pyrrolyl, R^1 = H, R^2 = Pr; R = 2-furyl, R^1 = H, R^2 = Ph;[72] and R = Ph, R^1 = H, R^2 = Ph; R = H, R^1 = R^2 = Ph; R = n-C_5H_{11}, R^1 = R^2 = Et.[73]

2. Structural Data

Structural data are available for $[Zr(\eta^1\text{-}NC_4H_2Me_2)_2Cp_2]$,[38] $[HfH(NHMe)Cp^*_2]$[56] (Figure 2), $[Hf\{N(2,6\text{-}Me_2C_6H_3)[(6\text{-methylpyridyl})vinyl]\}_2Cp_2]$,[60,61] $[Zr(NHPh)(OSO_2CF_3)Cp_2]$,[42] $[Zr\{N(SiMe_3)P(H)N(SiMe_3)_2\}(Cl)Cp_2]$,[65] $[Zr(\eta^2\text{-}NBu^tSiMe_2)(PMe_3)Cp_2]$[23] (see section II.2, Figure 1), $[Zr(NPhCPh{=}CPhNPh)Cp_2]$,[70] and $[Zr\{\eta^2\text{-}N(SiMe_3)CHPh\}(THF)Cp_2]$.[73]

The structure of the bis(2,5-dimethylpyrrolyl)zirconocene complex[38] is very similar to that of the previously described pyrrolyl derivative $[Zr(\eta^1\text{-}NC_4H_4)_2Cp_2]$,[37] although the presence of the methyl substituents on the ligand apparently weakens the Zr—N bond [Zr—N 2.171(2), 2.167(2) Å in pyrrolyl complex; Zr—N 2.22(2), 2.25(2) Å in the dimethyl-disubstituted derivative]. The Zr—N distances indicate a substantial $d_\pi-p_\pi$ interaction. The overall structure of the vinylamido complex $[Hf\{N(2,6\text{-}Me_2C_6H_3)[(6\text{-methylpyridyl})vinyl]\}_2Cp_2]$ is similar to those of the pyrrolyl derivatives. The Hf—N bond length is 2.182(12) Å.[60,61]

The most noteworthy feature of the structure of the monoamido complex $[HfH(NHMe)Cp^*_2]$ (Figure 2) is that the methylamido group is essentially planar, with the methyl group directed toward one Cp* ligand, and the hydrogen toward the other. The Hf—N bond length of 2.027(8) Å suggests considerable double-bond character, although the dihedral angle [C(Me)—N—Hf—H] of 63(3)° deviates significantly from the ideal 90° for perfect back-bonding, probably due to steric interactions.[56] The Zr—N bond length in $[Zr(NHPh)(OSO_2CF_3)Cp_2]$ (2.072(3) Å] and the amido ligand orientation also suggest π-donation from the amido group to Zr.[42]

The central ZrN_2C_2 five-membered ring of the enediamido complex $[Zr(NPhCPh{=}CPhNPh)Cp_2]$

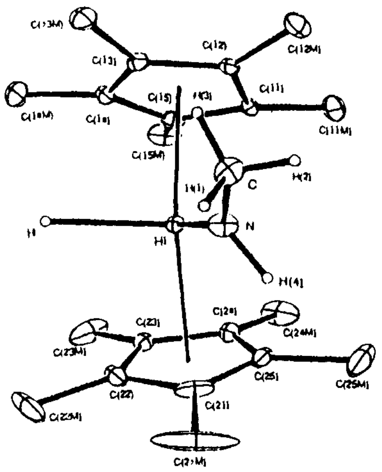


Figure 2. Molecular structure of [HfH(NHMe)Cp*$_2$]. (Reprinted from ref 56. Copyright 1988 American Chemical Society.)

[Zr—N 2.100(4), 2.123(5) Å] is folded along the N··N axis [dihedral angle 39.2(3)°], thus confirming the assumptions made from variable-temperature NMR data.[70]

The crystal structure of the η^2-imine complex [Zr{η^2-N(SiMe$_3$)CHPh}(THF)Cp$_2$] [Zr—C(1) 2.26(1), Zr—N 2.11(1), N—C(1) 1.41(1) Å] suggests the presence of a metallaaziridene due to significant π-donation from Zr to the π^* orbitals of the coordinated imine.[73]

In the crystal structure of the zirconaazaphosphirane [Zr{N(SiMe$_3$)P(H)N(SiMe$_3$)$_2$}(Cl)Cp$_2$] the endocyclic P—N1 bond [1.609(3) Å] is shorter than the exocyclic P—N2 bond [1.691(3) Å], which reflects a weak residual iminophosphorane character.[65] The difference between the Zr—N1—P [80.8(1)°] and Zr—P—N1 [60.9(1)°] angles is due to the differing Zr—P [2.562(1) Å] and Zr—N1 [2.267(3) Å] bond lengths.[65]

3. Chemical Properties

Metal—ligand bond disruption enthalpies have been determined for several metallocene amides.[74]

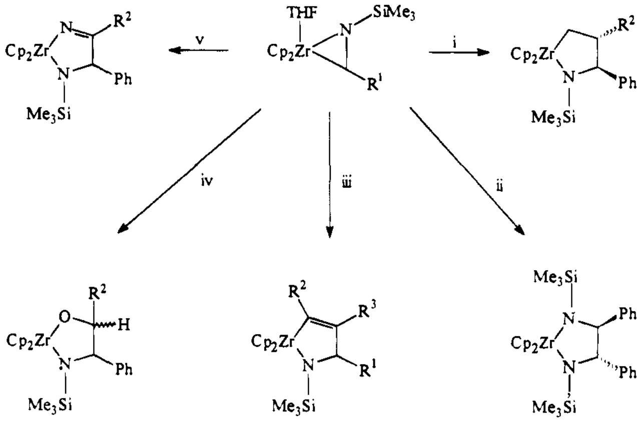
Amides of group 4 metallocenes with a direct M—NR$_2$ linkage exhibit a wide range of chemical behavior.[75] Loss of electron density at nitrogen through internal p$_\pi$—d$_\pi$ bonding weakens their donor capacity. Facile bond cleavage of the M—N bond with protic reagents (e.g., phenylacetylene, HXBu^t with X = O or S)[35,76] and group redistribution or scrambling with metal or metalloid halides are observed. [HfH(NH$_2$)Cp*$_2$] reacts with water to afford [HfH(OH)Cp*$_2$] (cf. section V.E) and ammonia; formation of [Hf(OH)(NH$_2$)Cp*$_2$] was not observed.[55]

Group exchange reactions have been observed in the reaction of [Zr(NMe$_2$)$_2$Cp$_2$] with MCl$_4$ (M = Si, Ge, Sn, Ti, Zr, Hf) to give [ZrCl$_2$Cp$_2$] and [MCl$_2$(NMe$_2$)$_2$].[77]

[ZrCl(NMe$_2$)Cp$_2$], prepared in situ from [ZrCl$_2$Cp$_2$] and [Zr(NMe$_2$)$_2$Cp$_2$], reacts with the metal—complex-substituted alkyne [Ru(C≡CH)(PMe$_3$)$_2$Cp] with elimination of dimethylamine and formation of the orange product [Cp(Cl)ZrC≡CRu(PMe$_3$)$_2$Cp] in 85% yield.[78]

The reaction between [Zr(NMe$_2$)(R)Cp$_2$] (R = Cl, NMe$_2$) and [ReH$_7$(PPh$_3$)$_2$] results in the formation of the heterometallic polyhydrides [Cp$_2$(R)Zr(μ-H)$_n${ReH$_{6-n}$(PPh$_3$)$_2$}] (n > 1) (see section VII.A, Scheme 33) with elimination of dimethylamine.[79]

Scheme 7[a]



[a] (i) CH$_2$=CHR^2 (R^1 = Ph, R^2 = H, Bu^n, Me); (ii) PhHC=N(SiMe$_3$) (R^1 = Ph); (iii) R^{2}C≡CR^3 (R^1 = R^2 = Ph, R^3 = H; R^1 = H, R^2 = R^3 = Ph; R^1 = C$_5$H$_{11}$, R^2 = R^3 = Et; R^1 = Ph, R^2 = CH$_2$(CH$_2$)$_2$C≡N, R^3 = H); (iv) R^{2}HC=O (R^1 = Ph, R^2 = Bu^t; R^1 = R^2 = Ph); (v) R^{2}CN (R^1 = Ph, R^2 = Pr^n, CH$_2$CH$_2$CH$_2$CH=CH$_2$, CH$_2$(CH$_2$)$_2$-C(OCH$_2$CH$_2$O)Me).

[Zr(NHPh)$_2$Cp$_2$] reacts with the molybdenum cyclohexadiene complex [Mo(CO)$_2$(η^2-chd)(η^5-indenyl)](OSO$_2$CF$_3$) (chd = cyclohexadiene) with ligand exchange and formation of [Zr(NHPh)(OSO$_2$CF$_3$)Cp$_2$] whose X-ray structure was determined (see section III.A.2).[42] The latter was also obtained from the zirconocene bisamido complex and CF$_3$SO$_3$H.[42]

[Zr(NMe$_2$)(OR)Cp$_2$] (R = 2,6-Bu$^t_2$C$_6$H$_3$) reacts with PhNCO in hexane with insertion and formation of [Zr{NPhC(=O)NMe$_2$}(OR)Cp$_2$].[46]

The zirconocene bisamido complexes [Zr(NHR)$_2$Cp$_2$] (R = 2,6-Me$_2$C$_6$H$_3$, Bu^t) catalyze the conversion of alkynes and amines to enamines.[41]

The azametallacyclopentenes obtained according to Scheme 6 react with CO under appropriate conditions to give substituted pyrroles;[72] hydrolysis affords a general route to geometrically pure allylic amines.[73]

The η^2-imido complex [Zr{η^2-N(SiMe$_3$)CHR^1}(THF)Cp$_2$] undergoes a number of chemo-, regio-, and diastereoselective coupling reactions with unsaturated organic compounds, forming zirconaazacyclopentane derivatives (Scheme 7).[73]

η^2-Ketimine complexes of zirconocene can be generated by a C—H activation process from α,α-disubstituted amines and react with a variety of unsaturated substrates to afford α,α,α-trisubstituted amines upon hydrolysis.[80]

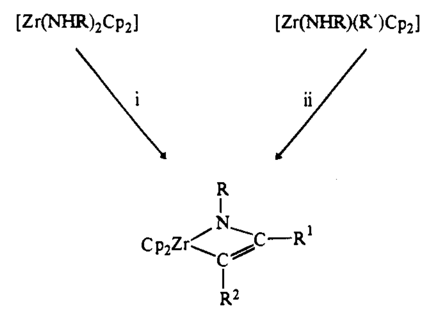
B. Dinuclear Amido-Bridged Metallocene(IV) Complexes

No dinuclear amido-bridged complexes of Zr and Hf were known up to 1991. One example of a titanium derivative is [CpTi(μ-NMe$_2$)$_3$M(CO)$_3$] (M = Cr, Mo, W).[81]

C. Zirconocene Imido Complexes [Zr(=NR)Cp$_2$]; Generation and Trapping

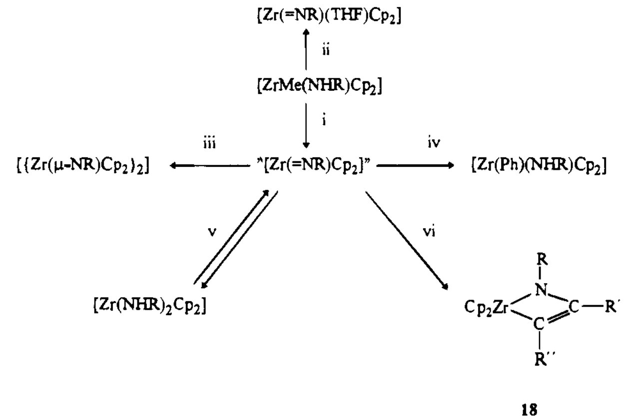
Thermolysis of certain amido zirconocene complexes shown in Scheme 8 in the presence of certain alkynes in benzene between 85 and 120 °C resulted

Scheme 8[a]



[a] (i) $-RNH_2$, $+R^1C{\equiv}CR^2$ (R = 2,6-$Me_2C_6H_3$, 4-$Bu^tC_6H_4$, Bu^t, $R^1 = R^2$ = Ph, R^1 = Me, R^2 = Ph, $R^1 = R^2$ = Me;[44] R = 2,6-$Me_2C_6H_3$, $SiMe_2Bu^t$, $R^1 = R^2$ = Ph;[41] R = 2,6-$Me_2C_6H_3$, $R^1 = R^2$ = Ph, *p*-Tol[41]); (ii) $-R'H$, $+R^1C{\equiv}CR^2$ (R = 2,6-$Me_2C_6H_3$, Bu^t, 4-$Bu^tC_6H_4$, R' = Me, Ph, $R^1 = R^2$ = Ph, R^1 = Me, R^2 = Ph, $R^1 = R^2$ = Me;[44] R = $CH_2CH_2Bu^t$, R' = Me[41]).

Scheme 9[a]



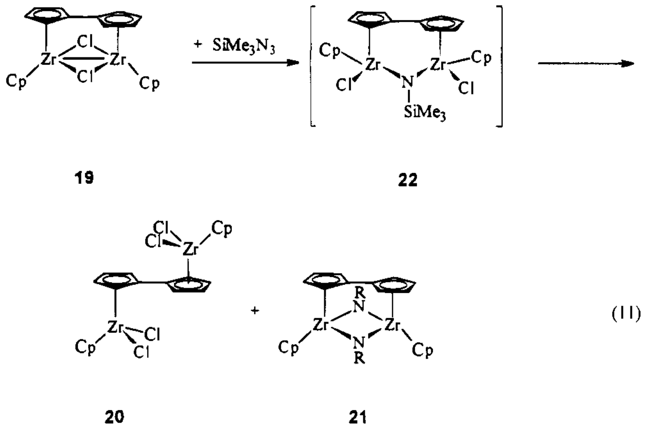
[a] (i) $-CH_4$; (ii) in THF, $-CH_4$; (iii) for R = 4-$Bu^tC_6H_4$; (iv) for R = Bu^t, benzene; (v) RNH_2; (vi) $R'C{\equiv}CR''$ (R' = Me, R'' = Ph; R' = R'' = Me, Ph).

in formation of azametallacyclobutenes.[41,44] No reaction was observed between $[Zr(NHSiMe_2Bu^t)_2Cp_2]$ and diphenylacetylene. The formation of the metallacycles shown in Scheme 8 was shown to be reversible. Formation of a transient zirconocene imido complex was suggested.

The generation of $[Zr(=NR)Cp_2]$ (R = 4-$Bu^tC_6H_4$, Bu^t, 2,6-$Me_2C_6H_3$)[44] is similar to that of transient complexes with a terminal Zr=O (cf. section V.G) or Zr=S (cf. section VI.C) bond. The thermolysis (Scheme 9) is a first-order process. The transient imidozirconocene complex either dimerizes (R = 4-$Bu^tC_6H_4$), or activation of a C—H bond of the solvent occurs (R = Bu^t). Alternatively, the intermediates can be stabilized in THF or trapped with alkynes or amines (Scheme 9).[44] The molecular structures of $[Zr(=NBu^t)(THF)Cp_2]$ and of dimeric $[\{Zr(\mu\text{-}NR)Cp_2\}_2]$ (R = 4-$Bu^tC_6H_4$) were determined. The Zr—N distances [2.098(2), 2.093(2) Å] and N—Zr—N angle [80.56(7)°] of the latter are typical of imido-bridged dimers. The Zr—N—C bond angle of the monomeric imido complex is 174.4(3)°, and the Zr—N bond length is 1.826(4) Å.[44] The THF adducts $[Zr(=NR)(THF)Cp_2]$ (R = 2,6-$Me_2C_6H_3$, Bu^t) dissociate rapidly and are therefore a convenient source of the reactive intermediate $[Zr(=NR)Cp_2]$. Thus, diphenylacetylene reacts rapidly with the THF adduct (R = 2,6-$Me_2C_6H_3$) to give the corresponding azametallacyclobutene **18** (R' = R'' = Ph).[41]

D. Dinuclear Imido-Bridged Metallocene(IV) Complexes

Only a few such complexes are known. The dimerization product of transient $[Zr(=NR)Cp_2]$ (R = 4-$Bu^tC_6H_4$) is discussed above (cf. section III.C). The orange complex **21** (R = $SiMe_3$) is obtained together with **20** from the reaction of **19** with trimethylsilyl azide (eq 11).[82] The formation of **20** and **21** is discussed in terms of an intermolecular exchange of the single-bridged μ-imido complex **22**.



(11)

Oxidation of $[\{CpZr(PMe_3)(\eta^1{:}\eta^5\text{-}C_5H_4)\}_2]$ by $SiMe_3N_3$ gave the deep-blue dinuclear imido-bridged complex $[\{CpZr(\eta^1{:}\eta^5\text{-}C_5H_4)\}_2(\mu\text{-}NSiMe_3)]$ in 88% yield.[83] The imido group of the latter is located in the region between the two $\eta^1{:}\eta^5$-cyclopentadienyl rings, and the short Zr—N distances [2.136(8), 2.103(9) Å] suggest appreciable Zr—N p_π—d_π interaction.[83]

E. Metallocene(IV) Alkylideneamido Complexes

1. Synthesis

The most common route to zirconocene(IV) alkylideneamido complexes [aldimido (M—N=CHR) and ketimido (M—N=CR_2) derivatives] is the hydrozirconation of nitriles R'CN with $[ZrH(X)(\eta\text{-}C_5R_5)_2]$ to give $[Zr(N{=}CHR')(X)(\eta\text{-}C_5R_5)_2]$ [for a recent review see ref 84; X = H, R = Me, R' = *p*-Tol;[85] X = Cl, R = H, R' = Me, Ph,[86,87] Bz,[86] $P(NPr^i{}_2)_2$[88]]. The products were obtained in 57% to quantitative yield, except for R' = Bz, which could not be obtained in pure form.[86] No reaction was observed between $[ZrMe_2Cp^*{}_2]$ and tolunitrile.[85]

The salt elimination route can successfully be employed for the synthesis of bis(alkylideneamido) complexes $[Zr(N{=}CR_2)_2Cp_2]$ from zirconocene dichloride and $LiN{=}CR_2$ (R = Ph),[89] as shown in 1971 (R = Ph, *p*-Tol, Bu^t).[90]

The amine displacement route was employed earlier in the synthesis of zirconocene and hafnocene bis(alkylideneamido) complexes.[90] An alternative synthesis is the reaction of a prereduced metal complex $[ZrLCp_2]$ (L = butadiene, 2 CO)[89] with benzophenone azine. The reaction of zirconocene dicarbonyl under UV irradiation gave the best result (80% yield). Unfortunately, this reaction seems to be limited to benzophenone azine, as the reaction of zirconocene butadiene with acetone azine yielded the C—C cou-

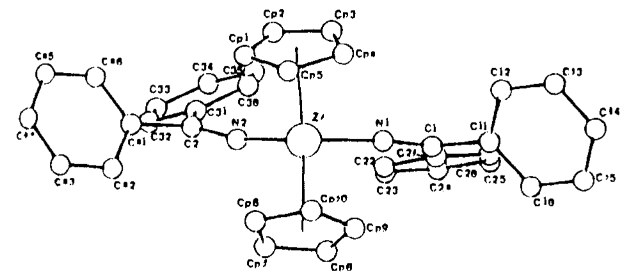


Figure 3. Molecular structure of $[Zr(N{=}CPh_2)_2Cp_2]$. (Reprinted from ref 89. Copyright 1988 American Chemical Society.)

pling product, and diphenyl zirconocene or zirconocene dicarbonyl gave only unidentified products.[89]

$[\{Zr(N_2)Cp^*_2\}_2(N_2)]$ reacts with 4 equiv of tolunitrile to form the metallacycle $[\overline{Zr\{NC(R)C(R)N}\}Cp^*_2]$. The latter reacts with H_2 to give the bis(alkylideneamido) complex $[Zr(N{=}CHR)_2Cp^*_2]$ (R = *p*-Tol).[85]

2. Structural Data

The molecular structures of $[Zr(N{=}CPh_2)_2Cp_2]$[89] and (*E*)-$[ZrCl(N{=}CHPh)Cp_2]$[87] have been determined. The short Zr—N bonds (2.013–2.063 Å) indicate some multiple-bond character. The C=N bond distances range from 1.259(1) to 1.266(4) Å.[87,89] The molecular symmetry of $[Zr(N{=}CPh_2)_2Cp_2]$ (Figure 3) differs from the apparent symmetry in solution (cf. section III.E.3).[89] The Zr—N—C linkages are nearly linear [173.7(2), 164.1(2)°]. The N—Zr—N angle [106.5(1)°] and the Zr—N bond lengths [2.058(2), 2.063(2) Å][89] are larger than those of (*E*)-$[ZrCl(N{=}CHPh)Cp_2]$. The core atoms of the alkylideneamido ligands are almost coplanar.

In (*E*)-$[ZrCl(N{=}CHPh)Cp_2]$ a nearly linear Zr—N—C arrangement [170.5(5)°] was found. The Zr—N bond is very short [2.013(5) Å]. The atoms Cl, Zr, N, C are coplanar with *E* orientation of the substituents of the Zr—N=C moiety (Cl and Ph group are *trans*).[87]

3. Spectroscopic Properties

The (alkylideneamido)zirconocene complexes are yellow or brown-yellow. In the IR spectra an absorption of high intensity is observed for the ν(C=N) mode between 1630 and 1700 cm^{-1}.[85,86,88,89]

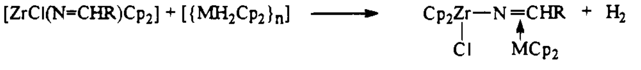
The solid-state structure of $[Zr(N{=}CPh_2)_2Cp_2]$ (cf. section III.E.2, Figure 3) shows a clear distinction of the (*E*)- and (*Z*)-oriented phenyl substituents at the $Ph_2C{=}NZr$ moiety.[89] This is not observed in solution. Even at low temperature (198 K) only one set of phenyl resonances is observed in the ^{13}C NMR spectrum, indicating a rapid equilibrium of (*E*)- and (*Z*)-phenyl groups.[89] This is an uncommon feature for heteroallene-type alkylideneamido metallocene complexes because earlier NMR studies of $[TiCl(N{=}CR_2)Cp_2]$ (R = *p*-Tol, Bu^t) had revealed the nonequivalence of the two C-substituents in the ketimides, implying a high rotational barrier about the C=N bond.[90]

In $[ZrCl(N{=}CHPh)Cp_2]$ only the (*E*)-isomer is present in the solid state.[87] The (*E*)-isomer was synthesized stereoselectively,[86] and it was shown that the isomerization (*E*) ⟷ (*Z*) could not be effected thermally or photochemically.[86,89]

Due to the molecular structure of $[ZrCl(N{=}CHPh)Cp_2]$ the Cp ligands are equivalent, and even at low temperature only one ^1H NMR signal was observed for the Cp protons for this complex as well as for $[ZrCl(N{=}CHMe)Cp_2]$.[87]

4. Chemical Properties

$[ZrCl(N{=}CHPh)Cp_2]$ reacts with tolyllithium with elimination of LiCl and formation of $[Zr(p\text{-}Tol)(N{=}CHPh)Cp_2]$;[86] with the polymeric metallocene dihydrides of Zr and Hf, the ochre dinuclear complexes **23** are formed in 60–68% yield with elimination of H_2 (eq 12; M = Zr, Hf, R = Ph; M = Zr, R = Me).[86] In **23** four signals for the four inequivalent cyclopentadienyl rings are observed.[86] The hydrido complex $[ZrH\{N{=}CH(p\text{-}Tol)\}Cp^*_2]$ reacts with methyl iodide with elimination of methane and formation of the corresponding iodo complex.[85]



$$[ZrCl(N{=}CHR)Cp_2] + [\{MH_2Cp_2\}_n] \longrightarrow \underset{\underset{Cl}{|}}{Cp_2Zr}{-}\underset{\underset{MCp_2}{\uparrow}}{N{=}}CHR + H_2 \quad (12)$$

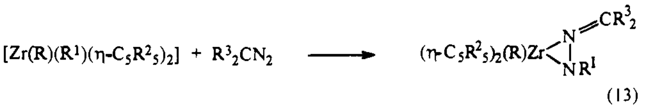
23

$[ZrCl\{N{=}CHP(NPr^i_2)_2\}Cp_2]$ is a useful starting material for the synthesis of a variety of *C*-phosphanyl-, *N*-phosphanyl-, or *N*-boranylimines. Thus, reaction with RR′MCl (M = P, R = R′ = Ph; M = P, R = NPr^i_2, R′ = Cl; M = P, R = R′ = NPr^i_2; M = B, R = R′ = NPr^i_2; M = B, R = $N(SiMe_3)N(SiMe_3)_2$, R′ = Cl; MRR′ = $SnMe_3$)[88] leads to formation of $[RR'M\{N{=}CHP(NPr^i_2)_2\}]$ with elimination of $[ZrCl_2Cp_2]$.

F. Metallocene(IV) Hydrazido and Hydrazonato Complexes

1. Synthesis

Salt elimination reactions have been employed for the synthesis of metallocene hydrazido complexes $[Zr(NR^1NPhR^2)(R)Cp_2]$ from $[ZrClRCp_2]$ and MNR^1NPhR^2 (R = Me, R^1 = Ph, R^2 = H, M = K;[91,92] R = $CH_2CH_2Bu^t$, R^1 = H, R^2 = Ph, M = Li[93]) in 72–83% yield. Insertion of diazoalkanes into Zr—C or Zr—H bonds yields hydrazonato(1−) complexes (eq 13; R = R^1 = Me, Bz, R^2 = H, R^3 = Ph; R = R^1 = Bz, R^2 = H, R^3 = CO_2Et;[94] R = Cl, R^1 = R^2 = H, R^3 = Ph;[95] R = OH, R^1 = R^2 = Me, R^3 = *p*-Tol;[96] R = R^1 = Me, R^2 = H, R^3 = Ph[95]) in 20–79% yield. A mechanism involving coordination of diazoalkane to zirconium followed by intramolecular migration of R^1 has been proposed (eq 13).[94,95]

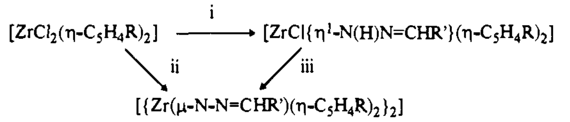


(13)

Zirconocene phosphido complexes react with diazoalkanes with insertion into the Zr—P bond and formation of phosphido hydrazonido(1−) ligands (cf. section IV.A.4).[97–99]

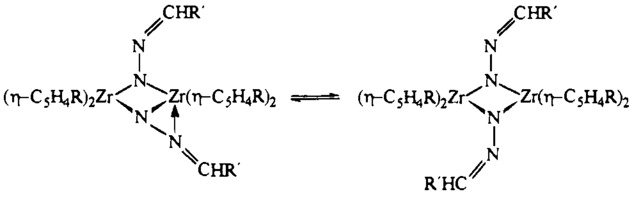
The hydrazone derivatives shown in Scheme 10 (R = H, Me, R′ = Ph;[100] R = H, R′ = 4-$MeOC_6H_4$,[100,101] Ph, 4-ClC_6H_4, 4-$(NC)C_6H_4$[101]) are readily available by

Scheme 10[a]



[a] (i) +LiN(H)N=CHR', $-2LiCl$; (ii) $+Li_2NNCHR'$, $-2LiCl$; (iii) $-HCl$.

ligand metathesis. The two-step synthesis gave higher yields.[100,101] The crystal structure of [{Zr(μ-NN=CHPh)(η-$C_5H_4Me)_2\}_2$] revealed an unusual unsymmetrical bridging ligand system (**24**) (cf. section III.F.4), while the ^{13}C NMR data suggest a fluxional behavior in solution (eq 14).[100]



24 **25** (14)

Bimetallic hydrazido(3−) complexes [Zr{N(H)N=$WMe_3Cp^*\}_n(R)_{2-n}Cp_2$] ($n$ = 1, 2, R = Me, Bz) are formed in the reaction of dimethyl or dibenzyl zirconocene with the tungsten hydrazido(2−) complex [W(=$NNH_2)Me_3Cp^*$].[102] The monosubstituted zirconocene complexes do not readily eliminate methane or toluene to generate hydrazido(4−) complexes. Thus, heating or irradiation in the presence of THF or PMe_3 led only to decomposition. They hydrolyze rapidly with formation of the tungsten starting material and zirconocene oxide derivatives.[102] The chemical shift of the N atoms ($W{=}N_{\alpha}N_{\beta}Zr$) in the ^{15}N NMR spectrum is 403−410 ppm for N_{α} and 246−260 ppm for N_{β}.[102]

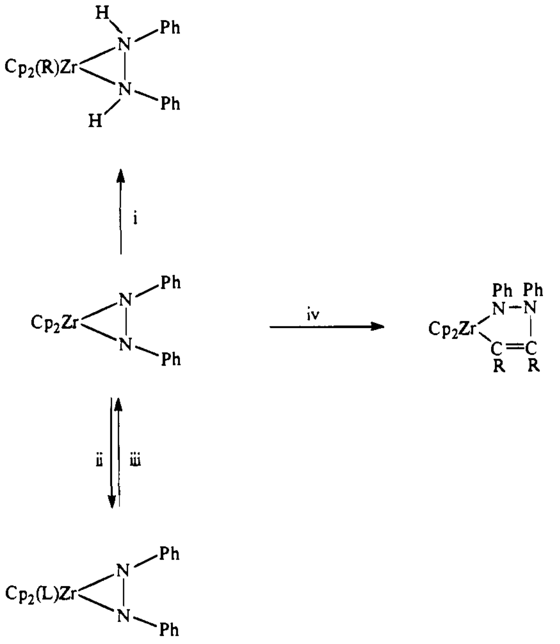
2. Spectroscopic Properties

The η^2-bonding of the hydrazido(1−) ligand in these complexes is appeared from ^1H and ^{13}C NMR spectroscopy; coordination of the β-nitrogen of the hydrazido ligand freezes the inversion at the N atom, thus making the cyclopentadienyl ligands chemically inequivalent.[91]

3. Chemical Properties

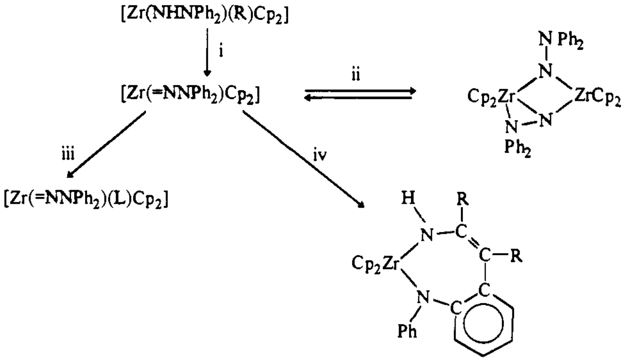
Heating [ZrMe{η^2-NPhN(H)Ph}Cp_2] in THF causes elimination of methane and generation of the transient hydrazido complex [$Zr(N_2Ph_2)Cp_2$], which is trapped as the THF adduct [$Zr(N_2Ph_2)(THF)Cp_2$] in 80% yield.[91,92] This adduct was also prepared in 60−80% yield by addition of monolithio-1,2-diphenylhydrazine to [{$ZrCl(H)Cp_2\}_n$] or most efficiently (90−95% yield) by adding [$ZrCl_2Cp_2$] to a solution of dilithio-1,2-diphenylhydrazide in ether/THF at room temperature.[91,92] The THF ligand can be replaced by a variety of σ-donor ligands to form [$Zr(N_2Ph_2)(L)Cp_2$] (L = py, PMe_3, PhCN, Bu^tNC).[91,92] The pyridine adduct has been structurally characterized (cf. section III.F.4). The THF adduct undergoes clean insertion of alkynes into the Zr—N bond (Scheme 11)(cf. Zr=O, section V.G; Zr=S, section VI.C; and

Scheme 11[a]



[a] (i) PhC≡CH or $PhCOCH_3$, R = C≡CPh or PhC(=CH_2)O; (ii) L (L = THF, py, PMe_3, Bu^tNC, PhCN); (iii) −THF; (iv) RC≡CR (R = Me, Et).

Scheme 12[a]



[a] (i) 110 °C, 12 h, −RH (R = $CH_2CH_2Bu^t$); (ii) 120 °C, 3 h; (iii) L (L = 4-(dimethylamino)pyridine); (iv) RC≡CR (R = Et, Ph, p-Tol).

Zr=NR, section III.C).[91,92] Phenylacetylene gives a product with an N—H bond, i.e. an η^2-hydrazido(1−) acetylide complex.[91] Acetophenone reacts in a similar fashion to give an enolato complex (Scheme 11).[91,92]

Thermolysis of the alkyl hydrazido complex [$Zr(CH_2CH_2Bu^t)(NHNPh_2)Cp_2$] results in loss of 2,2-dimethylbutane and generation of the transient intermediate [Zr(=$NNPh_2)Cp_2$], which, in the absence of trapping reagents, dimerizes (Scheme 12).[93] Trapping agents such as 4-(dimethylamino)pyridine give a monomeric adduct of the hydrazido(2−) complex. Trapping with alkynes or reaction with CO is also possible.[93]

The metalloazines **25** react with aldehydes or ketones (O=CR″R‴) to give olefins (R′HC=CR″R‴), N_2, azines (R′HC=N−N=CR″R‴), and zirconocene oxide.[101] The mechanism for this reaction is discussed.[101]

4. Structural Data

In [$Zr(N_2Ph_2)(py)Cp_2$],[91,92] the N−N bond length of 1.434(4) Å lies in the range of known N−N single-

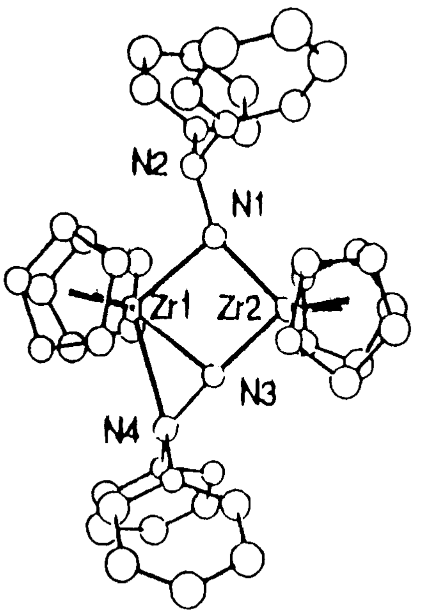
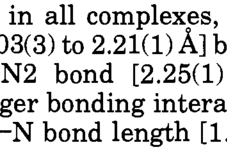


Figure 4. Molecular structure of $[\{Zr(=NNPh_2)Cp_2\}_2]$. (Reprinted from ref 93. Copyright 1991 American Chemical Society.)

bond distances. Both N atoms of the hydrazido(2−) ligand are pyramidal [torsion angle $C_{ipso}-N-N-C_{ipso}$ 91.3(4)°]. The Zr−N(hydrazido) bond lengths are 2.161(3) and 2.105(4) Å [N−Zr−N 39.25(12)°], Zr−N(py) is 2.431(4) Å.[91,92]

In $[Zr(CCPh)(NPhNHPh)Cp_2]$ the hydrazido(1−) ligand is bonded in an η^2-fashion with a dative Zr−N(HPh) bond [Zr−N 2.344(4) Å] and a Zr−N(Ph) σ-bond [2.122(5) Å] [N−N 1.410(6) Å, N−Zr−N 36.38(15)°].[91]

The molecular structures of the hydrazonato(1−) complexes (**26**; R = Ph, $R^1 = R^2$ = Me, R^3 = H;[94,95] R = CO_2Et, $R^1 = R^2$ = Bz, R^3 = H; R = Ph, R^1 = H, R^2 = Cl, R^3 = H;[94] R = p-Tol, R^1 = Me, R^2 = OH, R^3 = Me[96]) show an η^2-N,N′-bonding mode of the ligand. The structural data of the Zr,N1,N2,C,R^2 core in **26** are very similar in all complexes, with the central Zr−N1 bond [2.103(3) to 2.21(1) Å] being shorter than the lateral Zr−N2 bond [2.25(1) to 2.348(4) Å], implying a stronger bonding interaction between Zr and N1. The N−N bond length [1.30(2) to 1.349(5) Å] is shorter than that found in hydrazido(1−) complexes, suggesting multiple-bond character. The N−Zr−N bond angles range from 33.9(4) to 35.2(1)°.



26

The hydrazone derivative (**24**; R = Me, R′ = Ph; eq 14) shows an unusual unsymmetrical bridging ligand system. The Zr−N bond distances range from 2.004(7) to 2.232(7) Å, N−N distances are 1.36(1) and 1.32(1) Å.[100,101]

The dimerization product of transient $[Zr(=NNPh_2)Cp_2]$, shown in Figure 4, has a structure similar to the hydrazone derivative **24**, with Zr−N bond distances ranging from 1.996(7) to 2.446(6) Å.[93]

The structure of the monomeric hydrazido(2−) complex $[Zr(=NNPh_2)(4\text{-}NMe_2\text{-pyridine})Cp_2]$ is similar to that of the monomeric imido complex $[Zr(=NBu^t)(THF)Cp_2]$ (cf. section III.C). The Zr−N distance of 1.873(7) Å indicates a Zr−N double bond, while the N−N bond length of 1.364(10) Å is closer to the values observed for N−N single bonds. The hydrazido(2−) ligand is almost linear [Zr−N−N 168.7(6)°].[93]

IV. Metallocene(IV) Complexes with P-, As-, and Sb-Centered Anionic Ligands

A. Metallocene(IV) Phosphido Complexes

1. Synthesis

In 1966 Issleib et al. reported that the reaction of zirconocene dibromide and titanocene dichloride with $LiPR_2$ (R = Et, Bu) in THF at room temperature occurs with reduction to trivalent products $[\{M(\mu\text{-}PR_2)Cp_2\}_2]$ with concomitant formation of P_2R_4.[103] The first zirconocene(IV) phosphido complex, the spiro derivative $[\{Cp_2Zr(PPhCH_2)_2\}_2C]$, was reported in 1967.[104]

Metallocene(IV) phosphido complexes with terminal phosphido ligands have been known since 1983. If metallocene dichlorides are reacted with lithium phosphides with bulky ligands R, $LiPR_2$, bisphosphido complexes $[M(PR_2)_2Cp_2]$ (M = Zr, Hf, R = Ph, 76−84% yield;[105] M = Hf, R = Cy, 6% yield;[105] M = Zr, Hf, R = Et, Cy, Ph, 75−90% yield;[106] reaction conditions: M = Hf, THF, 80 °C, M = Zr, THF, −80 °C), are formed. However, if the steric demand of the ligand R is low or if the readily reduced titanocene dichloride is employed, phosphido-bridged dimetallic metallocene(III) complexes $[\{M(\mu\text{-}PR_2)Cp_2\}_2]$ (M = Ti, Zr, Hf, R = Me;[105] M = Ti, R = Ph;[105] M = Ti, Zr, R = Et;[107] M = Ti, Zr, R = Et, Bu[103]) and P_2R_4 are formed.

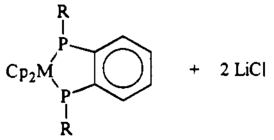
Metallocene monophosphido complexes with dialkyl- or diarylphosphido ligands are scarce. The bisphosphido complexes $[M(PPh_2)_2Cp_2]$ produce equilibrium mixtures with metallocene dihalides $[MX_2Cp_2]$ to give $[M(PPh_2)(X)Cp_2]$ (M = Zr, Hf, X = Cl, I).[105] The same mixture is obtained on mixing metallocene dihalide with 1 equiv of $LiPPh_2$.[105] However, the mixed PPh_2/X species accounted for only ca. 10% of the total Cp proton intensity (^1H NMR) and could not be isolated. The only isolable mono(dialkylphosphido) halide complex is the purple $[ZrCl(PPh_2)Cp_2]$, which was obtained in 5% yield at 0 °C from the reaction of $[Zr(PPh_2)_2Cp_2]$ with PPh_2Cl.[105]

Using bulky silylphosphido ligands, $Li(THF)_2P(SiMe_3)_2$, enables the synthesis of metallocene mono- and bisphosphido complexes $[M\{P(SiMe_3)_2\}_n(X)_{2-n}(\eta\text{-}C_5H_4R)_2]$ in 43−92% yield (M = Zr, X = Cl, R = H, $SiMe_3$, n = 1;[97,108] M = Zr, X = Me, R = H, n = 1;[97,108] M = Hf, X = Cl, R = H, n = 1;[109] M = Zr, Hf, X = Me, R = H, n = 1;[109] M = Zr, X = Cl, R = H, n = 2;[97,108] M = Zr, X = Cl, R = $SiMe_3$, n = 2;[108] M = Zr, Hf, X = Cl, R = H, n = 2;[109] M = Zr, X = Cl, R = Me, n = 2[110]). The reactions were carried out in THF or toluene at room temperature. No reaction was observed between $[ZrCl_2\{\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3\}_2]$ and the lithium phosphide.[97] $[ZrCl\{P(SiMe_3)(2,4,6\text{-}Bu^t_3\text{-}C_6H_2)\}Cp_2]$ was obtained in 85% yield from zirconocene dichloride and the corresponding lithium phosphide in THF at 0 °C.[111]

Extrusion of H_2 from hafnocene dihydride and primary or secondary alkyl- and arylphosphines (RR'PH) has been employed in the synthesis of hafnocene monophosphido hydride complexes $[HfH(PRR')Cp^*_2]$ (R = R' = Ph; R = H, R' = Ph; R = H, R' = Cy).[112] The reactions were carried out in petroleum ether at room temperature; yields range from 69–84%. Even in the presence of excess phosphine only the monophosphido complexes are formed. The bulkier Cy_2PH did not react even at 105 °C.[112]

Chelating *o*-phenylenebisphosphido ligands were employed in the synthesis of several metallocene bisphosphido complexes [eq 15; M = Zr, donor = TMEDA, R = Ph ($1,3\text{-}(SiMe_3)_2C_5H_3$ instead of Cp);[113] M = Ti, Zr, Hf, no donor, R = Ph;[114] R = Zr, donor = THF, R = H;[115] yields range from 56 to 79%). Alternatively, reaction of dimethyl metallocene with *o*-phenylenebisphosphine derivatives gives the metallacycles **27** (M = Ti, Zr, Hf, R = Ph;[114] M = Zr, R = H[115]) cleanly in 64–87% yield.

$[MCl_2Cp_2]$ + $[Li(donor)]_2[1,2\text{-}(PR)_2C_6H_4]$ ⟶



+ 2 LiCl (15)

27

The product of the reaction of metallocene dichlorides with primary lithium phosphides LiPHR strongly depend on the metal and its reducibility, the steric and electronic nature of the cyclopentadienyl ligands and the bulk of the alkyl or aryl group on phosphorus. Thus, complexes of the following type (i–vi) were obtained: (i) $[\{Zr(\mu\text{-}PHR')(\eta\text{-}C_5H_4R)_2\}_2]$, (ii) (*R*/*S*,*S*/*R*)-$[\overline{M(PR'{-}PR'{-}PR'})(\eta\text{-}C_5R_5)_2]$, (iii) $[M(PHR')(X)(\eta\text{-}C_5R_5)_2]$, (iv) $[M(PHR')_2(\eta\text{-}C_5R_5)_2]$, (v) $[\overline{M(PR{-}PR})L_2]$, (vi) $[\{ZrCl(\eta\text{-}C_5H_4R)_2\}_2(\mu\text{-}PMes)]$ (R = H, Me).

Metallocene(III) complexes of type i were first prepared with dialkylphosphido ligands.[105,107] *cis*-$[\{Zr(\mu\text{-}PHR')(\eta\text{-}C_5H_4Me)_2\}_2]$ (R' = Bu^t, adamantyl) are obtained from LiPHR' and the appropriate zirconocene dichloride.[116] The structurally characterized *trans*-$[\{Zr(\mu\text{-}PHCy)Cp_2\}_2]$ was obtained from the reaction of zirconocene dichloride with $CyPH_2$ in the presence of Mg in THF (vide infra).[117]

The 1,2,3-trisubstituted triphosphane-1,3-diyl complexes (ii) were first obtained as air-sensitive solids from the reaction of $[MX_2Cp_2]$ with polyphosphide anions (i.e. M = Ti, Zr, X = Cl, Br, $M'_2(PPh)_4$ with M' = Li, Na;[118] M = Ti, Zr, Hf, X = Cl, $K_2(PR')_n$, R' = Ph, Et, Me, Bu^t, n = 3–5[119]) in 28–84% yield. The titanocene derivatives are violet, and the hafnocene and zirconocene complexes yellow to orange.[119] Alternatively, complexes of type ii (M = Zr, Hf, R = H, R' = Ph;[120] M = Zr, Hf, R = H, R' = Bu^t;[121] M = Zr, Hf, R = Me, R' = Ph;[121] M = Zr, R = H, R' = Cy[122] or Ph[123]) have been obtained in low yield (15–27%) by reacting metallocene dichlorides with lithium phosphides (LiPHR'), whereby the metal and/or P atom have sterically less demanding ligands. Products of type ii (M = Zr, R = H, R' = Ph) have also been obtained in the reaction of dimethyl zirconocene or methyl zirconocene chloride with phenylphosphine.[120]

When zirconocene dichloride was reacted with 2 equiv of the bulkier $LiPHBu^t$, complex ii (M = Zr, R = H, R' = Bu^t) was formed in 15% yield as well as the reduced complex i (R' = Bu^t, R = H) in 50% yield.[121] Analogously, hafnocene dichloride reacts with $LiPHBu^t$ to give ii (M = Hf, R = H, R' = Bu^t), but the bisphosphido complex iv (M = Hf, R = H, R' = Bu^t) was also obtained in 60% yield.[121]

Terminal metallocene phosphido complexes of types iii (M = Hf, X = I, R = Me, R' = Ph, Cy;[112] M = Zr, Hf, X = Cl, R = Me, R' = Cy, 61–78% yield;[112] M = Zr, X = Cl, R = H, R' = $2,4,6\text{-}Bu^t_3C_6H_2$, 40% yield,[124] Mes, low yield[98]) and iv (M = Zr, R = H, R' = $2,4,6\text{-}Bu^t_3C_6H_2$,[124] Mes;[98] M = Zr, Hf, R = Me, R' = Bu^t, 30–71% yield[121]) are obtained when either the metal or the P atom bears a sterically demanding ligand.

$[ZrCl_2\{\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3\}_2]$ reacts with 2 equiv of $LiPHBu^t$ to give the terminal phosphido complex iv $[Zr(PHBu^t)_2\{\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3\}_2]$ (11% yield) and the diphosphene complex v (M = Zr, R = Bu^t, L = $\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3$) in 48% yield, while the hafnocene analogue gives only complex iv (M = Hf, R' = Bu^t, C_5R_5 = $\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3$) in 55% yield.[121]

$[ZrCl_2Cp^*_2]$ reacts with 2 equiv of LiPHMes to give $[Zr(PHMes)_2Cp^*_2]$ in 90% yield. In solution, this complex slowly eliminates H_2PMes with formation of transient $[Zr({=}PMes)Cp^*_2]$, which either rearranges to $[\overline{Zr(PMes{-}P}Mes)Cp^*_2]$ or $[\overline{Zr(1\text{-}PH\text{-}2\text{-}CH_2}\text{-}4,6\text{-}Me_2C_6H_2)Cp^*_2]$, or can be trapped with MeCN as $[\overline{Zr(N{=}CMe{-}PMes{-}CMe{=}N})Cp^*_2]$.[124b]

Diphosphene complexes (v) are obtained from the reaction of $[MCl_2L_2]$ with 2 equiv of LiPHR (M = Zr, Hf, L = $\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3$, R = Ph;[121] M = Zr, L = $\eta\text{-}C_5Me_4Et$, R = Mes[125]) in 26–70% yield.

The phosphinidene-bridged complex $[\{ZrCl(\eta\text{-}C_5H_4R)_2\}_2(\mu\text{-}PMes)]$ (R = H, Me) (vi) is obtained as dark green crystals on reaction of the corresponding zirconocene dichloride with LiPHMes, together with $[ZrCl(PHMes)(\eta\text{-}C_5H_4R)_2]$ or $[Zr(PHMes)_2(\eta\text{-}C_5H_4R)_2]$, depending on the stoichiometry employed.[126] The same product is obtained from the reaction of zirconocene dichloride with magnesium and $MesPH_2$ (vide infra).[117]

Oxidative addition of phosphine or diphosphanes to an in situ-generated zirconocene fragment or zirconocene(II) precursor was employed in the synthesis of zirconocene(III) and (IV) phosphido complexes.[117,127–129]

The metallocene(III) complexes $[\{M(\mu\text{-}PMe_2)Cp_2\}_2]$ (M = Zr, Hf) are obtained in 38–45% yield from metallocene dichloride, magnesium, and Me_2PPMe_2.[127] In the case of M = Zr, the byproduct $[(MCp_2)_2(\mu\text{-}Cl)(\mu\text{-}PMe_2)]$ was obtained in 10% yield.[127]

The complexity of the ^1H NMR spectrum of the final product $[\{ZrH(PH_2)Cp^*_2\}_2]$ which was obtained from $[\{Zr(N_2)Cp^*_2\}_2(N_2)]$ and PH_3 at low temperature is best explained by a dimeric structure. However,

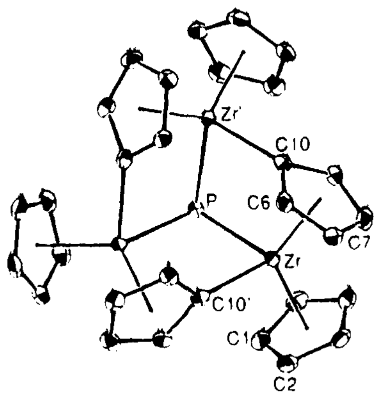
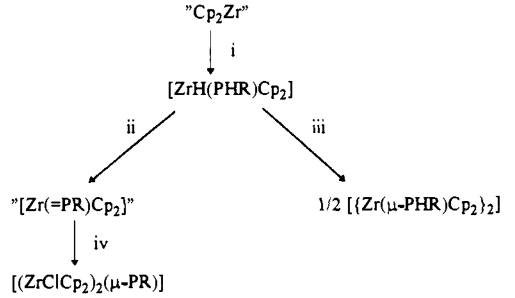


Figure 5. Molecular structure of a trimeric phosphido-capped complex. (Reprinted from ref 129. Copyright 1992 American Chemical Society.)

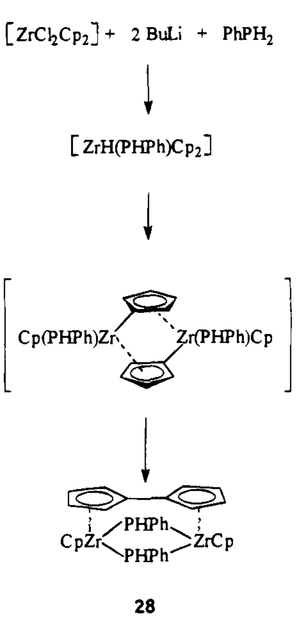
Scheme 13[a]



[a] (i) RPH_2; (ii) $-H_2$, intramolecular; (iii) $-H_2$, intermolecular; (iv) $[ZrCl_2Cp_2]$.

an unambiguous assignment to bridging or terminal ligands (H/PH_2) was not possible.[128]

C—H activation and subsequent C—C bond formation in the intermediate $[ZrH(PHPh)Cp_2]$ yields the Zr(III) complex **28** as the final product (eq 16).[129] In the analogous reaction with $(2,4,6\text{-}Bu^t_3C_6H_2)PH_2$ and Mg the isolated product (10% yield) is a trimeric phosphido-capped Zr(IV) species (Figure 5).[129] However, if $MesPH_2$ is employed instead of the bulkier $(2,4,6\text{-}Bu^t_3C_6H_2)PH_2$, the mono(phosphinidene)-bridged dinuclear complex $[(ZrClCp_2)_2(\mu\text{-}PMes)]$ was obtained.[117]



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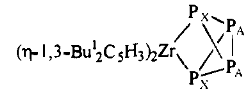
Zirconocene dichloride reacts with Mg and $CyPH_2$ with formation of *trans*-$[\{Zr(\mu\text{-}PHCy)Cp_2\}_2]$.[117] When the bulky $[ZrCl_2Cp^*_2]$ was used as the starting material, monitoring by ^{31}P NMR revealed the initial formation of $[ZrH(PHCy)Cp^*_2]$, which is unstable and loses H_2, yielding a compound which could not be isolated (^{31}P 220.2 ppm, no coupling to protons).[117] The route by which H_2 is lost appears to be controlled by steric factors (Scheme 13).[117]

$[M(CO)_2(\eta\text{-}1,3\text{-}Bu^t_2C_5H_3)_2]$ (M = Zr, Hf) reacts with white phosphorus in refluxing xylene to give **29**, which contains the P_4^{2-} anion.[130] The analogous Cp*-substituted complexes are only stable in solution and decompose in the solid state with formation of P_4.[130]



29

2. Spectroscopic Properties

Molecular weight measurements on $[M(PR_2)_2Cp_2]$ (M = Zr, Hf, R = Ph; M = Hf, R = Cy) showed these complexes to be monomeric in benzene.[105]

a. IR Spectra. A single weak absorption at ca. 350 cm^{-1} (M = Zr) and ca. 305 cm^{-1} (M = Hf) in $[M(PPh_2)_2Cp_2]$ was assigned as $\nu(M—P)$.[105] Two absorptions were observed for $[Hf(PCy_2)_2Cp_2]$ (299, 270 cm^{-1}).[105] In $[Zr\{1,2\text{-}(PH)_2C_6H_4\}Cp_2]$ the $\nu(Zr—P)$ mode was observed at 338 cm^{-1}.[115] The monophosphido chloro complexes $[ZrCl(PR_2)Cp_2]$ exhibit the ν(Zr—Cl) mode in the range of 330–350 cm^{-1} (R = Ph,[105] $SiMe_3$[97]). The complexes with primary phosphido groups (PHR) show the $\nu(P—H)$ mode between 2240 and 2340 cm^{-1}.[98,112,115]

b. ^{31}P and ^1H NMR. For terminal phosphido ligands generally two modes of coordination are possible. With 17-electron metal fragments the phosphido ligand acts as a one-electron σ-donor with a pyramidal configuration of the P atom. Fragments with 15 or fewer valence electrons can bind the ligand in the three-electron π-donor mode, with a planar P atom. The latter complexes exhibit ^{31}P NMR resonances that are usually significantly shifted to low field compared to the former.

Complexes in which the $P(SiMe_3)_2$ ligand acts as a one-electron donor resonate at high field between −203 and −287 ppm, while the chemical shifts of complexes in which the $P(SiMe_3)_2$ ligand acts as a three-electron donor are observed between −55 and −100 ppm [$[M\{P(SiMe_3)_2\}_2Cp_2]$, $[M\{P(SiMe_3)_2\}_2\{\eta\text{-}C_5H_4(SiMe_3)\}_2]$, M = Zr, Hf] and −108 and −154 ppm ($[ZrCl\{P(SiMe_3)_2\}\{\eta\text{-}C_5H_4(SiMe_3)\}_2]$, $[M\{P(SiMe_3)_2\}(X)Cp_2]$, M = Zr, Hf, X = Me; M = Hf, X = Cl].[97,109] For $[ZrI\{P(SiMe_3)_2\}Cp_2]$, the signal is shifted down field to −22.9 ppm.[97] The molecular structure determination of $[Hf\{P(SiMe_3)_2\}_2Cp_2]$ (cf. section IV.A.3) revealed the presence of both types of phosphido ligand (σ- and π-donor) in the solid state[109] while that of $[Zr\{P(SiMe_3)_2\}_2(\eta\text{-}C_5H_4Me)_2]$ shows a similar environment for both phosphido ligands.[110] In agreement with rapid equilibration between both coordination modes, single resonances at ca. −70 (M = Zr)[97,109] and −98.8 ppm (M = Hf)[109] were observed for $[M\{P(SiMe_3)_2\}_2Cp_2]$ and $[Zr\{P(SiMe_3)_2\}_2(\eta\text{-}C_5H_4\text{-}$

Me)$_2$] (−75.3 ppm)[110] at room temperature, with no change on cooling to −70 and −100 °C, respectively. The monophosphido complexes [$Zr\{P(SiMe_3)_2\}(X)Cp_2$] (X = Me, ca. −120 ppm;[97,109] X = Cl, −108.9 ppm[97]) and [$ZrCl\{P(SiMe_3)_2\}(\eta\text{-}C_5H_4Me)_2$] (−132.5 ppm)[131] show resonances at higher field than the bisphosphido complexes.[109] The ^{31}P resonance of [ZrCl{$P(SiMe_3)(2,4,6\text{-}Bu^t{}_3C_6H_2)$}$Cp_2$] (156 ppm) is shifted to low field compared to $P(SiMe_3)_2$ complexes.[111]

Metallocene complexes with silylphosphido ligands show a doublet (monophosphido complexes, 5.7−6.0 ppm, J(PH) ca. 1 Hz) or a triplet (bisphosphido complexes, 5.8−6.0 ppm, J(PH) ca. 1 Hz) in the ^1H NMR.[97,109]

The bis(dialkyl- or diarylphosphido) complexes [$M(PR_2)_2Cp_2$] (M = Zr, Hf, R = Et, Cy, Ph) show a singlet in the ^{31}P NMR spectra between 100 and 160 ppm.[105] As the crystal structure determination of [$Hf(PEt_2)_2Cp_2$] showed two different phosphido ligands (cf. section IV.A.3),[106] it was assumed that the interconversion of the M−P single and double bond is fast on the NMR time scale. Low-temperature freezing of the process is observed only for the bulky PCy_2 ligand. Thus, [$Hf(PCy_2)_2Cp_2$] shows two broad resonances (270.2, −15.3 ppm) at −126 °C, which coalescence at −100 °C ($\Delta G^{\ddagger} = 25.1 \pm 0.8$ kJ mol^{-1}). The Cp ligands appear as singlets in the ^1H NMR (5.7−5.9 ppm) with ^2J(PH) (if resolved) of ca. 1.5 Hz.[105,106]

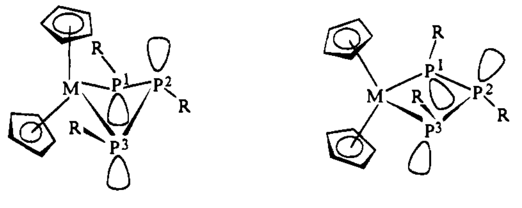
The hafnocene hydrido complexes [$HfH(PHR)Cp^*{}_2$] (R = Ph, Cy, J(PH) 227−232 Hz) and [$HfH(PPh_2)$-$Cp^*{}_2$] show singlets in the $^{31}P\{^1H\}$ NMR spectrum (30.5−96.3 ppm).[112] The ^1H chemical shift of the hydrido ligand in these complexes reflects the degree of π-donation from the phosphido ligand to Hf. Thus, δ(Hf−*H*) decreases in the order PPh_2 (14.7) > PHPh (13.9) > PHCy (12.9 ppm), indicating increasing π-interaction from PPh_2 to PHCy.[112] Apparently, for steric reasons the PPh_2 ligand is unable to adopt the geometry required for effective P⇒Hf π-donation. The halide derivatives [$M(PHR)(X)Cp^*{}_2$] (M = Hf, X = I, R = Ph, Cy; M = Hf, Zr, X = Cl, R = Cy;[112] δ = 34.4−72.1 ppm, J(PH) 203−226 Hz) and [$ZrCl(PHR)Cp_2$] (R = Mes, −5.6 ppm, J(PH) 230 Hz,[98] $2,4,6\text{-}Bu^t{}_3C_6H_2$, 90.4 ppm, J(PH) 271 Hz[124]) show a singlet in the $^{31}P\{^1H\}$ NMR spectra. A singlet is observed (1.87−2.02 ppm) for the Cp* ligands in the ^1H NMR spectrum.[112] The P*H*R resonance occurs as a doublet between 3.23 and 4.58 ppm (for R = Ph, Cy,[112] Mes[98]) or at 6.18 ppm (for R = $2,4,6\text{-}Bu^t{}_3C_6H_2$).[124]

The bisphosphido complexes [$Hf(PHBu^t)_2Cp_2$], [$M(PHBu^t)_2Cp^*{}_2$], and [$M(PHBu^t)_2\{\eta\text{-}1,3\text{-}(SiMe_3)_2\text{-}C_5H_3\}_2$] (M = Zr, Hf) show a singlet in the $^{31}P\{^1H\}$ NMR spectrum between 101 and 131 ppm.[121] The P*H*R resonance occurs between 3.6 and 4.4 ppm in the ^1H NMR (^1J(PH) 239−247 Hz, ^3J(PH) 11.1−11.8 Hz).[121] The complexes [$Zr(PHR)_2(\eta\text{-}C_5R'_5)_2$] show a singlet (R′ = H: 13.9, R = Mes;[98] 51.6 ppm, R = $2,4,6\text{-}Bu^t{}_3C_6H_2$;[124] R′ = Me: 39.0 ppm, R = Mes[124b]) in the $^{31}P\{^1H\}$ NMR, which splits into a multiplet on coupling to protons.

The diphosphene complexes [$M(PR{-}PR)\{\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3\}_2$] (M = Zr, Hf, R = Ph; M = Zr, R = Bu^t, δ = 193−271 ppm),[121] [$Zr(PMes{-}PMes)(\eta\text{-}C_5Me_4\text{-}Et)_2$] ($\delta$ = 138.7 ppm),[125] and [$Zr(PMes{-}PMes)Cp^*{}_2$] (δ = 134.9 ppm)[124b] show a singlet in the ^{31}P NMR spectrum.

Extreme down-field shifts are observed in [$\{ZrCl(\eta\text{-}C_5H_4R)_2\}_2(\mu\text{-}PMes)$] (ca. 325 ppm for R = H[117,126] or R = Me[126]) and for the μ_3-phosphorus atom in the trimeric complex shown in Figure 5 (782.6 ppm).[129] The transient terminal zirconocene phosphinidene complex [$Zr({=}PMes)Cp^*{}_2$] is believed to show a resonance at 537 ppm.[124b]

The complexes [$M(PR{-}PR{-}PR)Cp_2$] (M = Ti, Zr, Hf; R = Ph, Et, Me, Bu^t;[119] M = Zr, Hf, R = Ph;[121] M = Zr, R = Cy[122]) exhibit A_2X patterns in the ^{31}P NMR spectra, with the A_2 part at 182−254 (M = Ti), 92−138 (M = Zr), and 67−106 ppm (M = Hf) and the X part at −143 to −187 (M = Ti), −156 to −190 (M = Zr), and −160 to −195 ppm (M = Hf). In the analogous complexes [$M(PPh{-}PPh{-}PPh)Cp^*{}_2$], the ^{31}P resonances of the A_2 part are shifted to high field [M = Zr, (A_2 part) 60.87 (X part) −134.89 ppm; M = Hf, (A_2 part) 36.37, (X part) −128.75 ppm][121] and the coupling constant J(A−X) [244.95 (M = Zr), 215.80 Hz (M = Hf)] is smaller than in the Cp-substituted complexes. Only one diastereomer with *R* or *S* configuration at P^1 or *S* or *R* configuration at P^3 is present in solution (**30** and **31**, eq 17). In the ^1H NMR spectra two signals are observed for the inequivalent Cp or Cp* ligands [Cp, range 5.0−5.9 ppm, one multiplet, one triplet with J(P−H) 1.5−2.5 Hz].[119,121] The presence of a puckered (R = Ph) (**30**) or planar (R = Bu^t) (**31**) MP_3 metallacycle and a geometry between that shown in **30** and **31** for the Me and Et derivative was concluded on the basis of variable-temperature ^1H NMR studies.[119]

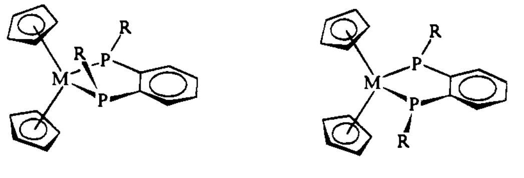


30 **31**

(17)

The o-phenylenebisphosphido metallocene derivatives (eq 18, M = Ti, Zr, Hf, R = Ph;[114] M = Zr, R = H[115]) exhibit two resonances in the ^{31}P NMR spectra due to the presence of both possible isomers, *cis* and *trans* [(R = Ph) M = Ti, −3.99, −6.87; M = Zr, −40.19, −41.50; M = Hf, −57.59, −58.80 ppm;[114] (R = H) M = Zr, −29.3 d, −77.5 (doublet with fine structure)[115]]. In the phenyl-substituted complexes the resonance of the *trans* isomer is shifted to high field compared to that of the *cis* isomer. Due to steric reasons the *trans*/*cis* ratio is 70/30 (M = Ti, R = Ph) and 95/5 (M = Zr, Hf, R = Ph).[114] No change is observed on heating to 98 °C.[114] The single signal observed for [$Zr\{1,2\text{-}(PPh)_2C_6H_4\}\{\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3\}_2$] at 30 °C (105 ppm) splits into two signals (−3.9 and +211.5 ppm) at −70 °C ($\Delta G^{\ddagger}$ = 45 kJ mol^{-1}). Thus, the limiting spectrum corresponds to the solid-state structure of the complex (cf. section IV.A.3).[113]

In [$Zr\{P(PR_2)PP(PR_2)P\}Cp_2$] (R = $SiMe_3$) six multiplets are observed for the six inequivalent P nuclei;



(18)

chemical shifts and coupling constants are given in Figure 6.[132]

The complexes **29** and the Cp* analogue (M = Zr) show A_2X_2 spectra with $\delta = 93-166$ ppm (P_X) and $\delta = -206$ to -219 ppm (P_A) [J(PP) = 193–201 Hz].[130]

The mass spectra of [M(PR–PR–PR)Cp_2] (M = Ti, Zr, Hf, R = Ph, Et, Me, Bu^t) exhibit the parent ion peak as well as the $P_3R_3^+$ fragment and fragmentation products thereof.[119] Parent ion peaks were also observed for [ZrCl{P($SiMe_3$)(2,4,6-$Bu^t_3C_6H_2$}Cp_2],[111] [M{P$(SiMe_3)_2$}(X)Cp_2] (M = Zr, Hf, X = P$(SiMe_3)_2$, Me; M = Hf, X = Cl),[109] [Zr{P$(SiMe_3)_2$}$_2$(η-C_5H_4-Me)$_2$],[110] and [M{1,2-$(PPh)_2C_6H_4$}Cp_2] (M = Ti, Zr, Hf).[114] In the latter, the fragment $(C_6H_4)_2P^+$ gives the most intense peak.

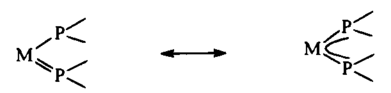
Elimination of $SiMe_3Cl$ or $SiMe_4$ was not detected in the fragmentation of monophosphido complexes with silylphosphido ligands.[109]

c. UV–Vis. Electronic spectra have been reported for the purple [HfH(PPh_2)Cp^*_2] (λ_{max} 580 nm) and the orange [HfH(PHR)Cp^*_2] (R = Cy, Ph; λ_{max} 415, 422 nm).[112]

3. Structural Data

Table 1 lists selected parameters of terminal phosphido complexes of Zr and Hf.

The Hf or Zr atom is coordinated in a distorted tetrahedral fashion in all complexes. The complexes [Hf$(PEt_2)_2Cp_2$],[106] [Hf{P$(SiMe_3)_2$}$_2$$Cp_2$],[109] and [Zr{1,2-$(PPh)_2C_6H_4$}{$\eta$-1,3-$(SiMe_3)_2C_5H_3$}$_2$][113] show two distinctly different bonding modes of the phosphido ligands. While the geometry about one P atom is pyramidal (sp^3), the other is trigonal planar (sp^2), suggesting donor interaction (**32**). Accordingly, unequal M–P bond lengths are observed (Δ = 0.20–0.09 Å). However, the difference in Zr–P bond lengths and P environments in [Zr{P$(SiMe_3)_2$}$_2$(η-C_5H_4Me)$_2$][110] and [Zr{PH(2,4,6-$Bu^t_3C_6H_2$)}$_2$$Cp_2$][124] is minor, suggesting the presence of delocalized π-electrons (**33**). According to Lauher and Hoffmann[133] π-interaction is strongest in these complexes if the trigonal-planar PR_2 ligand is orthogonal to the MP_2 plane. This is true for [Hf$(PEt_2)_2Cp_2$],[106] but the other complexes (Table 1) have a less favorable orientation for complete overlap of the ligand lone pair with the empty a_1 orbital of the $M^{IV}Cp_2$ moiety. In the monophosphido complexes the terminal phosphido unit functions as a three-electron donor, as evidenced by the approximately trigonal-planar geometry at phosphorus.



(19)

32 **33**

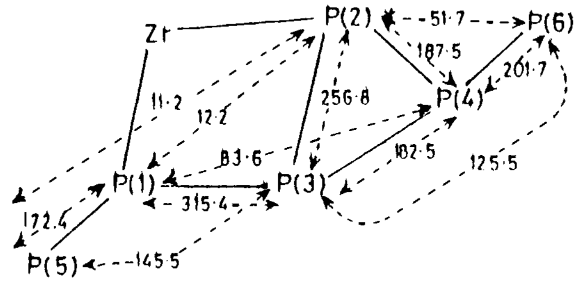


Figure 6. NMR coupling constants (hatched lines) (Hz) for [Zr{P(PR_2)PP(PR_2)P}Cp_2] (R = $SiMe_3$). Chemical shifts are P(1) 88.7, P(2) 62.9, P(3) −236.4, P(4) −110.6, P(5) −163.5, and P(6) −139 ppm. (Reprinted from ref 132. Copyright 1987 Chemical Society of London.)

Table 1. Selected Structural Parameters of Terminal Metallocene(IV) Phosphido Complexes

compound	M–P (Å)	sum of angles at P (deg)	refs
[ZrCl{P($SiMe_3$)(2,4,6-$Bu^t_3C_6H_2$)}Cp_2]	2.541(4)	359.5(5)	111
[Zr{1,2-$(PPh)_2C_6H_4$}{η-1,3-$(SiMe_3)_2C_5H_3$}$_2$]	2.560(4)	350	113
	2.647(6)	327	
[ZrCl{P$(SiMe_3)_2$}Cp_2]	2.547(6)	344.4	97,108
[ZrMe{P$(SiMe_3)_2$}Cp_2]	2.629(3)	349.2	97,108
[Hf$(PEt_2)_2Cp_2$]	2.488(1)	360	106
	2.682(1)	336	
[Hf{P$(SiMe_3)_2$}$_2$$Cp_2$]	2.553(1)	360	109
	2.654(1)	335	
[Zr{P$(SiMe_3)_2$}$_2$(η-C_5H_4Me)$_2$]	2.600(2)	351.2(1)	110
	2.634(2)	358.3(1)	
[HfH(PHPh)Cp^*_2][b]	2.549(8)		112
[Zr{PH(2,4,6-$Bu^t_3C_6H_2$)}$_2$$Cp_2$]	2.681(5)	356(1)[a]	124
	2.682(5)	321(2)	

[a] Proton not located crystallographically. [b] Crystallographic mirror plane exists, PHPh group is disordered.

Molecular structures of [M(PR–PR–PR)Cp_2] (M = Zr, R = Ph;[123] M = Hf, R = Ph;[120] M = Zr, R = Cy[122]) show that the central MP_3 core is essentially planar and only one diastereoisomer **31** is present in the solid state and in solution. The M–P bond lengths are comparable to those found in terminal phosphido complexes [M = Zr, R = Ph 2.622(3), 2.635(3) Å;[123] M = Hf, R = Ph 2.58(1), 2.59(1) Å;[120] M = Zr, R = Cy 2.618(4), 2.628(4) Å[122]]. The M··P distances (3.018–3.038 Å) suggest a weak transannular interaction.

In the trimeric phosphido-capped Zr(IV) complex shown in Figure 5 the P atom is located on a crystallographic 3-fold axis [Zr–P 2.575(1) Å].[129]

The phosphinidene-bridged complex [$(ZrClCp_2)_2$(μ-PMes)] has Zr–P bond lengths [2.597(6), 2.637(6) Å][117] comparable to those of terminal phosphido complexes. The Zr_2PC central core is planar with a Zr–P–Zr angle of 134.7(2)°.

[Zr{P(PR_2)PP(PR_2)P}Cp_2] (R = $SiMe_3$) (Figure 7) has a planar ZrP_3 four-membered ring with Zr–P bond lengths of 2.632(3) and 2.607(4) Å. Transannular Zr··P interaction, as in triphosphane-1,3-diyl complexes, is indicated by the Zr··P distance of 3.010(4) Å. In the solid state as well as in solution only one diastereoisomer is present [P atoms P(1) to P(4) all S or all R configuration].[132]

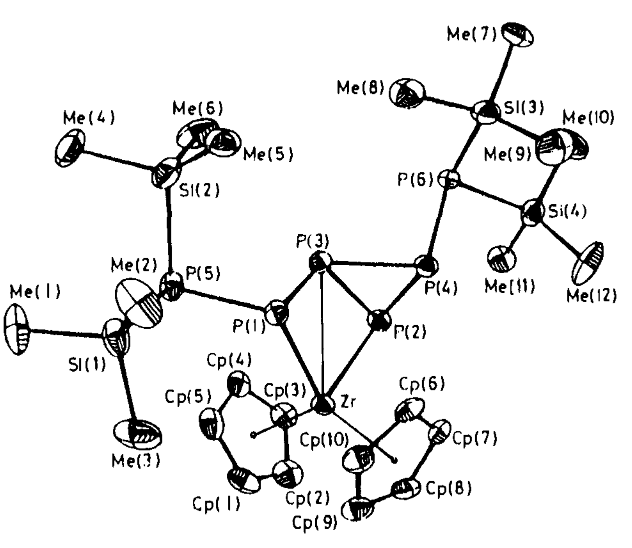
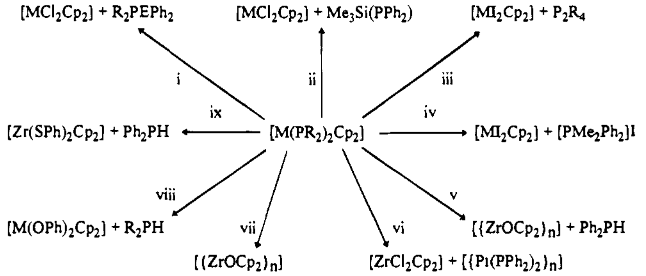


Figure 7. Molecular structure of $[\overline{Zr\{P(PR_2)PP(PR_2)P\}}Cp_2]$ (R = $SiMe_3$). (Reprinted from ref 132. Copyright 1987 Chemical Society of London.)

Scheme 14[a]



[a] (i) $2Ph_2ECl$ (M = Zr, Hf, R = Ph; M = Hf, R = Cy, E = P or As); (ii) Me_3SiCl (M = Zr, Hf, R = Ph); (iii) I_2 (M = Zr, Hf, R = Ph; M = Hf, R = Cy); (iv) 4MeI (M = Zr, Hf, R = Ph); (v) H_2O (M = Zr, R = Ph); (vi) $[PtCl_2(PhCN)_2]$; (vii) excess dry O_2 (M = Zr, R = Ph); (viii) 2PhOH (M = Zr, Hf, R = Ph; M = Hf, R = Cy); (ix) 2PhSH (M = Zr, R = Ph). For i–v and vii–ix ref 105; for vi ref 138.

Disorder of the 1,3-$Bu^t_2C_5H_3$ ligands in **29** (M = Zr, Hf) prevented determination of the crystal structure to complete crystallographic satisfaction.[130] However, the presence of a P_4-butterfly fragment with a $M(\eta$-1,3-$Bu^t_2C_5H_3)_2$ bridge was shown unambiguously.[130]

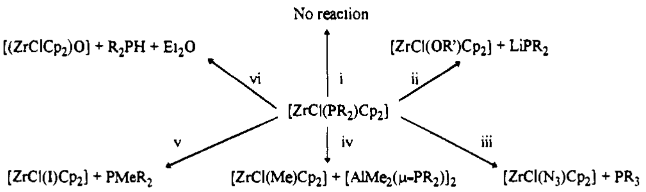
4. Chemical Properties

The terminal metallocene(IV) phosphido complexes are oxygen and moisture sensitive, especially in solution. They are intensely colored as solids and in solution (purple, red, or blue) and decompose rapidly in halogenated solvents.

The diphosphene complexes are green,[121,125] as is the bridging phosphinidene complex.[117]

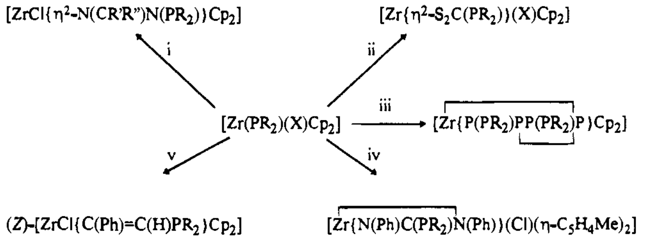
The complexes $[M(PR_2)_2Cp_2]$ (M = Zr, Hf, R = Ph; M = Hf, R = Cy) react with a variety of protic and halogen-containing species with cleavage of the M—P bond (Scheme 14).[105] When Me_2SiCl_2 instead of Me_3SiCl is reacted with $[Zr(PPh_2)_2Cp_2]$, an equilibrium mixture of starting materials and $[ZrCl(PPh_2)Cp_2]$, zirconocene dichloride, $Me_2SiCl(PPh_2)$, and $Me_2Si(PPh_2)_2$ is produced.[105] Aliphatic alcohols (MeOH, EtOH, Bu^tOH) and Et_2NH displace the PR_2 groups from $[Zr(PPh_2)_2Cp_2]$ as Ph_2PH, but the Zr products were poorly defined.[105]

Scheme 15[a]



[a] (i) LiMe; (ii) LiOR′ (R′ = 2,6-Bu^t_2-4-MeC_6H_2); (iii) $SiMe_3N_3$; (iv) $AlMe_3$; (v) MeI; (vi) EtOH; R = $SiMe_3$.

Scheme 16[a]



[a] (i) $N_2CR'R''$ (R′ = R″ = Ph; R′ = H, R″ = CO_2Et), X = Cl, ref 108; (ii) CS_2 (X = Cl, Me), ref 134; (iii) P_4 (X = PR_2), ref 132; (iv) PhN=C=NPh (X = Cl), ref 131; (v) Ph≡CH (X = Cl), ref 139; R = $SiMe_3$.

$[ZrCl\{P(SiMe_3)_2\}Cp_2]$ reacts with polar or protic reagents with displacement of the $P(SiMe_3)_2$ ligand (Scheme 15). Similarly, $[ZrMe\{P(SiMe_3)_2\}Cp_2]$ reacts with (2,4,6-$Bu^t_3C_6H_2$)PCl_2 to give $[ZrCl(Me)Cp_2]$ and the diphosphenes P_2(2,4,6-$Bu^t_3C_6H_2)_2$ and (2,4,6-$Bu^t_3C_6H_2$)P=$PSiMe_3$, the latter being unstable.[109] The reaction of $[Zr\{P(SiMe_3)_2\}_2Cp_2]$ with MeI led to elimination of $MeP(SiMe_3)_2$ and formation of $[ZrI\{P(SiMe_3)_2\}Cp_2]$.[97]

Reactions of $[HfH(PPh_2)Cp^*_2]$ with H_2, CO, and C_2H_4 proceed with reductive elimination of Ph_2PH and formation of the corresponding hafnocene derivatives $[HfL_2Cp^*_2]$ (L = H, CO, L_2 = butadiene).[112] Reaction of CO with $[M(PHBu^t)_2Cp^*_2]$ (M = Zr, Hf) led to reductive elimination of diphosphane $(PHBu^t)_2$ and formation of $[M(CO)_2Cp^*_2]$.[121] However, if a heterocumulene, white phosphorus, or phenylacetylene is reacted with $[Zr\{P(SiMe_3)_2\}(X)Cp_2]$ [X = Cl, $P(SiMe_3)_2$] insertion occurs with formation of novel P-functionalized ligands (Scheme 16, for CS_2 insertion cf. section VI.E.1; for diazoalkane insertion cf. section III.F.1).[97] $[ZrCl(PHMes)Cp_2]$ inserts diphenyl diazomethane into the Zr—P bond with formation of $[ZrCl\{\eta^2\text{-}N(CPh_2)N(PHMes)\}Cp_2]$.[98] No reaction was observed between $[Zr\{P(SiMe_3)_2\}_2\{\eta\text{-}C_5H_4(SiMe_3)\}_2]$ and Ph_2CN_2.[108] $[ZrCl\{P(SiMe_3)_2\}Cp_2]$ did not react with CO, while CO_2 led to decomposition.[97] However, $[HfH(PPh_2)Cp^*_2]$ undergoes successive insertion of CO_2 into the Hf—P and Hf—H bonds, with formation of $[HfH(\eta^2\text{-}O_2CPPh_2)Cp^*_2]$ and $[Hf\{OC(O)H\}\{OC(O)PPh_2\}Cp^*_2]$, respectively.[112]

Reaction of $[Zr\{P(SiMe_3)_2\}_2Cp_2]$ and $[ZrMe\{P(SiMe_3)_2\}Cp_2]$ with sulfur gives $[\{Zr(\mu\text{-}S)Cp_2\}_2]$ and unidentified P products.[134] In contrast, $[M(PR_2)_2Cp_2]$ (M = Zr, Hf, R = Cy, Ph) reacts cleanly with sulfur to give $[M(SPR_2)_2Cp_2]$ in 65–80% yield (^{31}P δ = 25.7–64.3 ppm) (cf. section VI.A.1).[135] The same products are obtained on reaction with SPR_2H.[135]

The dimeric complex $[\{ZrH(PH_2)Cp^*_2\}_2]$ selectively forms primary alkyl phosphines and zirconocene dihydride when treated with alkene and phosphine at 60–80 °C.[128]

Table 2

$$[M(PR_2)_2Cp_2] + M'LL_n \rightarrow [Cp_2M(\mu\text{-}PR_2)_2M'L_n] + L \qquad (21)$$

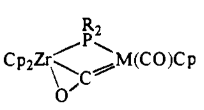
M	R	M′LL$_n$	M′L$_n$	yield (%)	refs
Zr,Hf	Et,Ph	$Rh(C_2H_4)_2$(η-indenyl)	Rh(η-indenyl)	86–90	150
Zr	Ph	*cis*-$Mo(NHC_5H_{10})_2(CO)_4$	$Mo(CO)_4$	80	144,147
Zr	Ph	$M'(PPh_3)_4$ (M′ = Ni, Pd, Pt) or $Pt(PPh_3)_2(CO)_2$	$M'(PPh_3)$	50–80	138,148
Zr	Ph	$Ni(CO)_2(PPh_3)_2$	$Ni(CO)_2$	85–90	138,148
Zr,Hf	Ph	$M'(H)(CO)(PPh_3)_2$ M′ = Rh, Ir	$M'(H)(CO)(PPh_3)$	65–75	149
Zr,Hf	Cy	$Rh(H)(CO)(PPh_3)_2$	$Rh(H)(CO)(PPh_3)$	65–75	149
Hf	Et	$Ni(CO)_4$	$Ni(CO)_2$	91	144
Hf	Et	$Fe_2(CO)_9$	$Fe(CO)_3$	45	144
Hf	Et	(nbd)$Mo(CO)_4$	$Mo(CO)_4$	44	144
Zr	$SiMe_3$	(nbd)$M'(CO)_4$ M′ = Cr,[a] Mo	$M'(CO)_4$	59–66	151
Zr	Ph	$Re_2(CO)_{10}$	$Re(H)(CO)_3$	17	145
Zr,Hf	Et	$Ni(cod)_2$	Ni(cod)	56–70	146
Zr,Hf[b]	Et	$Pd(PPh_3)_4$	$Pd(PPh_3)$	80	146
Zr,Hf	Et	$Pt(PPh_3)_4$	$Pt(PPh_3)$	80	146

[a] With C_5H_4Me ligands. [b] Product is contaminated with PPh_3 and $[Cp_2M(\mu\text{-}PEt)_2Pd(\mu\text{-}PEt)_2MCp_2]$.

Reduction of $[M(PR_2)_2Cp_2]$ (M = Zr, Hf, R = Et, Cy, Ph) with sodium naphthalenide (THF, 25 °C) produced the thermally stable Zr(III) and Hf(III) complexes $[Cp_2M(\mu\text{-}PR_2)_2Na(THF)_n]$ as shown by ESR spectroscopy.[106]

Metallocene bisphosphido complexes can be used for the synthesis of heterobi- and -trimetallic complexes if the reaction is with a potential precursor for a 12- or 14-electron fragment (cf. section IV.B.1). However, reaction of $[Zr(PR_2)_2Cp_2]$ (R = Ph, Cy) with $[\{M(CO)_3Cp\}_2]$ (M = Mo, W) results in reduction of the M—M bond and oxidation of one of the phosphido ligands with formation of yellow **34** (eq 20) in 70–85% yield.[136] **34** is also formed in the reaction of the zirconocene(III) complex $[\{Zr(\mu\text{-}PEt_2)Cp_2\}_2]$ with $[\{Mo(CO)_3Cp\}_2]$ in 70% yield.[137] Alternatively, **34** and Ph_2PH are formed in the reaction of $[MoH(CO)_3Cp]$ with $[Zr(PPh_2)_2Cp_2]$ in 80% yield.[136] A crystal structure determination was carried out on **34** (R = Et, M = Mo;[137] R = Ph, M = Mo[136]). The metal—metal distance [3.243(1),[137] 3.250(1) Å[136]] is comparable to that found in heterobimetallic phosphido-bridged complexes (cf. section IV.B.3), suggesting that direct Zr—Mo bonding is weak.

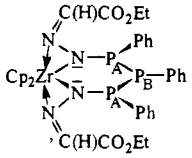
$$[Zr(PR_2)_2Cp_2] + 0.5\,[\{M(CO)_3Cp\}_2] \rightarrow$$



$+ R_2P\text{-}PR_2 + CO \qquad (20)$

34

The 1,2,3-trisubstituted triphosphane-1,3-diyl metallocene complexes $[M(PR—PR—PR)Cp_2]$ (M = Ti, Zr, Hf, R = Ph, Et, Me, Bu^t) react with CCl_4 and $CHCl_3$ with cleavage of the M—P bonds. Reaction with CS_2 was also observed, but the products were not characterized.[119] The reaction of $[Zr(PPh—PPh—PPh)Cp_2]$ with ethyl diazoacetate leads to insertion into both Zr—P bonds and formation of **35**. The stereochemistry of the P_3Ph_3 fragment of the starting material is retained in the product.[99]



35

The diphosphene complexes $[M(PR—PR)\{\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3\}_2]$ (M = Zr, Hf, R = Ph; M = Zr, R = Bu^t) are readily hydrolyzed to $[M(OH)_2\{\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3\}_2]$ and the *meso* and D,L isomers of $(PHR)_2$.[121]

It was not possible to generate a terminal phosphinidene complex by thermal or photochemical elimination of $SiMe_3Cl$ from $[ZrCl\{P(SiMe_3)(2,4,6\text{-}Bu^t_3C_6H_2)\}Cp_2]$.[111] Similarly, attempts to dehydrohalogenate $[M(PHR)(X)Cp^*_2]$ (M = Hf, X = I, R = Ph, Cy; M = Zr, Hf, X = Cl, R = Cy) with anionic bases [i.e. KH, BuLi, $NaN(SiMe_3)_2$] resulted in product mixtures.[112] However, when $[HfI(PHPh)Cp^*_2]$ was treated with $NaN(SiMe_3)_2$ at −78 °C, $HN(SiMe_3)_2$ and NaI were liberated and a red product of empirical formula $[Hf(PPh)Cp^*_2]_x$ was obtained (^{31}P 376 ppm).[112] Also, $[Zr(=PMes)Cp^*_2]$ is the proposed intermediate in the decomposition of $[Zr(PHMes)_2Cp^*_2]$, which yields $[Zr(PMes—PMes)Cp^*_2]$ or $[Zr(1\text{-}PH\text{-}2\text{-}CH_2\text{-}4,6\text{-}Me_2C_6H_2)Cp^*_2]$ as the final products.[124b]

B. Heterobimetallic and -trimetallic Phosphido-Bridged Metallocene(IV) Complexes

1. Synthesis

Although preparation of $[Cp_2Zr(\mu\text{-}PRR')_2Mo(CO)_4]$ (R = R′ = Me; R = H, R′ = Ph; R = Ph, R′ = $SiMe_3$) was reported as early as 1977,[140] it was only in 1985 that studies of heterobimetallic phosphido-bridged metallocene complexes were resumed. Some results are summarized in a review article.[141] Two synthetic routes have been described: (i) reaction of a metallocene bisphosphido complex with an appropriate transition metal compound (eq 21, Table 2), and (ii) reaction of zirconocene dichloride with a dilithio(bisphosphido)–transition metal complex $[M'L_n(PR_2Li)_2]$ to give $[Cp_2Zr(\mu\text{-}PR_2)_2M'L_n]$ [R = Ph, M′L$_n$ = $W(CO)_4$, 92% yield;[142] R = Ph, Cy, M′L$_n$ = $Fe(CO)_3$, 16–36% yield;[142] R = Ph, M′L$_n$ = $Fe(NO)_2$, 34% yield[143]].

In the reaction between $[Hf(PEt_2)_2Cp_2]$ and $Fe_2(CO)_9$ in hexane at room temperature the initially formed complex $[Cp_2Hf(PEt_2)(\mu\text{-}PEt_2)Fe(CO)_4]$ was isolated in 44% yield. Thermolysis of this product (toluene, 110 °C; solid state 139–140 °C) yields $[Cp_2Hf(\mu\text{-}PEt_2)_2Fe(CO)_3]$.[144]

Reaction of $[Zr(PPh_2)_2Cp_2]$ with $Re_2(CO)_{10}$ gave $[Cp_2Zr(\mu\text{-}PPh_2)_2Re(H)(CO)_3]$ in 17% yield. Monitoring of the reaction over 12 h by ^{31}P NMR showed the formation of numerous P species, including P_2Ph_4 and Ph_2PH.[145] The mechanism of formation and the source of the proton are unknown.

The reaction of metallocene bisphosphido complexes $[M(PR_2)_2Cp_2]$ with $[Pd(\eta\text{-}2\text{-}Me\text{-}allyl)Cp]$ or $[Pt(cod)_2]$ in the presence of equimolar amounts of a phosphine PR'_3 allows the synthesis of a variety of heterobimetallic complexes $[Cp_2M(\mu\text{-}PR_2)_2M'(PR'_3)]$ [(M′ = Pd) M = Zr, Hf, R = Cy, R′ = Ph; M = Zr, Hf, R = R′ = Ph; M = Zr, R = Ph, R′ = Me, Cy, OMe; M = Hf, R = Ph, R′ = O(*o*-Tol); (M′ = Pt) M = Zr, Hf, R = Cy, R′ = Ph; M = Zr, Hf, R = R′ = Ph; M = Hf, R = Ph, R′ = Me, Cy, OMe; M = Zr, R = Ph, R′ = O(*o*-Tol)].[146] The yellow to orange products are obtained in 44–84% yield.[146] With $P(OMe)_3$, mixtures of $[Cp_2M(\mu\text{-}PPh_2)_2M'\{P(OMe)_3\}_n]$ (M = Zr, M′ = Pd, *n* = 1, 2; M = Hf, M′ = Pt, *n* = 1, 2) were obtained.[146]

Several heterobimetallic phosphido-bridged complexes $[Cp_2M(\mu\text{-}PEt_2)_2M'L_n]$ have been reacted with $[M(PEt_2)_2Cp_2]$ (M = Zr, Hf) to give phosphido-bridged heterotrimetallic complexes $[\{Cp_2M(\mu\text{-}PEt_2)_2\}_2M']$ (M = Zr, Hf, M′ = Ni, L_n = 1,5-cod; M = Zr, Hf, M′ = Pd, L_n = PPh_3; M = Zr, Hf, M′ = Pt, L_n = PPh_3).[146] The products are obtained as orange or dark red crystals in 31–74% yield. The red-purple complex $[\{Cp_2Hf(\mu\text{-}PPhCH_2CH_2CH_2PPh)\}_2Ni]$ with unsymmetrically substituted phosphido ligands was prepared accordingly in 85% yield.[146]

Heterotrimetallic complexes (Zr/Pd/Hf or Zr/Pt/Hf) have been synthesized by reacting $[Zr(PEt_2)_2Cp_2]$ with $Pd(PPh_3)_4$ or $Pt(PPh_3)_4$ followed by addition of $[Hf(PEt_2)_2Cp_2]$.[146] The products were characterized in situ by ^{31}P NMR; the spectra also showed the presence of PPh_3 and the corresponding bimetallic complexes Zr/Pd or Zr/Pt and Hf/Pd or Hf/Pt.[146]

2. Spectroscopic Data

The complexes are yellow to red-orange crystalline solids (an exception is $[Cp_2Zr(\mu\text{-}PPh_2)_2Fe(NO)_2]$, which is purple), while the metallocene bisphosphido precursors are deep violet to deep red; this indicates that the charge-transfer system in the latter is disrupted on formation of heterobimetallic complexes.

a. ^1H NMR. The bimetallic complexes that have a quasi-mirror plane show one signal for the Cp protons in the ^1H NMR spectrum (range 4.8–5.6 ppm),[142–144,146–148] which is occasionally split into a triplet by coupling to the two bridging phosphido groups [^2J(P–H) 1–1.5 Hz].[146] The complexes without a quasi-mirror plane show two signals in the range 4.8–5.6 ppm consistent with the chemical inequivalence.[145,149]

In $[Cp_2M(\mu\text{-}PR_2)_2Rh(\eta\text{-}indenyl)]$ (M = Zr, Hf, R = Et, Ph) fluctuation of the indenyl ligand results in the observation of one signal for the Cp protons at 95 °C, while two signals are observed at −60 °C ($\Delta G^{\ddagger}$ = 58.2–62.8 kJ mol^{-1}).[150]

b. ^{31}P NMR. A singlet, which may be split into a doublet in the presence of coordinated phosphine ligands [^2J(P–P) 4–22 Hz], is observed for the bridging phosphido ligands of heterobimetallic complexes in the range 85–182 ppm (cf. chemical shift of the corresponding metallocene(IV) bisphosphido complexes, 100–160 ppm; section IV.A.2).[138,142–150] The phosphido-bridged heterotrimetallic complexes exhibit a singlet (symmetrical substitution) or two triplets [^2J(P–P) 20–25 Hz] for unsymmetrically substituted complexes in the range of 94–140 ppm in the ^{31}P NMR spectra, which is comparable to the range observed for heterodinuclear complexes.[146]

c. IR. A band at 347 cm^{-1} (M = Zr) and 302 cm^{-1} (M = Hf) was assigned to the ν(M–P) stretching mode in $[Cp_2M(\mu\text{-}PPh_2)_2M'(PPh_3)]$ (M = Zr, Hf; M′ = Pd, Pt).[146] In $[Cp_2M(\mu\text{-}PR_2)_2Rh(\eta\text{-}indenyl)]$ the ν(M–P) mode was assigned a medium to weak band at 325–338 cm^{-1} (M = Zr, R = Et, Ph) or 286–302 cm^{-1} (M = Hf, R = Et, Ph).[150] The ν(CO) modes of the heterobimetallic complexes with $M(CO)_n$ fragments closely resemble those of the depe-substituted analogues, suggesting a comparable bonding situation at the metal center in these complexes (i.e., no or weak metal–metal interaction).[142,144,147]

d. UV–Vis. The electronic spectra of $[Cp_2M(\mu\text{-}PPh_2)_2M'(H)(CO)(PPh_3)]$ (M = Zr, Hf, M′ = Rh, Ir) and $[Cp_2Zr(\mu\text{-}PCy_2)_2Rh(H)(CO)(PPh_3)]$ exhibit two absorption bands in the range 274–284 and 364–376 nm, respectively.[149] The orange-yellow complex $[Cp_2Zr(\mu\text{-}PPh_2)_2Mo(CO)_4]$ shows three absorptions at 306, 347, and 416 nm.[147]

e. Mass Spectra. The complexes $[Cp_2Zr(\mu\text{-}PR_2)_2M(CO)_n]$ (R = Ph, M = W, *n* = 4; R = Cy, Ph, M = Fe, *n* = 3)[142] and $[Cp_2Zr(\mu\text{-}PPh_2)_2Fe(NO)_2]$[143] exhibit parent ion peaks in the mass spectra as well as signals corresponding to successive loss of CO and NO, respectively.

3. Structural Data

Crystallographic data are available for one heterotrimetallic and for several heterobimetallic phosphido-bridged complexes (Table 3).

In the heterotrimetallic complex $[Cp_2Zr(\mu\text{-}PEt_2)_2Ni(\mu\text{-}PEt_2)_2HfCp_2]$ the Zr and Hf atoms are disordered with respect to their crystallographic positions (50:50 occupancy).[146] The MP_2Ni rings are nearly planar, with Ni showing a distorted tetrahedral coordination.[146]

The influence of the bridging PR_2 group on the observed metal–metal distance is exemplified by comparing the structure of $[Cp_2Hf(\mu\text{-}PEt_2)_2Mo(CO)_4]$[144] with $[Cp_2Zr(\mu\text{-}PPh_2)_2M'(CO)_4]$ (M′ = W[142] or Mo[147]). As the covalent radii of Zr and Mo are very similar to those of Hf and W the shorter M–M′ distance in the PPh_2-bridged complexes must result primarily from the bulkier PPh_2 bridges, which result in a decrease in the M–P–M′ angle and a shorter M–M′ distance (cf. Table 3).

In several complexes the MP_2M' core is essentially coplanar, while others exhibit a butterfly arrangement (dihedral angle up to 28°, cf. Table 3). The reason for this distortion of the core atoms is not clear; metal–metal interactions and crystal packing effects have been suggested.

Table 3. Selected Structural Parameters for $[(\eta\text{-}C_5H_4R)_2M(\mu\text{-}PR'_2)_2M'L_n]$

M	R	R′	$M'L_n$	M—P (Å)	M···M′ (Å)	$MP_2/M'P_2$ (deg)	M—P—M′ (deg)	ref
Zr	H	Ph	Rh(η-indenyl)	2.590(1)	3.088(1)	*a*	78.70(2)	150
Zr	H	Ph	$W(CO)_4$	2.619(3) 2.631(3)	3.289(1)	1.6	79.2(1)	142
Zr[b]	H	Ph	$Mo(CO)_4$	2.618(3) 2.631(3)	3.290(1)	2.8	79.2(1) 79.1(1)	152
Zr[b]	H	Ph	$Mo(CO)_4$	2.631(1) 2.630(1)	3.299(1)	*a*	79.1(1) 79.2(1)	147
Zr[c]	H	Ph	$Rh(H)(CO)(PPh_3)$	2.671(2) 2.698(2)	2.980(1)	9.94	72.4(1) 73.0(1)	149
Hf[c]	H	Ph	$Rh(H)(CO)(PPh_3)$	2.640(2) 2.672(2)	2.964(1)	9.73	73.2(1) 72.4(1)	149
Hf	H	Et	$Mo(CO)_4$	2.592(1) 2.596(1)	3.400(1)	7.7	83.01(3)	144
Zr	Me	$SiMe_3$	$Cr(CO)_4$	2.654(4) 2.657(4)	3.414(1)	14.7	82.65(7) 82.80(7)	151
Zr	H	$SiMe_3$	$Mo(CO)_4$	2.6585(7) 2.6711(9)	3.461(1)	14.2	81.56(2) 81.71(2)	151
Hf	H	Ph	$Pd(PPh_3)$	2.627(2) 2.615(2)	2.896(1)	24.49	71.43(5) 71.63(4)	146
Hf	H	Ph	Pd(dmpe)[d]	2.618(3) 2.607(3)	2.983(1)	27.25	74.30(7) 74.36(7)	146
Zr	H	Ph	$Re(H)(CO)_3$	2.629(3) 2.615(3)	3.274(1)	*a*	72.4(1) 73.0(1)	145

[a] Not reported. [b] The crystal structure was determined independently by two groups (refs 147 and 152); the only difference is that one crystal structure[152] has solvent of crystallization. [c] Zr and Hf complex are isostructural; the hydride was not located. [d] dmpe = $(Me_2PCH_2)_2$.

Extended Hückel molecular orbital calculations performed on the model complexes $[Cp_2Zr(\mu\text{-}PH_2)_2M'L_n]$ [$M'L_n$ = $Pt(PH_3)$, Pt(dmpe) (dmpe = $(Me_2PCH_2)_2$), Rh(η-indenyl), $Ni(\mu\text{-}PH_2)_2ZrCp_2$, $Mo(CO)_4$] indicate the presence of M′ ⇒ Zr donor–acceptor metal–metal bonds that become weaker along the series Pt > Rh > Ni > Mo.[146]

4. Chemical Reactivity

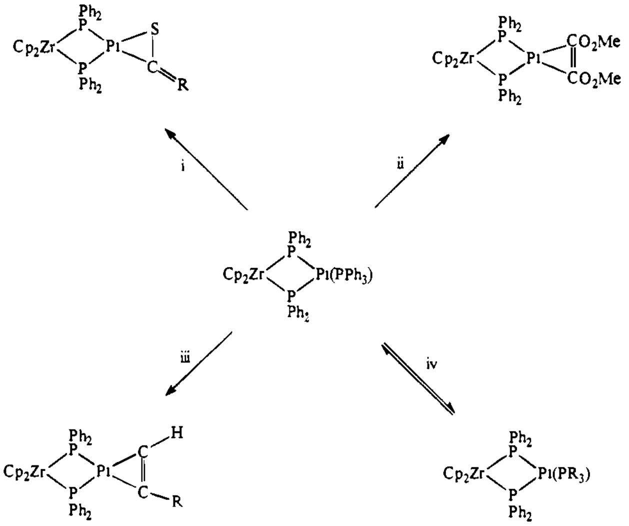
The complexes $[Cp_2M(\mu\text{-}PPh_2)_2M'(H)(CO)(PPh_3)]$ (M = Zr, Hf, M′ = Ir, Rh) and $[Cp_2M(\mu\text{-}PCy_2)_2Rh(H)(CO)(PPh_3)]$ (M = Zr, Hf) are air stable.[149] Some heterobimetallic complexes with $M'(CO)_n$ fragments [$M'(CO)_n$ = $W(CO)_4$, $Fe(CO)_3$] are air stable in the solid state but decompose rapidly in solution on exposure to air.[142,144,147] Complexes with $M'(PPh_3)$ fragments (M′ = Ni, Pd, Pt) are air sensitive.[148]

Ligand substitution reactions at the late transition metal center of $[Cp_2Hf(\mu\text{-}PEt_2)_2Ni(cod)]$,[146] $[Cp_2M(\mu\text{-}PPh_2)_2M'(PPh_3)]$ (M = Hf, M′ = Pd; M = Zr, M′ = Pt),[146] and $[Cp_2Zr(\mu\text{-}PPh_2)_2Rh(H)(CO)(PPh_3)]$[149] have been intensively studied.

The electrophilic substitution reactions shown in Scheme 17 are typical for Pt(0). However, oxidative addition of MeI and $Me_3O^+BF_4^-$ was not observed, which is unusual for Pt(0) complexes. The diminished reactivity of Pt in these complexes is possibly due to metal–metal interaction (cf. section IV.B.3).[148] However, reaction of $[Cp_2M(\mu\text{-}PEt_2)_2Rh(\eta\text{-}indenyl)]$ (M = Zr, Hf) with MeI proceeds with formation of $[Cp_2M(\mu\text{-}PEt_2)_2Rh(Me)(\eta\text{-}indenyl)]^+I^-$, while no reaction is observed with H_2 (1 atm), CO (1 atm), or acetyl chloride.[150]

No reaction was observed between $[Cp_2M(\mu\text{-}PPh_2)_2M'(PPh_3)]$ (M = Hf, M′ = Pd; M = Zr, M′ = Pt) and CO, H_2, ethylene (1 atm), excess Bu^{t}CN, benzaldehyde, paraformaldehyde, or MeI.[146] More reactive oxidative agents such as acetyl bromide react with disruption of the PPh_2 bridge.[146]

Scheme 17[a]



[a] (i) SCNPh or CS_2, ref 148 [R = S, NPh (for NPh product was not isolated)]; (ii) $MeO_2CC{\equiv}CCO_2Me$, ref 148; (iii) HC≡CPh or $HC{\equiv}CO_2Me$, with MeI, refs 138, 148 (R = CO_2Me, Ph), $-[PPh_3Me]I$; (iv) PEt_3 or PCy_3, ref 148 (R = Et, Cy; an equilibrium mixture is obtained, products were not isolated).

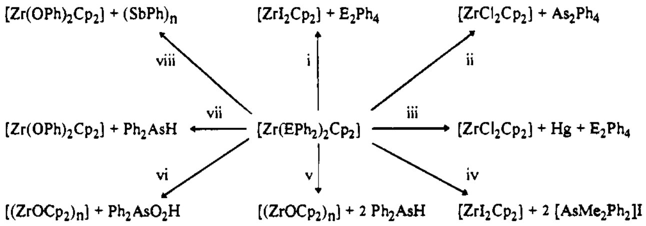
$[Cp_2Zr(\mu\text{-}PPh_2)_2W(CO)_4]$ did not react with diphenylacetylene, $PMePh_2$, or CS_2 thermally or photochemically.[142] The reaction with LiR (R = Me, Bu, Ph, BEt_3H) led to unidentifiable products.[142]

$[Cp_2Zr(\mu\text{-}PPh_2)_2Rh(H)(CO)(PPh_3)]$ acts as a catalyst precursor for the catalytic hydroformylation of 1-hexene. The rate is considerably slower than that of known monometallic rhodium catalysts; however, with the heterobimetallic complex a dramatic increase in selectivity for the terminal aldehyde product was observed.[149]

C. Metallocene(IV) Arsenido and Antimonido Complexes

1. Synthesis

Scheme 18[a]



[a] I_2 (E = As, Sb); (ii) Ph_2AsCl, (E = As); (iii) $HgCl_2$ (E = As, Sb); (iv) excess MeI (E = As); (v) H_2O (E = As); (vi) moist air (E = As); (vii) 2PhOH (E = As); (viii) 2PhOH (E = Sb).

Only a small number of zirconocene arsenido and antimonido complexes $[Zr(ER'_2)_2(\eta\text{-}C_5H_4R)_2]$ (E = As, Sb, R = H, R′ = Ph;[153] E = As, R = H, Me, R′ = $SiMe_3$[154]) is known. The synthesis is based on salt-elimination reactions between zirconocene dichloride and the appropriate lithium reagent. Only one monoarsenido complex $[Zr\{As(SiMe_3)_2\}(Cl)(\eta\text{-}C_5H_4Me)_2]$ has been synthesized to date.[154] The complexes are deeply colored (red), highly air and moisture sensitive, and decompose in halogenated solvents.

2. Spectroscopic Properties

Although IR data were reported for all complexes, the ν(Zr—E) mode (E = As, Sb) was not unambiguously assigned.[153]

The ^1H NMR spectra show a single resonance for the Cp protons of $[Zr(EPh_2)_2Cp_2]$ with a down-field shift in the order Sb > As > P, which is the reverse of that expected from electronegativity values and implies that d_π—p_π back-bonding is more pronounced for Zr—Sb than Zr—P.[153]

Mass spectrometric studies on $[Zr(AsPh_2)_2Cp_2]$ failed to detect Zr-containing fragments; only ions derived from polyarsenic species were observed.[153]

3. Structural Data

The crystal structures of $[Zr\{As(SiMe_3)_2\}(Cl)(\eta\text{-}C_5H_4Me)_2]$ and $[Zr\{As(SiMe_3)_2\}_2Cp_2]$ have been determined.[154] The bisarsenido complex exhibits two distinctly different Zr—As bond lengths [Zr—As1 2.799(2), Zr—As2 2.616(2) Å], which indicates the presence of a Zr—As single and double bond. The geometry of the arsenido groups is in agreement with this formulation [sum of angles at As1, 329.2(2), and at As2, 360.0(2)°]. In the monoarsenido complex, the Zr—As bond length [2.7469(7) Å; sum of angles at As is 328.9(5)°] is intermediate between those of the bisarsenido complex.[154]

4. Chemical Properties

Reactions of $[Zr(EPh_2)_2Cp_2]$ (E = As, Sb) with protic species and halogenated reagents lead to cleavage of the Zr—E bond (Scheme 18).[153] No evidence was found for a mixed halide/EPh_2 complex in the reactions with halogen sources.[153]

V. Metallocene(IV) Complexes with O-Centered Anionic Ligands

A. Metallocene Alkoxides and Aryloxides

1. Synthesis

Zirconocene alkoxides were first reported in the patent literature in 1960,[155] but the compounds were not fully characterized. Two major preparative routes have been employed. These are, first, the reaction of a metallocene dihalide with excess alcohol in the presence of excess base to give $[M(OR)_2(\eta\text{-}C_5H_4R')_2]$ (M = Ti, Zr, Hf, R′ = H, Me, R = Ph, 4-$Bu^tC_6H_4$, 2,4-$Cl_2C_6H_3$, 2,4,6-$Cl_3C_6H_2$, 2,5-$Me_2C_6H_3$, *m*-Tol, base = $NaNH_2$ or NaH;[156] M = Hf, R′ = $SiMe_3$, R = Me, Et, base = NEt_3;[157] M = Zr, R′ = H, R = 3,5-$Me_2C_6H_3$, 2,4-$Me_2C_6H_3$, base = NEt_3;[158] M = Ti, Zr, Hf, R′ = alkyl, R = Ph, Tol, halophenyl, base = $NaNH_2$, NEt_3;[159] M = Ti, Zr, Hf, R′ = Me, R = aryl, base = $NaNH_2$;[160] M = Ti, Zr, Hf, R′ = H, R = aryl, base = $NaNH_2$, NEt_3;[161] M = Zr, R′ = H, Me, ROH = 2,2′-dihydroxybiphenyl, 1,1′-dihydroxy-2,2′-binaphthyl, resorcinol;[162] M = Ti, Zr, R′ = Me, R = α- or β-nap, base = NEt_3;[163] M = Ti, Zr, R′ = H, R = α- or β-nap, base = NEt_3[164]) and, second, the reaction of a metallocene dichloride with alkali metal alkoxides or aryloxides (M′OR) to give $[MCl(OR)(\eta\text{-}C_5H_4R')_2]$ (M = Zr, R′ = H, M′ = Li, R = 2,6-$Pr^i_2C_6H_3$, 2,6-$Bu^t_2C_6H_3$, 2,6-Bu^t_2-4-MeC_6H_2, 2,4,6-$Bu^t_3C_6H_2$;[46] M = Hf, R′ = $SiMe_3$, M′ = Na, R = Me[157]).

Excess of alcohol and base is necessary to prevent formation of inseparable mixtures of the mono- and disubstituted products.[157] However, with the bulky α- or β-nap ligand either the mono- or the disubstituted products can be obtained in 60–65% yield.[163,164] The disubstituted complexes have also been obtained from $[ZrCl_2(\eta\text{-}C_5H_4Me)_2]$ and NaOR (R = α- or β-nap).[163,164] Treatment of $[(ZrClCp_2)_2O]$ with ROH (R = Ph, 4-ClC_6H_4, 4-BrC_6H_4) in the presence of NEt_3 gives $[\{Zr(OR)Cp_2\}_2O]$.[156] The reaction of $[MCl_2\{(\eta\text{-}(C_5H_4)_2X\}]$ [M = Ti, Zr, Hf, X = $(Me_2Si)_n$ with n = 2 or 3, $Me_2SiOSiMe_2$] with phenols was studied.[165]

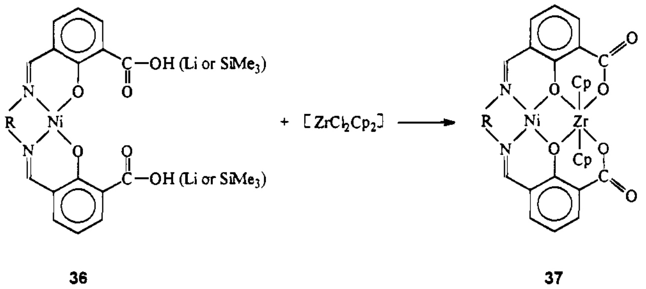
The reaction of zirconocene dichloride with bulky lithium aryloxides $[Li(OEt_2)(OR)]_2$ [R = 2,6-$Pr^i_2C_6H_3$, 2,6-$Bu^t_2C_6H_3$, 2,6-Bu^t_2-4-MeC_6H_2, 2,4,6-$Bu^t_3C_6H_2$] is slow in refluxing THF (2–4 days), but addition of TMEDA leads to significant acceleration.[46] No further substitution was observed when an excess of lithium reagent[46] or the sodium alkoxide[157] was used. No reaction of the lithium reagents was observed with $[ZrCl_2\{\eta\text{-}1,3\text{-}(SiMe_3)_2C_5H_3\}_2]$, $[ZrCl_2\{\eta\text{-}C_5H_4(SiMe_3)\}_2]$, or $[ZrCl_2(\eta\text{-}C_5H_4Bu^t)_2]_2$,[46] and zirconocene dichloride did not react with $[Li(OEt_2)(OR]_n$ (R = 3,5-$Bu^t_2C_6H_3$, 2,4-$Bu^t_2C_6H_3$).[46]

Zirconocene bisaryloxides with bulky aryloxo ligands $[Zr(OR)_2Cp_2]$ (R = 2,6-$Pr^i_2C_6H_3$, 3,5-$Bu^t_2C_6H_3$) are obtained from $[Zr(NMe_2)_2Cp_2]$ and the corresponding alcohol with facile elimination of dimethylamine.[46] Use of 1 equiv of alcohol also gave the disubstituted product. By contrast, the sterically demanding phenols ROH (R = 2,6-$Bu^t_2C_6H_3$, 2,6-Bu^t_2-4-MeC_6H_2) gave only the monosubstituted products $[Zr(OR)(NMe_2)Cp_2]$ regardless of the stoichiometry employed.[46] However, reaction of $[Zr(OR)(NMe_2)Cp_2]$ (R = 2,6-$Bu^t_2C_6H_3$) with methanol gave $[Zr(OMe)(OR)Cp_2]$ in 11% yield.[46]

Schiff base derivatives of zirconocene have been obtained from zirconocene dichloride and the bidentate Schiff bases SBH (SBH = 2-HO-C_6H_4CH=NR; with R = Ph, *o*-, *m*-, or *p*-Tol;[166] R = Bz, nap, $C_6H_4R^1$, with R^1 = 2- or 3-MeO, 2-EtO, 2- or 3-Cl, 3-NO_2;[167] R = 4-$R^2C_6H_4$, with R^2 = Cl, Br, I, NO_2, OMe, OEt[168]), the terdentate Schiff bases $SB'H_2$ [$SB'H_2$ = *N*-(3-oxo-

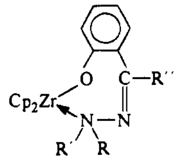
1-methylbutylidene)-*o*-aminophenol and *N*-(3-oxo-1-phenylbutylidene)-*o*-aminophenol],[166] and the quadridentate Schiff base SB″H_2 (SB″H_2 = *N,N′*-disalicylidene-*o*-phenylenediamine)[166] in the presence of NEt_3. The resulting products show *O,N*-, *O,O′,N*-, or *O,O′,N,N′*-coordination of the Schiff base derivatives.

The Ni(II) complex of a quadridentate Schiff base **36** [R = $(CH_2)_2$, $(CH_2)_3$, *o*-C_6H_4] has been employed as a ligand for Cp_2Zr in **37** (eq 22).[169]



36 37 (22)

Hydrazone **38** (R = Bz, R′ = R″ = H; R = Ac, R′ = Ph, R″ = H;[170] R = H, Ph, 2,4-$(NO_2)_2C_6H_3$, R′ = H, R″ = H, Me[171]) and azine derivatives **39** (R = Me, R′ = Me, Ph, R″ = 2- or 3-py; R = H, Me, R′ = *o*-OC_6H_4, R″ = 2- or 3-py; R = Me, R′ = Me, Ph, R″ = 2- or 3-py)[172] of Zr have been prepared by treating $[ZrCl_2Cp_2]$ with the appropriate hydrazone or azine at elevated or room temperature in the presence of butylamine or NEt_3. Complexes of type **39** with the tetracoordinated ligands $\{OCR''{=}N{-}N{=}C(Me){-}\}_2$ (R″ = 4-$MeOC_6H_4$)[173] and $(o\text{-}OC_6H_4{-}CR''{=}N{-})_2$ (R″ = H, Me)[171] were prepared analogously. The products were characterized by IR, NMR, and UV–vis spectroscopy.[171–173]



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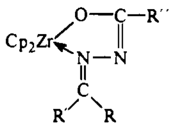

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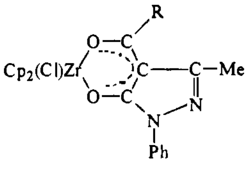
$[ZrCl_2Cp_2]$ reacts with pyrazolone derivatives in the presence of NEt_3 with formation of the monosubstituted complexes **40** (R = Me, Et, Ph, 4-ClC_6H_4).[174]



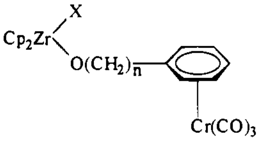
40

The solubility of polyoximes of zirconocene or hafnocene was evaluated. Monomeric model complexes such as $[M(ON{=}R)_2Cp_2]$ (M = Zr, Hf, R = Cy) were prepared and their solubility studied.[175]

The reaction of $[ZrMe_2Cp_2]$ with alcohols proceeds rapidly with elimination of methane and formation of the corresponding alkoxide or aryloxide.[176,177] Thus, R_3SiOH (R = Et, Ph) gives $[Zr(OSiR_3)_2Cp_2]$ in 60% (R = Ph) or quantitative (R = Me) yield,[177] and Bu^tMe_2SiOH yields $[ZrMe(OSiBu^tMe_2)Cp_2]$.[178] Similarly, (*E*)-HOCRR′CH=CHR″ gives (*E*)-[ZrMe(OCRR′CH=CHR″)Cp_2] (R = R′ = Me, R″ = H; RR′ = $(CH_2)_4$, R″ = H; R = H, R′ = R″ = Me) in 74–95% yield.[179] The diols 2,2-dimethylpropane-1,3-diol and 1,3-benzenedimethanol afford the macrocyclic zirconocene dialkoxides $[Cp_2Zr(\mu\text{-}OCH_2{-}X{-}CH_2O)_2ZrCp_2]$ (X = CMe_2, C_6H_4) in 65 and 29% yield, respectively.[180]

Elimination of toluene was employed in the synthesis of $[ZrBz(OR)Cp_2]$ from dibenzyl zirconocene and ROH (R = 2-Me-6-$Bu^tC_6H_3$, 2,4-Me_2-6-(α-methylcyclohexyl)C_6H_2)[181] in boiling toluene or at ambient temperature (R = Me).[182]

Complexes **41** in which a difunctional ligand bridges two or three metals were obtained from dibenzyl zirconocene (*n* = 1, X = Bz) or dimethyl zirconocene [*n* = 1, X = $OCH_2C_6H_5Cr(CO)_3$] and $[(HOCH_2C_6H_5)Cr(CO)_3]$ in 32–46% yield,[183] or from $[ZrCl_2Cp_2]$ or $[Zr(NMe_2)_2Cp_2]$ and $[NEt_4][OC_6H_5Cr(CO)_3]$ (*n* = 0, X = $OC_6H_5Cr(CO)_3$) in 60% yield.[184]



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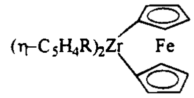
Complex **42** (R = Bu^t) reacts with R′OH (R′ = Me, Bz, 3,5-$(MeO)_2Bz$) with successive formation of $[Zr(OR')(Fc)(\eta\text{-}C_5H_4Bu^t)_2]$ and $[Zr(OR')_2(\eta\text{-}C_5H_4Bu^t)_2]$.[185]



42

Oligomeric zirconocene hydride chlorides react with methanol at −75 °C with formation of $[ZrCl(OMe)(\eta\text{-}C_5H_4R)_2]$ (R = H, Me) and elimination of H_2.[186]

Other synthetic routes include:

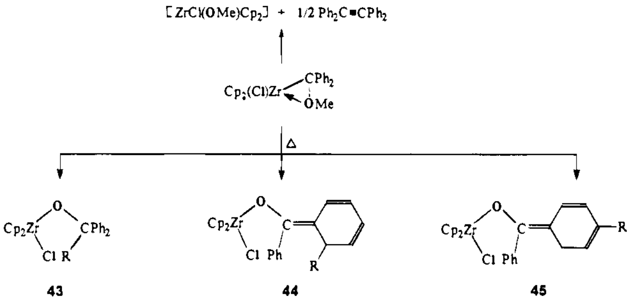
(i) Autoxidation of dialkyl zirconocenes gives $[Zr(OR)_2Cp_2]$ (R = Me,[179] R = Me, Bz, substituted Bz[187]) in good yield. Kinetic studies showed these reactions to be free-radical chain reactions involving an S_H2 type displacement of an alkyl radical from the metal center by an alkylperoxyl radical.[179,187] Peroxo complexes $[Zr(O_2R)(R)Cp_2]$ are the proposed intermediates. In the autoxidation of $[ZrR(X)Cp^*_2]$ (R = Me, Bz, X = R, Cl) and $[ZrBz_2CpCp^*]$ formation of alkoxo complexes is not observed.[182] Rates of initiation and oxidation have been compared with those of the corresponding Cp_2Zr complexes.[182] However, the reaction of Bu^tCOOH with $[HfH(R)Cp^*_2]$ gives stable *tert*-butyl peroxo complexes $[Hf(OOBu^t)(R)Cp^*_2]$ (R = Cl, H, Me, Et, Pr, CH=CHBu^t, Ph, 3,5-$Me_2C_6H_3$,[188] or $CH_2CH_2CMe_3$[189]); $[Hf(CH_2CHMeCH_2)Cp^*_2]$ and $[Hf(CH_2CH_2CH_2CH_2)Cp^*_2]$ yield $[Hf(OOBu^t)RCp^*_2]$ (R = CH_2CHMe_2, Bu).[188] The thermal stability of these complexes is sufficient for their isolation, except for $[HfH(OOBu^t)Cp^*_2]$, which decomposes above −35 °C. In the IR spectra the ν(OO) mode is observed at

835–850 cm^{-1}.[188] The mode of decomposition of these complexes depends on the ligand R. Only for R = H, Me, Et, Pr, Bu, CH_2CHMe_2,[188] and $CH_2CH_2Bu^t$ [189] is smooth decomposition to $[Hf(OBu^t)(OR)Cp^*_2]$ observed. Neohexyl migration from Hf to oxygen in *threo-* and *erythro-*$[Hf(CHDCHDBu^t)(OOBu^t)Cp^*_2]$ to give *threo-* and *erythro-*$[Hf(OCHDCHDBu^t)(OBu^t)Cp^*_2]$ occurs with retention of the configuration at the migrating carbon center.[189] Kinetic studies suggest an intramolecular rearrangement.

(ii) Insertion of propylene oxide into the Zr–Cl bond of $[ZrCl_2Cp_2]$ furnishes both $[ZrCl\{OCH(CH_2Cl)CH_3\}Cp_2]$ (90%) and $[ZrCl(OCH_2CHClCH_3)Cp_2]$ (10%).[190]

(iii) From zirconocene alkyl ethers the following routes are followed:

(a) Thermolysis of $[ZrCl\{CHMe(OEt)\}Cp_2]$ at 145 °C gives $[ZrCl(OEt)Cp_2]$ and ethylene.[191] Similarly, $[Zr\{CH_2(OMe)\}_2(\eta\text{-}C_5H_4R)_2]$ (R = H, Me) lose ethylene upon heating at 70 °C with formation of $[Zr(OMe)_2(\eta\text{-}C_5H_4R)_2]$.[186] Rearrangement of $[ZrCl\{CPh_2(OMe)\}Cp_2]$ at ambient temperature proceeds with elimination of alkene (eq 23).[192] At elevated temperature rearrangement to **43**, **44** and **45** (R = Me) is observed.[192]



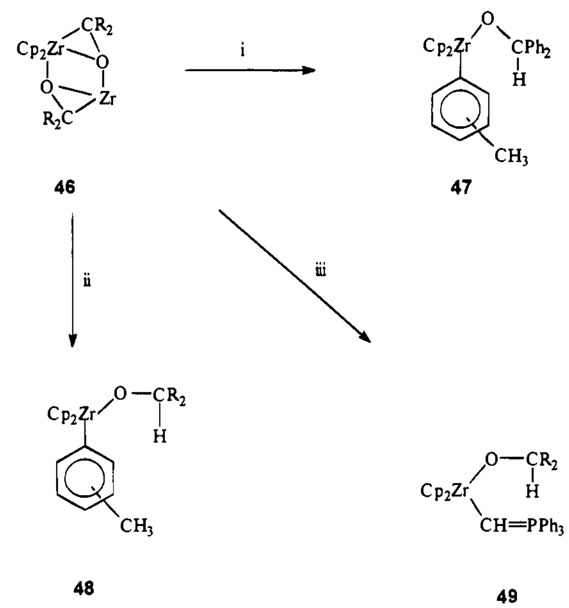
(23)

Comparable is the reaction of the ketone complex $[\{Zr(\eta^2\text{-}CPh_2O)Cp_2\}_2]$ with alkyl halides, which yields the products **43**–**45** (R = Me, Et, tetrahydrofurfuryl, allyl, 2-propyl, 2-octyl, Bu^t).[193,194] $[ZrCl\{CH_2(OCH_2Ph)\}Cp_2]$ underwent a Wittig rearrangement at 110 °C to give $[ZrCl(OCH_2CH_2Ph)Cp_2]$ as the major product.[195] A radical mechanism is discussed for all these reactions.

(b) Reaction of the zirconocene alkyl ether $[ZrCl\{CH_2(OMe)\}Cp_2]$ with zirconocene hydride chloride at 40 °C gives $[ZrCl(OMe)Cp_2]$ and methyl zirconocene chloride.[196] Similarly, $[ZrCl\{CPh_2(OMe)\}Cp_2]$ gives $[ZrCl(OMe)Cp_2]$ and $[ZrCl(CHPh_2)Cp_2]$, but also $[ZrCl_2Cp_2]$ and $[Zr(CHPh_2)(OMe)Cp_2]$.[197] Therefore, two different pathways have been suggested for this reaction.

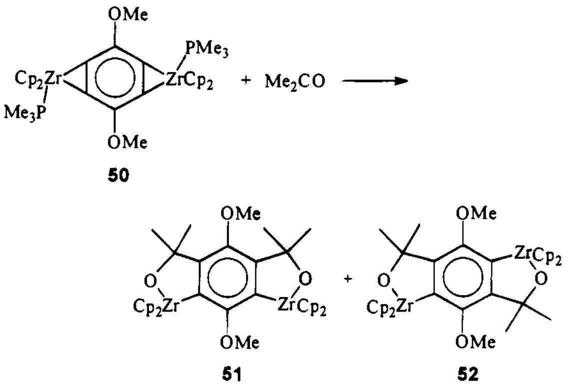
(c) Ring-opening reactions of η^2-diaryl ketone metallocenes are observed in the following reactions, which occur via activation of a C–H bond. Thermolysis of the ketone complex **46** (R = Ph) at 100 °C in toluene gives a mixture of isomers **47** (Scheme 19).[194,198] If the thermolysis of **46** (R = *p*-Tol) is carried out in benzene, **48** is obtained.[199] With the phosphorus ylide $CH_2{=}PPh_3$, **49** is obtained at 70 °C in hexane.[199]

Scheme 19[a]



[a] (i) Toluene, 100 °C; (ii) benzene, Δ; (iii) $CH_2{=}PPh_3$.

(iv) **50** and **53** undergo a bis-coupling reaction with acetone to give the bis-metallacycles **51** and **52** (ratio 1.7/1)[200] and **54**,[201] respectively, as determined by ^{1}H NMR (eqs 24 and 25). The same reaction was observed for the alkyne complex $[Zr(\eta^2\text{-}SiMe_3C{\equiv}CPh)(PMe_3)Cp_2]$, which reacts with acetophenone with replacement of the phosphine and CC coupling of the π-ligands at the zirconocene template to give the oxametallacyclopentene $[\overline{\mathrm{Zr\{OCMePhCPh{=}C}}\mathrm{(SiMe_3)\}Cp_2}]$.[202]



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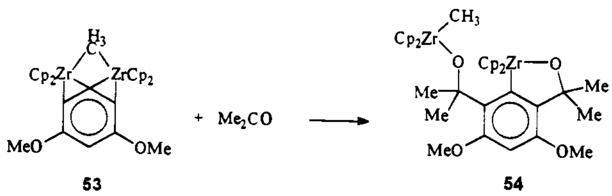
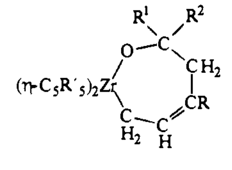


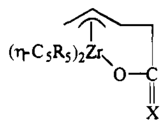
(25)

The diene complexes $[Zr(diene)Cp^*_2]$ (diene = *s-cis*-isoprene, *s-trans*-butadiene) react with 2,4-dimethyl-3-pentanone regio- and stereoselectively to give **55** (R = H, Me, R′ = Me, $R^1 = R^2 = Pr^i$).[203] The crystal structure analysis revealed the *Z* configuration with respect to the C–C double bond.[203] An isomeric mixture of (*s-trans-* and *s-cis-*η^4-butadiene)zirconocene reacts with carbonyl compounds $R^1R^2C{=}O$ to give **55** (R = R′ = H for all complexes, $R^1 = R^2$ = Ph, Me; R^1 = Me, R^2 = Ph; R^1 = Me, $R^2 = Bu^t$; R^1 = H, $R^2 = CH_2CHMe_2$; CR^1R^2 = cyclododecane).[204]



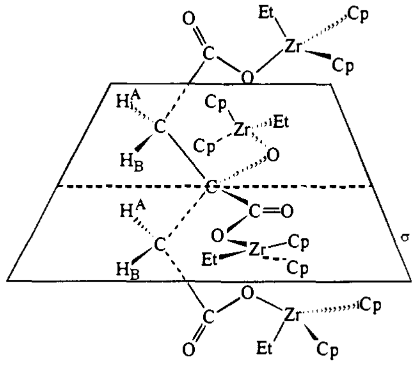
55

The 1:1 reactions of [Zr(butadiene)(η-C_5R_5)$_2$] (R = H, Me) with CO_2, Bu^{t}NCO, PhNCO, or PhMeC=C=O yield Zr—O bound complexes having (σ, syn-η^3-allyl) metal structures **56** (X = NBu^t, NPh, CMePh, O), while [Zr(isoprene)(η-C_5R_5)$_2$] (R = H, Me) gave seven-membered rings with (*Z*)-oxametallacyclic structures [Zr{OC(=X)CH_2CH=CHCH_2}(η-C_5R_5)$_2$] (X = NBu^t, NPh, CMePh, O).[205] [Zr(isoprene)(η-C_5R_5)$_2$] (R = H, Me) reacts with Ph_2C=C=O to give a six-membered oxametallacycle [Zr{OC(=CPh_2)CHMeCMe=CH}(η-C_5R_5)$_2$].[205]



56

(v) With equimolar amounts of ROH, [Zr(C_2H_4)(PMe_3)Cp_2] undergoes protonation of the ethylene ligand to give [ZrEt(OR)Cp_2] (R = Me, Et, Ph);[206,207] excess ROH leads to formation of [Zr$(OR)_2Cp_2$].[206] Trifunctional alcohols X$(OH)_3$ afford bridged trinuclear complexes [{Cp_2(Et)ZrO}$_3$(μ_3-X)] [X = CH_2CHCH_2, $CH_2CMe(CH_2)CH_2$, 2,4,6-C_6H_3],[208] and tetrahydroxy compounds such as citric acid or pentaerythritol give tetranuclear complexes **57** (cf. section V.D.1).[208] However, when the difunctional 1,2-dihydroxybenzene is employed, the reaction products are the dinuclear complex [{ZrEtCp_2}$_2$(μ-1,2-$O_2C_6H_4$)] and [Zr(1,2-$O_2C_6H_4$)Cp_2].[209] The latter was described in 1969 but not fully characterized.[210]



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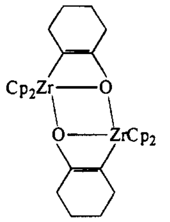
(vi) Oxygen atom transfer from N_2O to [HfH(Ph)Cp^*_2) gives [Hf(OH)(Ph)Cp^*_2] and [HfH(OPh)Cp^*_2].[211] An intermediate benzyne complex was implicated in the scrambling process, and it was shown that [Zr(η^2-cyclohexyne)(PMe_3)Cp_2] reacts with N_2O to give the dimeric oxametallacyclobutene derivative **58** with elimination of N_2 and PMe_3.[212] Similarly, [Zr(C_2Ph_2)Cp^*_2] reacts with N_2O to yield the adduct **59**, which loses N_2 at ambient temperature to give **60** (eq 26).[69]



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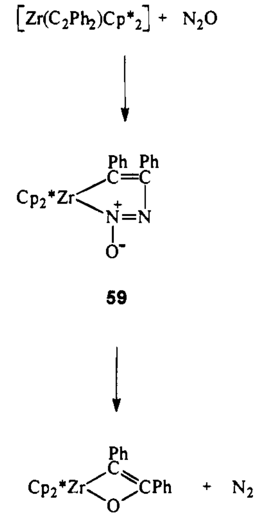


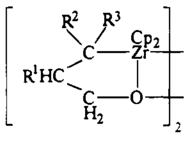
(26)

59

60

(vii) Elimination and intramolecular hydrozirconation: The reaction of silylated unsaturated alcohols with zirconocene hydride chloride is dependent on the length and branching of the alkenyl chain. Thus, Me_3SiH and the yellow complex [Cp_2(Cl)Zr($CH_2CH_2CY_2O$)Zr(Cl)Cp_2] (Y = Me) or [{Zr($OCY_2CH_2CH_2$)Cp_2}$_2$] (Y = H) are obtained.[213]

Zirconocene hydride chloride reacts with KO$(CH_2)_n$CR=CH_2 (*n* = 1, R = H, Me; *n* = 2, R = H) with elimination of KCl and intramolecular hydrozirconation to give dimeric 1-oxa-2-zirconacyclopentanes **61** (R^1 = R^2 = R^3 = H; R^1 = Me, R^2 = R^3 = H; R^1 = R^2 = H, R^3 = Me; R^1 = H, R^2 = R^3 = D) in 10–40% yield.[214,215] The dimeric nature was confirmed by mass spectroscopy and X-ray crystallography (R^1 = R^2 = H, R^3 = Me).[215] However, when [$ZrCl_2Cp^*_2$] was reacted with XMg$(CH_2)_n$OMgX (*n* = 3 or 4, X = halide) the monomeric complexes [Zr{$CH_2(CH_2)_n$O}Cp^*_2] (*n* = 2 or 3) were obtained due to the presence of the bulky Cp* ligands.[214]



61

(viii) When [Hf(CO)$_2$Cp*$_2$] is reacted with H_2 (3 atm) at 125 °C, clean reduction of one CO ligand is observed with formation of [HfH(OMe)Cp*$_2$] and CO.[216]

(ix) in 1971/1972 the synthesis of metallocene bisalkoxo or bisaryloxo complexes from tetra(cyclopentadienyl) metal complexes and ROH was reported.[217,218]

2. Spectroscopic Properties

Metal—ligand bond disruption enthalpies have been determined for the series [MX$_2$(η-C$_5$R$_5$)$_2$] (R = H, Me) and [MX$_3$Cp*] (M = Zr, Hf, X = hydrocarbyl, hydride, alkoxide, amide, halide).[74]

Bis(alkylcyclopentadienyl)di(aryloxide)titanium, -zirconium, and -hafnium complexes have been separated by thin-layer chromatography. R_f values were determined for various adsorbents and solvents, and a relation between the structure of the compounds and their R_f values was established.[219]

The ν(CO) mode is generally observed in the range 1280−1300 cm^{-1} for aryloxides and 1090−1140 cm^{-1} for alkoxides. The Zr—O stretching modes are observed in the range 420−570 cm^{-1}. The ν(M—O—C) mode occurs at 620−630 cm^{-1} in [Zr(Cl)$_{2-n}$(OR)$_n$(η-C$_5$H$_4$Me)$_2$] (n = 1,2, R = α-, or β-nap).[163]

The complexes [Zr(OR)$_2$Cp$_2$] (R = 2,6-Bu$^t_2$C$_6$H$_3$, 2,6-Bu$^t_2$-4-MeC$_6$H$_2$, 2,4,6-Bu$^t_3$C$_6$H$_2$)[46] and [Zr(OR)(X)Cp$_2$] (R = 2,6-Bu$^t_2$C$_6$H$_3$, X = NMe$_2$;[46,220] 2,6-Bu$^t_2$-4-MeC$_6$H$_2$, X = NMe$_2$; R = 2,6-Bu$^t_2$C$_6$H$_3$, X = OMe[46]) show a 1:1 doublet for the o-Bu^t groups in the ^{1}H NMR, which is attributed to restricted rotation about the carbon—oxygen bond.[46] In the NMR spectra of [M(OR)$_2$Cp$_2$] (M = Ti, Zr, Hf, R = Ph, 4-Bu^{t}C$_6$H$_4$, 2,4-Cl$_2$C$_6$H$_3$, 2,4,6-Cl$_3$C$_6$H$_2$, 2,5-Me$_2$C$_6$H$_3$, m-Tol), the deshielding of the Cp protons by the center metal decreases in the order Ti > Zr > Hf.[156] A ^{13}C NMR study on [M(O-4-RC$_6$H$_4$)$_2$Cp$_2$] (M = Ti, Zr, Hf, R = H, MeO, Cl, Br, I) showed that the chemical shifts of the Cp carbon atoms decreases in the series Ti > Zr > Hf.[221]

[Hf(OR)$_2${η-C$_5$H$_4$(SiMe$_3$)}$_2$] (R = Me, Et) and [HfCl(OMe){η-C$_5$H$_4$(SiMe$_3$)}$_2$] exhibit molecular parent ion peaks in their field desorption mass spectra.[157]

The ^{91}Zr NMR spectrum of [ZrMe(OSiMe$_2$Bu^t)Cp$_2$] exhibits a signal at −110 ppm (80 °C).[178]

3. Structural Data

Crystal structures have been reported for the following complexes containing either terminal alkoxo or aryloxo ligands: [ZrBz{O-2,4-Me$_2$-6-(α-methylcyclohexyl)C$_6$H$_2$}Cp$_2$] [Zr—O 1.981(6) Å, Zr—O—C 165.3(5)°],[181] [ZrCl(O-2,6-Bu$^t_2$-4-MeC$_6$H$_2$)Cp$_2$] [Zr—O 1.98(2) Å, Zr—O—C 150(1)°],[220] [Zr(NMe$_2$)(O-2,6-Bu$^t_2$C$_6$H$_3$)Cp$_2$] [Zr—O 2.056(1) Å, Zr—O—C 142.7(1)°],[220] [Cp$_2$(Cl)Zr(μ-OCMe$_2$CH$_2$CH$_2$)Zr(Cl)Cp$_2$] [Zr—O 1.921(4) Å, Zr—O—C 165.9(4)°],[213] and the isostructural complexes [M(OR)$_2$(η-C$_5$H$_4$Me)$_2$] (R = 2,6-Cl$_2$C$_6$H$_3$, M = Hf[222] or Zr[223]). The ligands in these complexes occupy positions about the Zr atom typical of [ZrX(Y)Cp$_2$] type compounds. The large Zr—O—C angle of 165.3(5)° in [ZrBz{O-2,4-Me$_2$-6-(α-methylcyclohexyl)C$_6$H$_2$}Cp$_2$] results in the aryloxo ligand occupying a "wedge-like" space within the coordination sphere.[181] A very similar arrangement of the aryloxo ligands has been observed in [Zr(OR)(X)Cp$_2$] (R = 2,6-Bu$^t_2$-4-MeC$_6$H$_2$, X = Cl; R = 2,6-Bu$^t_2$C$_6$H$_3$, X = NMe$_2$).[220] The short Zr—O bond distances indicate a partial double bond, ascribable to π-donation from the oxygen atom to the empty 1a$_1$ orbital of Zr.

Crystal structures of the macrocyclic complexes [Cp$_2$Zr(μ-OCH$_2$XCH$_2$O)$_2$ZrCp$_2$] [(X = CMe$_2$) Zr—O 1.945(6) Å, Zr—O—C 142.5(5)°; (X = 1,3-C$_6$H$_4$) Zr—O 1.939(5), 1.935(5) Å, Zr—O—C 154.9(4), 152.8(4)°] have been determined.[180]

In the trinuclear complexes [Zr{OC$_6$H$_5$Cr(CO)$_3$}$_2$Cp$_2$][184] and [Zr{OCH$_2$C$_6$H$_5$Cr(CO)$_3$}$_2$Cp$_2$][183] the O—Zr—O bond angles of 95.8(3)[184] and 98.12(13)° [183] lie in the normal range for zirconium bent-sandwich complexes. The Zr—O bond distances [1.992(6)[184] and 1.956(2), 1.948(2) Å[183]] as well as the Zr—O—C bond angles of 153.6(6)[184] and 155.9(2), 157.9(3)° [183] are comparable to those of monoalkoxo complexes.

Several complexes which have an oxametallacycloalkane or -alkene fragment have been structurally characterized. The complexes **58** [Zr—O 2.159(8), 2.227(7) Å, Zr—O—C 150.4(6)°][212] and **60** [Zr—O 2.065(5) Å][69] contain an oxametallacyclobutene fragment. In [Zr{CH$_2$(CH$_2$)$_3$O}Cp*$_2$] the Zr—O distance [2.008(13) Å] is comparable to that of acyclic alkoxo ligands, but the Zr—O—C bond angle is only 141.1(12)°.[214] The oxametallacycloheptene complexes of zirconocene **55** [R = H, Me, R′ = Me, R^1 = R^2 = Pr^i, Zr—O 1.961(7) (R = H), 1.964(8) (R = Me) Å;[203] and R = R′ = H, R^1 = R^2 = Ph, Zr—O 1.946(4) Å[204]] are mononuclear in solution and in the solid state, whereas a structurally characterized oxametallacyclopentane derivative has a dimeric structure[215] similar to that of the oxametallacyclobutene derivative **58**. Zr—O bond distances of the dimeric complexes [(five-membered) 2.190(3) and 2.234(7) Å;[214,215] (four-membered ring) 2.159(8) and 2.227(7) Å[212]] are slightly longer due to the bridging alkoxo ligands.

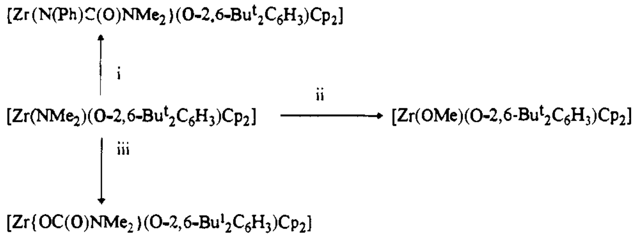
Crystallographic data for [HfEt(OOBu^t)Cp*$_2$] show an η^1-bonding mode for the peroxo ligand. The short Hf—O bond length [1.970(8) Å] and the Hf—O—O—C dihedral angle of 70.9° suggest substantial π-donation from oxygen to the empty a$_1$ orbital of the hafnocene moiety.[188]

4. Chemical Properties

The metallocene alkoxides or aryloxides are white to yellow, air-sensitive compounds. The M—O bond is readily cleaved by protic reagents. Thus, [M(OPh)$_2$(η-C$_5$H$_4$R)$_2$] (M = Ti, Zr, Hf, R = Et, Pr, Bu) react with HX (X = Br, I) to give the corresponding dihalide complexes.[224] The complexes [M(OR′)$_2$(η-C$_5$H$_4$R)$_2$] (M = Ti, Zr, Hf, R = H, Me, R′ = Ph, 4-Bu^{t}C$_6$H$_4$, 2,4-Cl$_2$C$_6$H$_3$, 2,4,6-Cl$_3$C$_6$H$_2$, 2,5-Me$_2$C$_6$H$_3$, m-Tol) react with HCl or AcCl to give [MCl$_2$(η-C$_5$H$_4$R)$_2$].[156] Protonation of **55** (R = R′ = H for all complexes, R^1 = R^2 = Ph, Me; R^1 = Me, R^2 = Ph; R^1 = Me, R^2 = Bu^t; R^1 = H, R^2 = CH$_2$CHMe$_2$; CR^{1}R^2 = cyclododecane) gives MeCH=CHCH$_2$CR^{1}R^{2}OH and CH$_2$=CH(CH$_2$)$_2$CR^{1}R^{2}OH.[204]

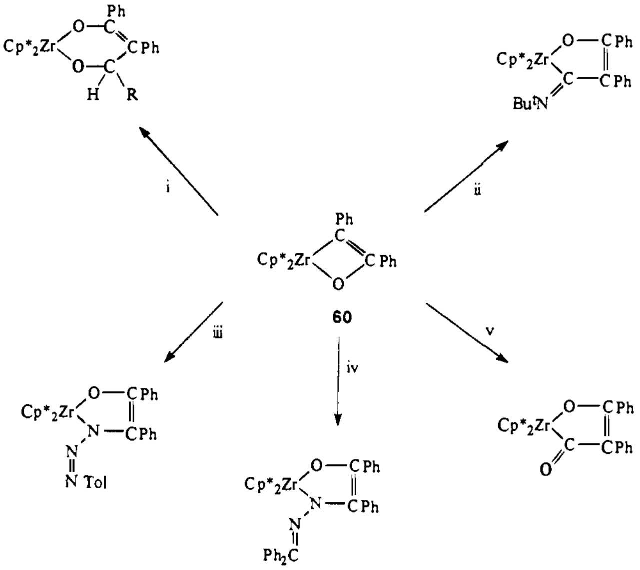
Some reactions that leave the alkoxo ligand unaffected are summarized in Scheme 20.[46] The oxametallacyclobutene complex **60** inserts a variety of compounds to give five- and six-membered metalla-

Scheme 20[a]



[a] (i) PhNCO; (ii) MeOH, Δ, benzene, $-Me_2NH$; (iii) CO_2.

Scheme 21[a]



[a] (i) RC(=O)H (R = H, Tol, Hex); (ii) Bu^{t}NC; (iii) $TolN_3$; (iv) Ph_2CN_2; (v) CO.

cycles (Scheme 21).[69] [ZrBz{*O*-2,4-Me$_2$-6-(α-methylcyclohexyl)C_6H_2}Cp_2] reacts with Bu^{t}NC to give the η^2-iminoacyl derivative [Zr(η^2-NBu^{t}CBz){*O*-2,4-Me$_2$-6-(α-methylcyclohexyl)C_6H_2}Cp_2].[181]

B. Metallocene Complexes with Transition Metal-Substituted Alkoxo Ligands

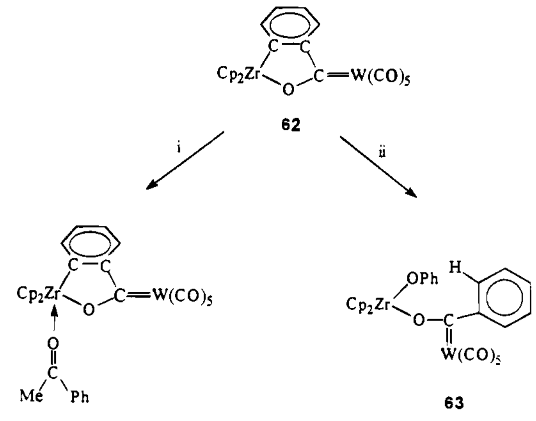
Two major synthetic approaches are used for the synthesis of metallocene complexes with transition metal-substituted alkoxo ligands: (i) transfer of hydrogen from a transition metal hydride to a metallocene acyl complex and (ii) transfer of hydrogen from a metallocene hydride derivative to a transition metal complex.

(i) Whereas molybdocene dihydride reacts with the acyl complex [Zr(η^2-OCMe)(Me)Cp_2] with reduction of the acyl ligand by hydrogen transfer and formation of [ZrMe(OCH_2Me)Cp_2], rhenocene hydride and tungstocene dihydride give heterodinuclear complexes [Cp_2(Me)Zr—OCHMe—M(X)Cp_2] (M(X) = Re, WH).[225] The tungsten complex has a limited lifetime of several minutes.

(ii) For a recent review article on metallocene oxycarbene complexes see ref 84.

(Zirconoxy)carbene complexes [Cp_2(R)M=C(H)—O—Zr(H)Cp$^*_2$] [M = Nb, R = H;[226] M = Nb, R = H, Me, Bz, $CH_2C_6H_4OMe$, Ph, $CH_2OZr(H)Cp^*_2$;[227] M(R) = Cr, Mo,[226] or W[226,228]] are prepared by reacting [NbR(CO)Cp_2] (R = H, Me, Bz, $CH_2C_6H_4OMe$, Ph, $CH_2OZr(H)Cp^*_2$)[227] or [M(CO)Cp_2] (M = Cr, Mo,[226] or W[226,228]) with [$ZrH_2Cp^*_2$] at −78 °C in toluene. The molecular structure of the tungsten derivative [M(R) = W] shows strong W=C [2.008(7) Å] and Zr—O bonds [1.970(4) Å] and a moderately long C=O bond [1.350(8) Å].[226,228] The mechanism of the reaction with niobocene derivatives has been discussed.[227]

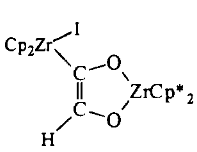
Scheme 22[a]



[a] (i) MeC(=O)Ph; (ii) PhOH.

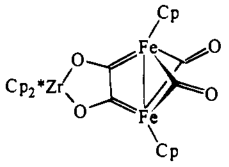
The (zirconoxy)carbene complex **62** is obtained by thermolysis of diphenyl zirconocene in the presence of $W(CO)_6$. The reactive intermediate is a zirconocene—aryne complex.[229] **62** forms an adduct with acetophenone, and with phenol **63** is obtained (Scheme 22). The latter is also accessible from the reaction of [ZrCl(OPh)Cp_2] with [$(CO)_5$W=C(OLi)(Ph)].[229] **62** was shown to be polymeric in the solid state [Zr—O 2.082(7) Å].[229] However, the $C_5H_4Bu^t$ analogue of **62** is monomeric in the solid state [Zr—O 2.082(7) Å], as is **63** [Zr—O(C=W) 2.056(6), Zr—O(Ph) 1.971(6) Å].[229]

Treatment of [ZrL(CO)Cp_2] (L = CO, PMe_3) with [$ZrH_2Cp^*_2$] affords the (zirconoxy)carbene complexes [Cp_2(L)Zr=CHO—Zr(H)Cp$^*_2$]. The reaction of the PMe_3 adduct with MeI gives methane and the corresponding iodo complex [Cp_2(L)Zr=CHO—Zr(I)Cp$^*_2$].[230] The latter reacts with HCl to give [$ZrCl_2Cp_2$], PMe_3, and [ZrI(OMe)Cp$^*_2$]; with CO the purple complex **64** is formed. **64** is also obtained from the reaction of [Cp_2(CO)Zr=CHO—Zr(H)Cp$^*_2$] with MeI (elimination of CH_4).[230] The X-ray structure of **64** confirmed the formulation of the structure as a Zr-substituted enediolate zirconocycle [Zr—O 1.999(7), 2.073(7) Å].[230]



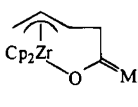
64

The structurally characterized complex **65** [Zr—O 2.11(1) Å] was obtained from the reaction of [{Zr(N_2)Cp$^*_2$}$_2$(N_2)] with [{Fe$(CO)_2$Cp}$_2$], or from [$ZrI_2Cp^*_2$] and Na[Fe$(CO)_2$Cp].[231,232]



65

(Butadiene)zirconocene reacts with L_nM—CO with formation of **66** [ML_n = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$, $Fe(CO)_4$, $Fe(CO)_3PPh_3$, $Rh(CO)Cp$, $Co(CO)Cp$, $Co(CO)(\eta\text{-}C_5H_4Cl)$, $Ni(CO)_3$, $Zr(CO)Cp_2$, $Hf(CO)Cp_2$, $V(CO)_3Cp$].[84] (Butadiene)hafnocene reacts with [$M(CO)_4Cp$] (M = V, Nb) to give an equilibrium mixture of hafnocene oxycarbene complexes (eq 27).[84]



66

(27)

The complexes [$M(Cl)_{2-n}\{OCCo_3(CO)_9\}_nCp_2$] (M = Zr, Hf, n = 1, 2) have been prepared from metallocene dichloride and $Li\{OCCo_3(CO)_9\}$, and their crystal structures have been reported.[233]

Reaction of zirconocene hydride chloride with metal enolates [$W(CHR'COX)(CO)_3Cp$] (X = OEt, Me, Ph) gives [$Cp_2(Cl)Zr(OCHRCHR')W(CO)_3Cp$] (X = OEt, R = R′ = H; X = R = Me, Ph, R′ = H; X = R = R′ = Ph).[234] The phenyl derivative (R = R′ = Ph) exists as two diastereomers which are separable by recrystallization.[234] The crystal structure of the derivative with R = Me, R′ = H has been determined.[234] Photolysis of [$Cp_2(Cl)Zr(OCHRCHR')W(CO)_3Cp$] gives [$Cp_2(Cl)Zr\text{-}O\text{-}W(CO)_3Cp$] via elimination of $R'CH{=}CHR$. The dinuclear complex rapidly decomposes at room temperature to give [$(ZrClCp_2)_2O$] and [$W(CO)_3Cp$]$_2$ as major products; however, it can be trapped with alkynes or PMe_3.[234] The thermal sensitivity led to considerable loss of [$Cp_2(Cl)Zr\text{-}O\text{-}W(CO)_3Cp$] on isolation (36% yield) (cf. section V.F.1).[234]

Comparable heterobimetallic complexes with metal—metal interaction are dealt with in section VII.

C. Metallocene Enolates and Enediolates

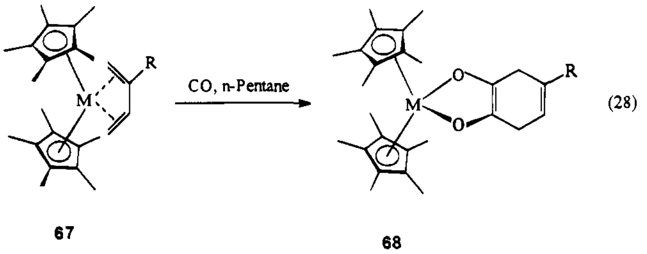
1. Synthesis

Several synthetic routes to metallocene enolates and enediolates are employed.

a. Salt Elimination. The complexes [$Zr\{OC(R^1)(=CR^2R^3)\}(X)Cp_2$] (X = Me, $R^1 = R^2 = R^3$ = H; X = Me, R^1 = H, $R^2 = R^3$ = Me; X = $OCH{=}CH_2$, $R^1 = R^2 = R^3$ = H; X = $OCH{=}CH_2$, R^1 = H, $R^2 = R^3$ = Me;[235] X = Cl, R^1 = SBu^t, R^2 = H, R^3 = Me;[236] X = Cl, R^1 = Et, R^2 = Me, R^3 = H;[237] X = Cl, $C(=CR^2R^3)R^1$ = 1-cyclopentenyl, 2-cyclohexenyl;[237] X = Cl, R^1 = $N(CHMe_2)_2$, $R^2 = R^3$ = H;[238] X = Cl, R^1 = PPh_2, $R^2 = R^3$ = H;[239] X = Cl, R^1 = $Fe(CO)(PPh_3)Cp$, $R^2 = R^3$ = H[240]) are obtained from zirconocene chloride derivatives and the appropriate lithium reagent in 60–87% yield. Where $R^2 \neq R^3$ both isomers (*E*) and (*Z*) are obtained in varying ratios.

b. Reductive Coupling. Reductive coupling of two CO molecules with formation of enediolato complexes [$M\{OC(R){=}C(R)O\}Cp^*_2$] has also been employed (M = Hf, R = $CH{=}CH_2$;[214] MR_2 = $HfCH_2(CH_2)_2CH_2$, $RC{=}CR$ = $CH_2CH_2C{=}CCH_2CH_2$;[242] M = Zr, R = Me[243]). Molecular orbital calculations together with an isotope-crossover study showed the formation of the Me derivative to be an intramolecular process.[244]

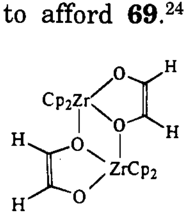
The (η^4-*s-cis*-diene) metallocene complexes **67** (M = Hf, R = H, Me; M = Zr, R = Me) react with CO to give the metal enediolates **68** in 80–90% yield (eq 28).[241] However, reaction of the corresponding η^4-*s-trans*-diene complexes with CO affords carbonyl complexes.[241] Alternatively, the enediolato complex [$Zr\{OC(Bu^t){=}C(Bu^t)O\}Cp^*_2$] is obtained from the oxidative addition of $Bu^tC(=O)C(=O)Bu^t$ to [$\{Zr(N_2)Cp^*_2\}_2(N_2)$].[245]



(28)

67 **68**

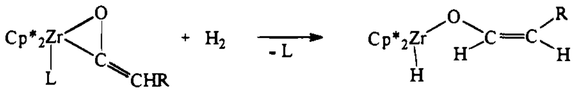
c. CO Insertion. Carbonylation of [$HfH(CH{=}CBu^tH)Cp^*_2$] gives [$Hf(OCH{=}CHCBu^tH)Cp^*_2$] (−10 °C) which reacts with further CO at 25 °C to give [$Hf(OCH{=}CHCBu^t{=}CHO)Cp^*_2$].[242] A possible mechanism for this process is discussed. Carbonylation of zirconocene hydride chloride gives the η^2-formaldehyde complex [$(ZrClCp_2)_2(\mu\text{-}CHO)$], which reacts slowly with further CO to afford **69**.[246] Carbonylation of [$ZrCl\{CH(SiMe_3)R\}Cp_2$] (R = 9-anthryl) stereospecifically yields (*E*)-[$ZrCl\{OC(SiMe_3){=}CHR\}Cp_2$] via 1,2-$SiMe_3$ migration.[247] The insertion of CO into the Zr—C bond(s) in the 1-sila-3-zirconacyclobutane ring of [$Zr(CH_2SiMe_2CH_2)(\eta\text{-}C_5R_5)_2$] (R = H, Me) has been examined. For the Cp derivative, insertion of 1 equiv of CO is followed by an intramolecular 1,2-silyl shift and formation of an oligomeric zirconaoxirane species, [$Zr\{OC(=CH_2)SiMe_2CH_2\}Cp_2$]$_n$. Comparable studies of the carbonylation of the Cp* derivative have shown that this reaction can lead to the formation of two different diinsertion products—a cyclic



69

dienolate, $[Zr\{OC(=CH_2)SiMe_2C(=CH_2)O\}Cp^*{}_2]$, and a bicyclic enediolate $[Zr\{OC(CH_2SiMe_2CH_2)=CO\}Cp^*{}_2]$.[248]

d. Hydrogenation. Hydrogenation of the ketene complexes **70** gives zirconocene enolates **71** (eq 29; R = H, L = py; R = Bu^t, L = CO, CH_2PMe_3).[249] The enolate geometry for R = Bu^t is >96% *cis*, as deduced from the vinylic H—H coupling constant. Treatment of this complex with MeI gives $[ZrI(OCH=CBu^tH)Cp^*{}_2]$, which isomerizes to the *trans* isomer.[249]


(29)

70 **71**

$[Hf(CO)_2Cp^*{}_2]$ reacts with $[MH_2Cp^*{}_2]$ (M = Zr or Hf) under H_2 to produce *cis*-$[Cp^*{}_2(H)Hf(\mu\text{-}OCH=CHO)M(H)Cp^*{}_2]$.[216] Warming of $[HfH_2(CO)Cp^*{}_2]$ above −10 °C under H_2 gives *cis*- or *trans*-$[(HfHCp^*{}_2)_2(\mu\text{-}OCH=CHO)]$, $[(HfHCp^*{}_2)_2(\mu\text{-}OCH_2CH_2O)]$, and $[HfH(OMe)Cp^*{}_2]$,[216] while the *trans* enediolate dimer is the sole product in the thermal reaction of the Zr analogue $[ZrH_2(CO)Cp^*{}_2]$.[250] The oxametallacyclobutene complex **60** reacts with H_2 to give the enolate $[ZrH(OCPh=CHPh)Cp^*{}_2]$.[69]

e. Acidic Hydrogen. Substrates with acidic hydrogen R—H (HO—H, PhO—H, $MeC(=O)CH_2$—H, HCC—H, PhCC—H, Bu^tCC—H) react with the oxametallacyclobutene complex **60** to give $[Zr(OCPh=CHPh)(R)Cp^*{}_2]$.[69]

f. Coordinated CO. The aldehyde complex $[Zr(CO)(\eta^2\text{-}OCHCH_2CHMe_2)Cp^*{}_2]$ slowly loses its coordinated CO and rearranges to the enolate hydride complex $[ZrH(OCH=CHCHMe_2)Cp^*{}_2]$.[242] By contrast, the Hf derivative rearranges without loss of CO to give the cyclic enolate tautomer $[Hf\{OCH=C(CH_2CHMe_2)O\}Cp^*{}_2]$, most likely by a 1,2-hydrogen shift of the cyclic acyl derivative $[Hf(\eta^2\text{-}COCH(CH_2CHMe_2)O\}Cp^*{}_2]$.[242] The acyl complex $[Zr(\eta^2\text{-}COCH_2CHMe_2)(H)Cp^*{}_2]$ reacts with ethylene or 2-butyne to give the metallacycles $[Zr\{OCH(CH_2CHMe_2)CH_2CH_2\}Cp^*{}_2]$ or $[Zr\{OCH(CH_2CHMe_2)CMe=CMe\}Cp^*{}_2]$.[242]

g. Insertion of Diphenyl Ketene. Insertion of diphenyl ketene into the Zr—C bonds of $[ZrR_2Cp_2]$ (R = Me, Bz, Ph) gives $[Zr(OCR=CPh_2)_n(R)_{2-n}Cp_2]$ (n = 1, 2, R = Me; n = 1, R = Bz; n = 2, R = Ph).[68]

2. Spectroscopic Properties

The zirconocene enolates are yellow[235,238] or orange,[239] and the enediolato complexes are red, violet,[241,245] or blue.[245] The unusual color of zirconocene enediolato complexes gives rise to an absorption in the UV—vis spectrum at 433—570 nm,[241,245] which is due to an electronic transition from the HOMO (π) to the LUMO (y^2). This absorption is shifted to higher wavenumbers if the ZrO_2C_2 ring is less puckered (Figure 8).[245] Accordingly, $[Zr\{OC(Bu^t)=C(Bu^t)O\}Cp^*{}_2]$, which was shown to contain a planar ZrO_2C_2 ring by X-ray crystallography, exhibits a maximum at 570 nm, while for $[Zr\{OC(Me)=C(Me)O\}Cp^*{}_2]$, which has a puckered ring, the absorption is observed at 495 nm.[245]

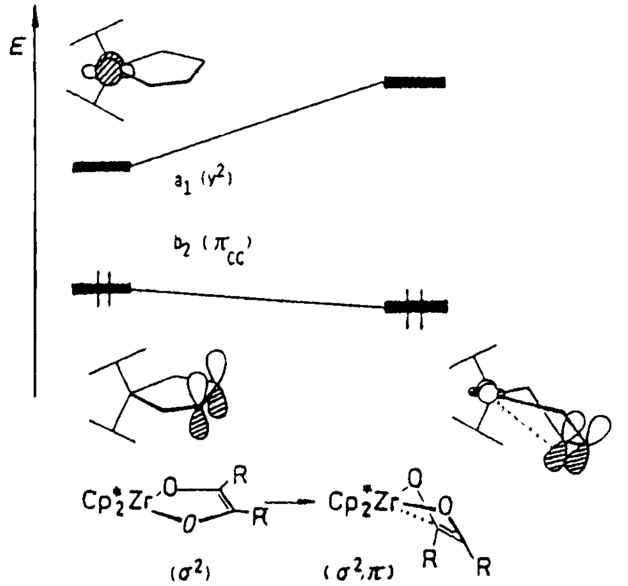


Figure 8. Energy of the frontier orbitals in planar and puckered enediolate complexes. (Reprinted from ref 245. Copyright 1985 VCH Publishers, Inc.)

All compounds have been characterized by NMR spectroscopy. In the ^{13}C NMR spectrum the resonance of the C=C bond of the enediolato ligand is observed between 132 and 158 ppm.[241] For the enolato complexes $[ZrCl(OCR=CH_2)Cp_2]$ (R = NPh_2,[238] PPh_2[239]) and $[ZrH(OCH=CH_2)Cp^*{}_2]$[249] the O—*C* resonance is observed between 154.2 and 169.2 ppm, while the $=CH_2$ resonance appears at 78.1 (X = NPh_2) or 103.0 ppm (X = PPh_2) in the former, and at 89.4 ppm in the latter. For $[ZrI(OCH=CHBu^t)Cp^*{}_2]$ the H—H coupling constants for the *cis* (J(HH) = 7.9 Hz) and *trans* (J(HH) = 13.2 Hz) isomer have been determined.[249]

In the IR spectrum the ν(C=C) mode is observed between 1600 and 1700 cm^{-1}, and the ν(CO) mode between 1200 and 1270 cm^{-1}.[241,249]

3. Structural Data

Structural data are available for the enolato complexes $[ZrCl(OCR=CH_2)Cp_2]$ [R = NPh_2, Zr—O 1.976(3), O—C 1.337(5) Å, Zr—O—C 147.3(3)°;[238] R = PPh_2, Zr—O 1.960(3), O—C 1.339(5) Å, Zr—O—C 163.6(3)°;[239] R = $Fe(CO)(PPh_3)Cp$, Zr—O 1.948(8), O—C 1.364(14) Å[240]], (E)-$[ZrCl\{OC(SiMe_3)=CHR\}Cp_2]$ [R = 9-anthryl, Zr—O 1.950(4), O—C 1.360(6) Å, Zr—O—C 157.7(3)°],[247] $[ZrMe(OCMe=CPh_2)Cp_2]$ [Zr—O 1.975(3), O—C 1.341(7) Å, Zr—O—C 150.8(3)°],[68] and $[Zr(OCMe=CPh_2)_2Cp_2]$ [Zr—O 1.989(7)—2.004(6), O—C 1.35(1), Zr—O—C 143.5(6)—153.8(5)°].[68] The cyclic dienolate $[Zr\{OC(=CH_2)SiMe_2C(=CH_2)O\}Cp^*{}_2]$ [Zr—O 1.990(2), 1.987(2) Å, Zr—O—C 139.6° (av)] has two exocyclic methylene groups [C=C 1.318(6), 1.316(6) Å].[248]

Crystallographic studies of the enediolato complexes $[Zr\{OC(R)=C(R)O\}Cp^*{}_2]$ (R = Me, Bu^t) show a planar ZrO_2C_2 ring for R = Bu^t [Zr—O 2.031(4), 2.048(6) Å], and a nonplanar ring for R = Me [dihedral angle ZrO_2/O_2C_2 16.8°, Zr—O 2.022(6), 2.011(6) Å].[245] The distance between Zr and the C—C double bond is 0.12 Å shorter in the methyl derivative.[245] EHMO calculations indicate that the nonplanar configuration is more stable, allowing a $\sigma^2-\pi$ interaction with the Cp^*_2Zr fragment (Figure 8).[245]

4. Chemical Reactivity

The nucleophilicity of the methylene carbon in the enolates $[ZrCl(OCR{=}CH_2)Cp_2]$ (R = NPh_2,[238] PPh_2[239]) has been exploited to form complexes with $Cr(CO)_5$. Crystal structures have been reported for $[ZrCl\{OCRCH_2Cr(CO)_5\}Cp_2]$ (R = NPh_2,[238] PPh_2[239]).

$[ZrCl\{OC({=}CH_2)PPh_2\}Cp_2]$ reacts rapidly with benzaldehyde to form $[ZrCl\{OCHPhCH_2C({=}O)PPh_2\}Cp_2]$.[239] Both (*E*)- and (*Z*)-zirconocene enolates have been shown to undergo selective kinetic aldol condensation to give mainly *erythro*-β-hydroxy ketones, esters, and amides.[236,237] Low-temperature transmetalation of the lithium dienolate of 2-cyclohexen-1-one or 2-cyclopenten-1-one with zirconocene dichloride gives the (*Z*)- and (*E*)-zirconocene dienolates. These complexes, generated in situ, participate in aldol reactions with achiral aldehydes RCHO (R = Ph, Bu, 2-furyl, nap) forming syn β-hydroxy enone systems.[251]

In situ-prepared zirconocene enolates, derived from *S*-*tert*-butyl alkanethioates ($RCH_2C({=}O)SBu^t$) (R = Me, Et, $CHMe_2$), underwent syn-selective condensation with the imine $4\text{-}MeOC_6H_4CH_2N{=}CHC{\equiv}CSiMe_3$ to give β-amino acid derivatives.[252]

5. Related Complexes

The reaction of zirconocene dichloride with dipotassium dithiooxalate (dto) in CH_2Cl_2 gives $[(ZrClCp_2)_2(dto)]$ in 49% yield. In the complex each Zr is five-coordinate, being bound to an O and an S atom of the dto ligand [Zr—O 2.277(3), 2.258(3), Zr—S 2.698(1), 2.698(1) Å].[253] The $ZrCl(\mu\text{-}dto)ZrCl$ fragment is planar.

D. Metallocene Carboxylates

1. Synthesis

Reaction of metallocene halides with carboxylic acids in the presence of excess base for 1—2 days is a general synthetic route to metallocene carboxylates $[Zr(O_2CR)_n(Cl)_{2-n}Cp_2]$ [base usually NEt_3, $n = 1$ or 2; R = Pr^i, $MeC({=}O)NHCHMe$—;[254] RCO_2H = 2- or 4-pyridinecarboxylic acid, 2,6-pyridinedicarboxylic acid,[255] 2-thiophenecarboxylic acid, 2-thiopheneacetic acid, 3-pyridinecarboxylic acid,[256] 3-thiophenecarboxylic acid, 3-thiopheneacetic acid, 2-thiophenebutyric acid,[257] palmitic acid, stearic acid, behenic acid ($[ZrCl_2Cp_2]$ and $[ZrCl_2(\eta\text{-}C_5H_4Me)_2]$ were used as starting materials),[258] *N*-phthaloyl amine acids $o\text{-}C(O)C_6H_4C(O)NCHR'CO_2H$ (with R′ = H, Me, Bz, Pr^i, CH_2CH_2SMe),[259] *trans*-cinnamic acid, dihydrocinnamic acid[260]]. The dibasic benzilic acid acts as a tridentate ligand.[260]

Reaction with excess carboxylic acid results in cleavage of a metal—cyclopentadienyl bond and formation of trisubstituted complexes $[Zr(O_2CR')_3(\eta\text{-}C_5H_4R)]$ (R = H, Me, $R'CO_2H$ = palmitic acid, stearic acid, behenic acid)[258] (cf. section VI.E.1).

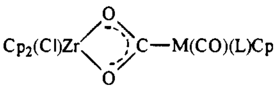
Reaction of $[MCl_2Cp_2]$ (M = Ti, Zr) with 3-indole derivatives (i.e., 3-indoleacetic acid, 3-indolepropionic acid, 1-tryptophan, 3-indolebutyric acid) in the presence of NEt_3 gave the monosubstituted (1:1 reaction) and disubstituted (1:2) carboxylato complexes.[261] Hafnocene dichloride (1:1, 1—2 days) gives the monosubstituted products $[HfCl(O_2CR)Cp_2]$. However, the 1:2 reaction yields $[HfCl(O_2CR)_2Cp]$.[262]

$[(ZrBrCp_2)_2O]$ reacts with CCl_3COOH with cleavage of the Zr—O—Zr bond to give the intermediate $[ZrBr(O_2CCCl_3)Cp_2]$ which disproportionates to $[ZrBr_2Cp_2]$ and $[Zr(O_2CCCl_3)_2Cp_2]$.[263] With organic acids RCOOH (R = Me, Ph) the mixed compound $[ZrBr(O_2CR)Cp_2]_4[Zr(O_2CR)_2Cp_2]$ is formed.[263] Treatment of $[(ZrClCp_2)_2O]$ with excess RCO_2H gave $[ZrCl(O_2CR)Cp_2]$ (R = H, Me, Bu^t, Ph) in 75—83% yield.[264] The complexes (R = Me, Ph) were prepared as early as 1969 but not fully characterized.[265] Earlier attempts to prepare the acetates $[Zr(O_2CMe)(X)Cp_2]$ (X = Cl, O_2CMe) by treating zirconocene dichloride or zirconocene dihydride with acetic acid resulted in Zr—Cp bond cleavage.[266,267] The analogous trifluoroacetate complexes, however, have been prepared by these and other routes,[266—268] and the monoacetate can be obtained by treating methyl zirconocene chloride with acetic acid.[264]

The reaction of zirconocene dichloride with TFA in the two-phase system $CHCl_3/H_2O$ yields the dinuclear complex $[\{Zr(O_2CCF_3)(\mu\text{-}OH)Cp_2\}_2]$, which contains five-coordinate Zr, in 30% yield.[269] $[Zr(\eta^2\text{-}CHPhNMe_2)(Me)Cp_2]$ reacts with TFA with replacement of the Me ligand by CF_3COO.[270] In these trifluoroacetate complexes η^1-coordination of the carboxylato ligand is observed (cf. section V.D.3).[269,270]

The reaction of zirconocene dichloride with the sodium salt of a carboxylic acid has been employed for the synthesis of monocarboxylato complexes $[ZrCl(O_2CR')(\eta\text{-}C_5H_4R)_2]$ (R = H, R′ = 2-, 3-, or $4\text{-}BrC_6H_4$, 2- or $4\text{-}ClC_6H_4$, 2- or $4\text{-}IC_6H_4$, 2- or $3\text{-}FC_6H_4$, 3- or $4\text{-}NO_2C_6H_4$, *p*-Tol, $4\text{-}CNC_6H_4$, $2\text{-}NH_2C_6H_4$, Ph;[271] R = Me, R′ = nap;[272] R = H, Me, R′ = nap, $\alpha\text{-}CH_2C_{10}H_7$, $PhCH{=}CH$, $p\text{-}ClC_6H_4OCH_2$;[273] R = Me, R′ = nap[274]) in 67—91% yield, as well as for the synthesis of zirconocene complexes containing ferrocenylcarboxylato ligands $[\{ZrCl(\eta\text{-}C_5H_4R)_2\}_n(Y)]$ [$n = 1$, R = H, Me, Y = $FcCO_2$, $FcCH_2CO_2$, $Fc(CH_2)_3CO_2$, $FcC(O)(CH_2)_2CO_2$, $FcC(O)(C_7H_8)CO_2$ (C_7H_8 = 5,6-norbornene);[275] $n = 1$, R = H, Y = $FcC(O)(CH_2)_2CO_2$;[276] $n = 2$, R = H, Me, Y = $Fe\{C_5H_4C(O)(CH_2)_2CO_2\}_2$;[275] $n = 1$, R = H, Me, Y = $FcCO_2$, $FcCH_2CO_2$, $FcCOCH_2CH_2CO_2$[277]]. The monothiocarbamato complex $[ZrCl(SOCNMe_2)Cp_2]$ was prepared accordingly (cf. section VI.E.1).[278]

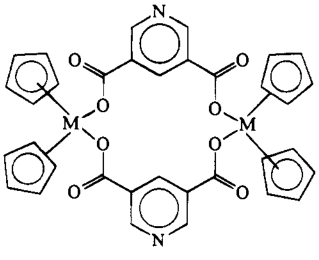
The dicarbonyl complex **72** (M = Re, L = CO) is obtained by salt elimination from zirconocene dichloride and $Na[Re(CO)_2(COO)Cp]$.[279] Analogously, zirconocene dichloride reacts with $Na[M(CO)_2(COO)Cp]$ (M = Fe, Ru) at low temperature to give **72** (M = Fe, Ru, L = CO).[280] Treatment of methyl zirconocene chloride with $[Re(CO)(CO_2H)(NO)Cp]$ results in elimination of methane and formation of light yellow **72** (M = Re, L = NO) in 82% yield.[281] The titanocene analogues (M = Fe, Ru, L = CO) are unstable above −30 °C.[280]



72

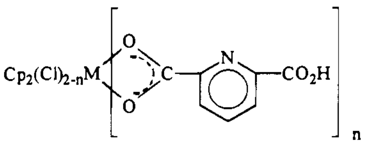
Complex **42** (R = Bu^t) reacts with PhCOOH to give [$\mathrm{Zr(O_2CPh)_2(\eta\text{-}C_5H_4Bu^t)_2}$]; excess of carboxylic acid yields [$\mathrm{Zr(O_2CPh)_3Cp}$].[185]

Utilization of aromatic dicarboxylato ligands allows the synthesis of monomeric,[255] dimeric,[282] or trimeric[283] metallocene complexes, depending on the position of the carboxyl groups. Thus, reaction of metallocene dichloride with pyridine-3,5-dicarboxylic acid in the presence of triethylamine gives the homodinuclear species **73** (M = Ti, Zr) quantitatively.[282] The crystal structure of the Ti derivative has been determined.[282] Both pyridine ligands in **73** can act as Lewis bases toward [$\mathrm{M'(CO)_2Cl}$] (M′ = Rh, Ir).[282]



73

In contrast, when titanocene or zirconocene dichloride was reacted with pyridine-2,6-dicarboxylic acid and $\mathrm{NEt_3}$ in varying molar ratios, the complexes **74** (M = Ti, Zr, n = 1 or 2) were obtained.[255]

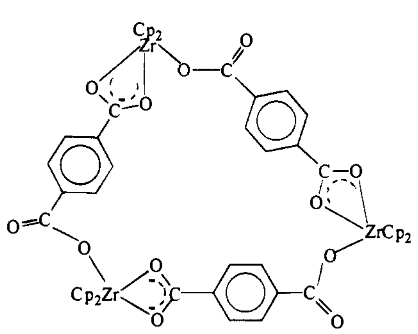


74

A monomeric product [$\mathrm{Zr\{OC({=}O)CH_2OCH_2C({=}O)O\}Cp_2}$] was also obtained from the reaction of zirconocene dichloride with the disodium salt of oxydiacetic acid in $\mathrm{CHCl_3/H_2O}$. Titanocene dichloride gives a mononuclear or dinuclear product, depending on the solvent employed.[284]

The trinuclear complex **75** is obtained on reacting zirconocene dichloride with disodium terephthalate in $\mathrm{H_2O/CHCl_3}$.[283]

The reaction of titanocene dichloride with tetrasodium pyrazinetetracarboxylate gives the tetrametallic complex **76** (M = M′ = Ti).[285] Attempts to prepare the Zr analogue (**76**, M = M′ = Zr) were unsuccessful.[285] However, if the tetrasodium salt is reacted with equimolar amounts of titanocene and zirconocene dichloride, **76** (M = Zr, M′ = Ti) is obtained.[285]



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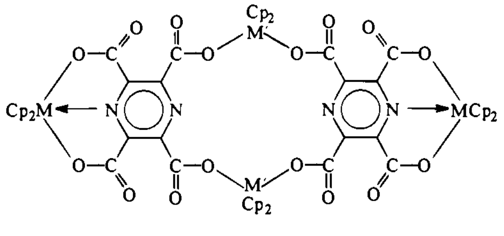


76

The polymeric complexes [$\mathrm{Zr(\mu\text{-}OCOC{\equiv}COCO)Cp_2}$]$_n$ and [$\mathrm{Zr(\mu\text{-}OCOC{\equiv}COCO)Cp_2{\cdot}CHCl_3}$]$_n$ are obtained from zirconocene dichloride and acetylenedicarboxylic acid in $\mathrm{H_2O/CHCl_3}$ or $\mathrm{H_2O/CH_2Cl_2}$,[286] while the analogous Ti system gave [$\mathrm{Ti(\mu\text{-}OCOC{\equiv}COCO)Cp_2}$]$_n$ (n = 2, 4)[287] with tetracoordinate Ti.

[$\mathrm{Zr(C_2H_4)(PMe_3)Cp_2}$] reacts with carboxylic acids RCOOH, undergoing protonation of the ethylene ligand and formation of mononuclear ethyl carboxylato complexes [$\mathrm{ZrEt(O_2CR)Cp_2}$] (R = H, Me, $\mathrm{CF_3}$).[206] Excess TFA gives [$\mathrm{Zr(O_2CCF_3)_2Cp_2}$].[206] With bifunctional H-acidic compounds, such as dicarboxylic acids or salicylic acid, bridged dinuclear ethyl complexes [$\mathrm{Cp_2(Et)Zr(\mu\text{-}O_2CXCO_2)Zr(Et)Cp_2}$] are obtained (X = $\mathrm{CH_2}$, $\mathrm{CH_2CH_2}$, *cis*- and *trans*-CH=CH, CH=CMe).[288] Reactions with tetrafunctional carboxylic acids (citric acid, pentaerythritol) yield tetranuclear complexes **57** (cf. section V.A.1).[208]

2. Spectroscopic Properties

The heterocarboxylates [$\mathrm{ZrCl(O_2CR)Cp_2}$] and [$\mathrm{Zr(O_2CR)_2Cp_2}$] ($\mathrm{RCO_2H}$ = 2- or 4-pyridinecarboxylic acid, 2,6-pyridinedicarboxylic acid;[255] 2-thiophenecarboxylic acid, 2-thiopheneacetic acid, 3-pyridinecarboxylic acid;[256] 3-thiophenecarboxylic acid, 3-thiopheneacetic acid, 2-thiophenebutyric acid;[257] 3-indoleacetic acid, 3-indolepropionic acid, 1-tryptophan, 3-indolebutyric acid[261]) are brown (M = Zr) or yellow to brown (M = Hf) and exhibit one fairly intense absorption between 242 and 301 nm in their electronic spectra. The complexes [$\mathrm{ZrCl(O_2CR)Cp_2}$], [$\mathrm{ZrCl(O_2CR)(\eta\text{-}C_5H_4Me)_2}$], [$\mathrm{Zr(O_2CR)_2Cp_2}$], and [$\mathrm{Zr(O_2CR)_2(\eta\text{-}C_5H_4Me)_2}$] ($\mathrm{RCO_2H}$ = palmitic, stearic, and behenic acid),[258] [$\mathrm{ZrCl(O_2CR)Cp_2}$] (R = 2-, 3-, or 4-$\mathrm{BrC_6H_4}$, 2- or 4-$\mathrm{ClC_6H_4}$, 2- or 4-$\mathrm{IC_6H_4}$, 2- or 3-$\mathrm{FC_6H_4}$, 3- or 4-$\mathrm{NO_2C_6H_4}$, *p*-Tol, 4-$\mathrm{CNC_6H_4}$, 2-$\mathrm{NH_2C_6H_4}$, Ph;[271] R =

H, Me, Bu^t, Ph[264]), and $[Zr(Cl)_{2-n}(O_2CR)_nCp_2]$ (n = 1, 2, O_2CR = N-phthaloyl amino acids)[259] are white or light yellow. Electronic spectra showed a single band in the range 242 to 245 nm. Electrical conductivity measurements showed these complexes to be monomeric nonelectrolytes.

a. IR. In the IR spectrum, the difference between ν_{as}(COO) and ν_s(COO) is indicative of the bonding mode of the carboxylato ligand. Thus, for η^2-coordination a difference of 60 to 100 cm^{-1} is expected and observed in most carboxylato complexes, which show the ν_{as}(COO) and ν_s(COO) mode in the range 1495–1640 and 1430–1525 cm^{-1}, respectively.[255–263,272–274] A difference of 190 cm^{-1} was observed for $[ZrCl(O_2CR)Cp_2]$ (R = 2-, 3-, or 4-BrC_6H_4, 2- or 4-ClC_6H_4, 2- or 4-IC_6H_4, 2- or 3-FC_6H_4, 3- or 4-$NO_2C_6H_4$, p-Tol, 4-CNC_6H_4, 2-$NH_2C_6H_4$, Ph), and a bidentate coordination was suggested.[271]

In **72** the ν_{as} and ν_s(COO) mode are displaced to lower energies (1350, 1278 cm^{-1}, M = Re, L = NO;[281] 1312, 1264 cm^{-1}, M = Re, L = CO;[279] 1345, 1290 cm^{-1}, M = Ru, L = CO;[280] 1365, 1270 cm^{-1}, M = Fe, L = CO[280]) with respect to analogous monometallic complexes.

For the bridged dinuclear products $[Cp_2(Et)Zr(\mu\text{-}O_2CXCO_2)Zr(Et)Cp_2]$ ν_{as} and ν_s(COO) are observed at 1526–1567 and 1426–1460 cm^{-1}, respectively.[288]

The ν(Zr—O) mode occurs in the range 460 to 480 cm^{-1}.[255–259,261–264,269,272–274]

The monomeric nature of **74** (n = 1) is indicated by the IR spectrum, which shows absorptions for both the free CO_2H and coordinated carboxylato group.[255] In $[Zr\{OC(=O)CH_2OC_6H_4\text{-}p\text{-}Cl\}(Cl)Cp_2]$ a five-membered ring is observed (by IR) instead of η^2-coordination of the carboxylato ligand.[273] Observation of the ν(ZrCl) mode at 250–280 cm^{-1} in $[ZrCl(L)Cp_2]$ (L = N-phthaloyl amino acids) was attributed to the presence of chloro-bridged dimers.[259]

The solution and solid-state IR spectra of $[ZrCl(O_2CR)Cp_2]$ (R = H, Me, Bu^t, Ph) are consistent with η^2-bonding of the carboxylato ligand [ν_{as}(COO) 1493–1528 cm^{-1}, ν_s(COO) 1410–1477 cm^{-1}], although the formato complex (R = H) is in equilibrium with unidentate η^1-carboxylate as shown by variable-temperature ^1H and ^{13}C NMR studies.[264] In THF solution all these complexes exist as solvated η^1-carboxylato complexes.[264]

b. NMR. An up-field shift of the Cp protons of $[ZrCl(O_2CR)Cp_2]$ (R = 2-, 3-, or 4-BrC_6H_4, 2- or 4-ClC_6H_4, 2- or 4-IC_6H_4, 2- or 3-FC_6H_4, 3- or 4-$NO_2C_6H_4$, p-Tol, 4-CNC_6H_4, 2-$NH_2C_6H_4$, Ph) (6.20–6.45 ppm)[259,271] and $[ZrCl(O_2CR)(\eta\text{-}C_5H_4R')_2]$ (R′ = H, Me, R = nap, α-$CH_2C_{10}H_7$, PhCH=CH, p-$ClC_6H_4OCH_2$) (6.01–6.36 ppm)[273] compared to zirconocene dichloride was observed in the ^1H NMR spectra.

In the ^{13}C NMR spectra the chemical shift of the carboxylate C atom $-CO_2-$ is observed between 187.1 and 213 ppm.[280,281] In $[ZrCl(L)Cp_2]$ (L = N-phthaloyl amino acids) chemical shifts are observed between 170 and 175 ppm.[259]

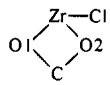
The mass spectra of some bis(cyclopentadienyl)-substituted benzoato zirconium chlorides have been reported and the main fragmentation pathways proposed.[289]

The zirconocene complexes containing ferrocenylcarboxylato ligands are orange and sensitive to light and air.[275] The ν_{as}(COO) and ν_s(COO) modes at 1510–1550 and 1380–1420 cm^{-1} indicate bidentate coordination of the ferrocenylcarboxylato ligand.[275] The protons of the cyclopentadienyl ligands on Zr are shifted up-field in the proton NMR spectra (Cp, 6.14–6.27 ppm; C_5H_4Me, 5.80–6.23 ppm) compared with those of $[ZrCl_2Cp_2]$ and $[ZrCl_2(\eta\text{-}C_5H_4Me)_2]$.[275] Four absorption bands are observed between 220 and 466 nm for these complexes in the UV spectra.[275]

3. Structural Data

It was not until 1988 that crystallographic studies on carboxylato complexes were reported.

The monomeric carboxylato complex $[ZrCl(O_2CR)(\eta\text{-}C_5H_4Me)_2]$ (R = nap) has a bidentate carboxylato ligand with Zr—O bond distances of 2.260(2) and 2.317(2) Å; O—Zr—O and O—C—O are 56.3(1) and 117.2(3)°, respectively.[272,274] As in dithiocarbamato complexes, the Zr—O distances are different, with Zr—O2 being shorter than Zr—O1 (**77**). Accordingly, the C—O1 bond is shorter (1.259 Å) than C—O2 (1.269 Å).[272,274] In this complex and in $[ZrCl\{O_2C(CH_2)_2C(O)Fc\}Cp_2]$ which contains a ferrocenylcarboxylato ligand [Zr—O 2.248(3), 2.287(3) Å][276] the Zr—O bond lengths are much larger than Zr—O distances found in oxo-bridged dimeric complexes (1.94–1.97 Å, cf. section V.F.3). The C—O bond length of the O—C—O fragment (1.280, 1.253 Å;[276] 1.259, 1.269 Å[272,274]) are 0.03–0.06 Å longer than a normal C=O bond length (1.22 Å).



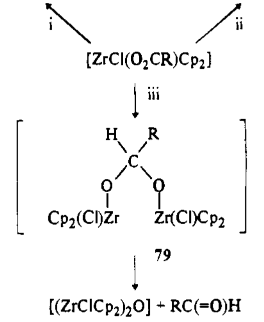
77

The dimetallic tetranuclear complex **76** (M = Zr, M′ = Ti) exhibits Zr—O bond lengths of 2.17(1) and 2.20(1) Å. The molecule lies on a crystallographic mirror plane.[285]

A monodentate carboxylato ligand is observed in $[Zr(\eta^2\text{-}CHPhNMe_2)(O_2CCF_3)Cp_2]$ [Zr—O 2.205(3) Å],[270] $[Zr\{OC(=O)CH_2OCH_2C(=O)O\}Cp_2]$ [Zr—O 2.156(2) Å],[284] and $[\{Zr(O_2CCF_3)(\mu\text{-}OH)Cp_2\}_2]$ [Zr—O 2.217(4) Å].[269] The Zr—O bonds are shorter than in complexes with η^2-bonding of the carboxylato group.

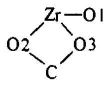
The carboxylato ligand acts as a (2 + 1)-dentate ligand in the cyclic trinuclear complex **75**[283] and polymeric $[Zr(\mu\text{-}OCOC{\equiv}COCO)Cp_2]_n$ and $[Zr(\mu\text{-}OCOC{\equiv}COCO)Cp_2{\cdot}CHCl_3]_n$.[286] In **75** three bridging dicarboxylato ligands are present, and each Zr atom has three ligating O atoms (**78**), with long Zr—O3 distances [2.30(1)–2.37(1) Å], short Zr—O1 distances [2.06(1)–2.08(1) Å], and intermediate Zr—O2 [2.22(1)–2.25(1) Å]. The 27-membered central ring is puckered.[283] The polymeric complexes consist of chains with 2_1 symmetry, packed parallel to each other in the crystals.[286] As in **75**, three different Zr—O distances are observed [Zr—O1, 2.113(2), 2.120-

Scheme 23[a]



[a] (i) $[ZrH(\mu\text{-}H)(\eta\text{-}C_5H_4Me)_2]$ (R = Me); (ii) THF (R = H, Me, Bu^t, Ph); (iii) $[ZrCl(H)Cp_2]_x$ (R = H, Me, Ph).

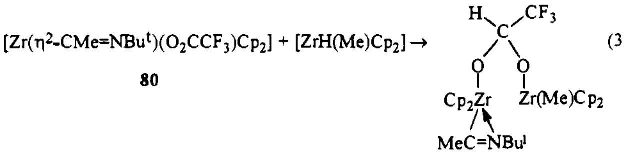
(7); Zr—O2, 2.261(3), 2.275(8); Zr—O3, 2.332(2), 2.316-(8) Å].[286]



78

4. Chemical Properties

Reduction of the coordinated carboxylato ligand in $[ZrCl(O_2CR)Cp_2]$ to the aldehyde (R = H, Me, Ph) or alcohol (R = Me) has been reported (Scheme 23).[264] Similarly, the dimeric complexes **72** (M = Re, L = NO;[281] M = Ru, L = CO[279]) react with zirconocene hydride chloride to give $[Cp_2(Cl)Zr{-}OCH_2{-}M(CO)(L)Cp]$.[279,281] No direct evidence for the postulated $\mu\text{-}\eta^1$-O,O′ *gem*-diolate intermediate **79** exists.[264] However, the reaction of the iminoacyl complex **80** with methyl zirconocene hydride results in reduction of the trifluoroacetate ligand and formation of **81** (eq 30), which has been crystallographically characterized [Zr—O, 2.099(3), 1.968(3) Å].[270]



(30)

81

The complexes $[ZrCl(O_2CR)Cp_2]$ (R = Pr^i, MeC(=O)NHCHMe—) react with amines (benzylamine, α-methylbenzylamine) to give the corresponding *N*-benzylisobutyramide and *N*-acetyl-L-alanine-α-methylbenzylamide.[254]

Thermal degradation of the heterobimetallic carboxylates **72** (M = Fe, Ru, L = CO) gives $[\{M(CO)_2Cp\}_2]$ and $[(ZrClCp_2)_2O]$, indicating partial deoxygenation of CO_2.[280]

5. Related Complexes

The nitronato complexes $[Zr(O_2N{=}CMeR)(X)Cp_2]$ (R = Me or H, X = Cl; R = Me, X = CH_2CMe_2Ph) were prepared from the reaction of $Li(O_2N{=}CMeR)$ with the appropriate zirconocene derivative in 80% yield.[290] The crystal structure of $[ZrCl(O_2N{=}CMe_2)Cp_2]$ shows the η^2 bonding mode of the nitronato ligand (cf. section VIII.B).[290] The ligand "bite" is similar to that observed in carboxylato and dithiocarbamato complexes.

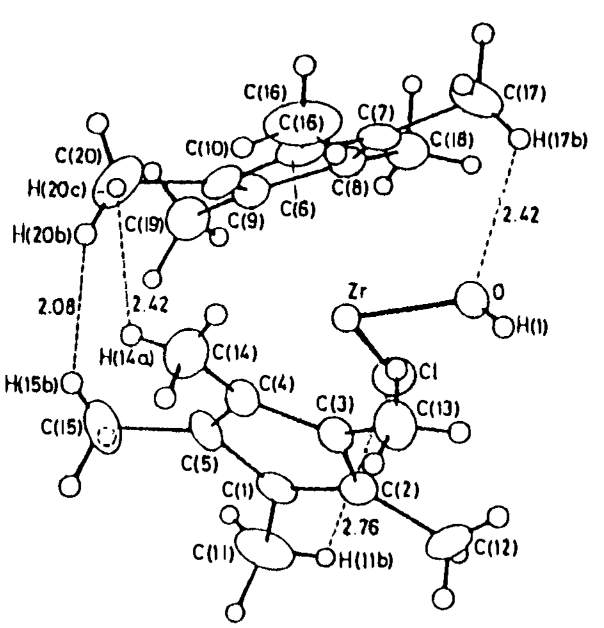


Figure 9. Molecular structure of $[ZrCl(OH)Cp^*_2]$. Short intermolecular contacts are shown. (Reprinted from ref 292. Copyright 1985 Chemical Society of London.)

E. Metallocene Hydroxides

Monohydroxides of zirconocene derivatives $[Zr(OH)(X)Cp_2]$ (X = Cl, Br, I, NO_3;[291] C_6F_5[176]) and zirconocene dihydroxide[176] have been known since 1966. However, using bulky Cp* ligands allows the synthesis and isolation of metallocene hydroxo complexes that are not accessible from the corresponding Cp-substituted complexes. Thus, the reaction of $[ZrMe_2(\eta\text{-}C_5R_5)_2]$ or $[ZrCl(Me)(\eta\text{-}C_5R_5)_2]$ with water affords for R = H the well-known oxo-bridged dimers $[(ZrXCp_2)_2O]$ (X = Cl, Me), and for R = Me, the structurally characterized complexes $[ZrCl(OH)Cp^*_2]$ [Zr—O, 1.950(2) Å] and $[Zr(OH)_2Cp^*_2]$ [Zr—O, 1.975(8), 1.982(7) Å].[292] The former is also obtained on hydrolysis of $[ZrCl(R)Cp^*_2]$ (R = Bu[292] or H[55]); alternatively, the dihydroxo complex is obtained from hydrolysis of $[(ZrHCp^*_2)_2O]$ or by hydrolysis of the reaction mixture of $[ZrCl_2Cp^*_2]$ and BuLi.[55] The monohydroxo complex shows the presence of significant intramolecular nonbonding contacts (Figure 9).[292] The mass spectrum of $[Zr(OH)_2Cp^*_2]$ shows the parent ion peak and an intense signal for $[Zr(=O)Cp^*_2]$.[292]

The hafnocene analogues $[Hf(OH)(X)Cp^*_2]$ (X = H, Cl) were prepared from $[HfH(X)Cp^*_2]$ or $[HfH(NH_2)Cp^*_2]$ (X = H) and water.[55] The monohydroxo complex (X = H) reacts further with H_2O to give the dihydroxo complex.[55] The latter is also obtained from hydrolysis of $[(HfHCp^*_2)_2O]$.[55]

Extended Hückel MO calculations performed on the model complex $[Zr(OH)_2Cp_2]$[180] are consistent with the predictions by Hoffmann and Lauher.[133] An energy minimum occurs when O—Zr—O is 97.9°; however, the energy varies only slightly over the range 96–101°, suggesting $d_\pi{-}p_\pi$ interaction between the $1a_1$ orbital of the Cp_2Zr fragment and the oxygen p orbitals.[180]

[$ZrCl_2Cp_2$] reacts with TFA in $CHCl_3/H_2O$ to give the hydroxo-bridged complex [{$Zr(O_2CCF_3)(\mu\text{-}OH)Cp_2$}$_2$] [Zr—O, 2.217(4) Å] (cf. section V.D.1).[269] The Zr—O(H) bond lengths of 2.152(3) and 2.158(3) Å are ca. 0.2 Å longer than the Zr—O distances of oxo-bridged complexes (cf. section V.F.3).[269]

The alkyne complex [$Zr(C_2Ph_2)Cp^*_2$] reacts with H_2O to give the monohydroxide [Zr(CPh=CHPh)(OH)Cp^*_2].[69] Similarly, **42** (R = Bu^t) reacts with stoichiometric amounts of water to give [$Zr(Fc)(OH)(\eta\text{-}C_5H_4Bu^t)_2$].[185]

Hydrolysis of [$M(CO)_2Cp_2$] affords [$Cp_6Ti_6O_8$] (M = Ti) and crude ZrO_2 (M = Zr), respectively;[293,294] no reaction of [$M(CO)_2Cp^*_2$] (M = Ti[293,294] or Zr[294]) with water was observed.

Complexes [$(ZrXCp_2)_2O$] (X = Cl, Br, OPh), [$Zr(OPh)_2Cp_2$] and [ZrCl(Y)Cp_2] (Y = NO_3, $O_2C_{15}H_{11}$ (β-diketonate)) are hydrolyzed by excess water, primarily undergoing elimination of one Cp ligand.[295]

N_2O reacts with [$HfH_2Cp^*_2$] under mild conditions to yield N_2 and [HfH(OH)Cp^*_2] quantitatively. Competitive oxidation of the hydrido and aryl ligands in [HfH(Ph)Cp^*_2] occurs with N_2O at 80 °C, affording [Hf(OH)(Ph)Cp^*_2] and [HfH(OPh)Cp^*_2] (3:2).[211] Independently, [Hf(OH)(Ph)Cp^*_2] has been prepared from [HfH(Ph)Cp^*_2] and water.[211]

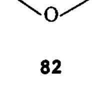
F. Oxo-Bridged Metallocene Dimers

1. Synthesis

The two major synthetic routes employed in the synthesis of oxo-bridged metallocene dimers are (a) hydrolysis of metallocene complexes and (b) oxidation of low-valent metallocene compounds.

a. Hydrolysis. Hydrolysis of metallocene dialkyls or dihalides [$MX_2(\eta\text{-}C_5H_4R)_2$] (M = Hf, R = H, X = *o*-, *m*-, or *p*-Tol, Ph;[296] M = Zr, R = H, X = Cl;[297,298] M = Hf, R = H, Me, X = $4\text{-}ClC_6H_4$, $4\text{-}MeOC_6H_4$, $3,4\text{-}Me_2C_6H_3$;[299] M = Zr, R = Bu^t, X = Me[300,301]) and of [MCl_2{$(\eta\text{-}C_5H_4)_2Y$}] (M = Zr, Y = $(SiMe_2)_n$, n = 2, 3;[297,165] M = Ti, Zr, Hf, Y = $Me_2SiOSiMe_2$, $(SiMe_2)_n$, n = 2, 3[165]) or solvolysis of [ZrX_2Cp_2] (X = Cl, *o*-Tol)[302] with ethanol yields the corresponding oxo-bridged dimetallic derivatives in high yield. [$ZrEt(O_2CR)Cp_2$] (R = H, Me, CF_3) is hydrolyzed to [{$Zr(O_2CR)Cp_2$}$_2$O].[206] Kinetic studies have been reported for the hydrolysis of [$ZrCl_2Cp_2$].[303,304]

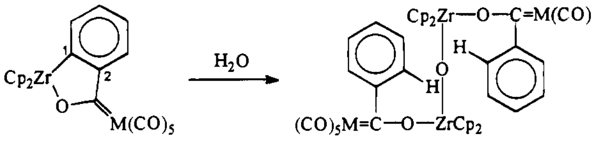
Hydrolysis of the dinuclear complexes [$(ZrCl_2Cp)_2${$(\eta\text{-}C_5H_4)_2Y$}] (Y = $SiMe_2$, CH_2)[305] and [$(ZrMe_2Cp)_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)$][306] gives **82** (X = Cl, Y = $SiMe_2$, CH_2; X = Me, no Y). The structurally characterized Cl derivative **82** (X = Cl, no Y) was obtained from oxidation of [{$Zr(\mu\text{-}Cl)Cp$}$_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)$] with oxygen.[307] The close similarity of the fulvalene pattern in the ^1H NMR spectrum of the Me derivative with that of the Cl complex indicates that the two compounds are probably isostructural.[306]



82

[$MH_2Cp^*_2$] (M = Zr, Hf) react in a clean stepwise manner with water to afford [MH(OH)Cp^*_2], [$(MHCp^*_2)_2O$], and finally [$M(OH)_2Cp^*_2$]·H_2O with evolution of H_2.[55] The dihydrides react with [M(OH)(X)Cp^*_2] (X = Cl, OH, H) to give [Cp^*_2(X)M—O—M(H)Cp^*_2] (M = Zr, Hf).[55]

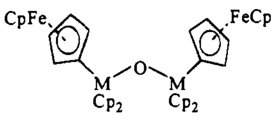
Hydrolysis of **83** gives **84** (M = Mo, W) (eq 31).[308] Similarly, [$Zr(C_2H_4)(PMe_3)Cp_2$] reacts with water with protonation of the ethylene ligand and formation of [$(ZrEtCp_2)_2O$];[206] [ZrEt(OH)Cp_2] is proposed as intermediate.



(31)

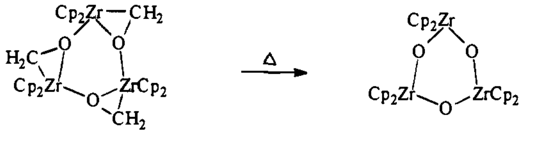
83 **84**

b. Oxidation. Oxidation of dimethylzirconocene, [$(Zr(\mu\text{-}Cl)${$(\eta\text{-}C_5H_4)_2SiMe_2$})$_2$], or **42** (R = H) with oxygen (air) gave [$(ZrMeCp_2)_2O$] (10% yield),[309] [(ZrCl{$(\eta\text{-}C_5H_4)_2SiMe_2$})$_2$O] (identified in solution as intermediate),[310] and **85** (M = Zr, Hf, ca. 30% yield),[311] respectively.



85

Ph_3PO or CO_2 have been used as oxidizing agents for [{$Zr(\mu\text{-}Cl)Cp$}$_2${$(\eta\text{-}C_5H_4)_2SiMe_2$}]. O atom abstraction gives **82** (X = Cl, Y = $SiMe_2$).[312] Similarly, [{$Zr(\mu\text{-}O)Cp_2$}$_3$] (**87**) was first prepared from [$Zr(CO)_2Cp_2$] and CO_2.[313] Complex **87** was also obtained on thermolysis of tris[(η^2-formaldehyde)zirconocene] (**86**) (eq 32).[314]



(32)

86 **87**

Reaction of the Zr(III) complexes [{$Zr(\mu\text{-}Cl)Cp$}$_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)$] and [$Zr(\mu\text{-}Cl)Cp_2$]$_2$ with [ReO_3Cp^*] gives **82** (X = Cl, no Y) and [{$Zr(\mu\text{-}O)Cp_2$}$_3$] (**87**), respectively.[315]

c. Others. Zirconocene dichloride reacts with [WO_3Cp^*]$^-$ to give the heterobimetallic μ-oxo complex [$Cp^*WO_3Zr(Cl)Cp_2$] in 69% yield.[316]

Photolysis of [$Cp_2(Cl)Zr(OCHRCHR')W(CO)_3Cp$] (R = R' = H; R = Me, Ph, R' = H; R = R' = Ph) gives [$Cp_2(Cl)Zr$—O—$W(CO)_3Cp$] via elimination of R'CH=CHR.[234] The heterobimetallic complex is thermally sensitive and decomposes at 25 °C.[234]

Mixed chalcogenido-bridged metallocene dimers are dealt with in section VI.B.2.

2. Spectroscopic Properties

The oxo-bridged metallocene dimers display the characteristic IR band associated with the Zr—O—Zr unit as an intense absorption between 750 and 790 cm^{-1}.[263,291,301,317] For **82** (X = Cl, no Y) the ν(ZrOZr) mode is observed at lower wavenumbers (735, 702 cm^{-1}).[315] The trimeric complex [{Zr(μ-O)Cp_2}$_3$] exhibits a broad band at 750 cm^{-1}.[315] In [Cp_2(Cl)-Zr—O—W$(CO)_3$Cp] the ν(ZrOW) mode is observed at 789 cm^{-1}.[234]

The FIR and Raman spectra of [$(MFCp_2)_2O$] (M = Zr, Hf) have been reported.[318]

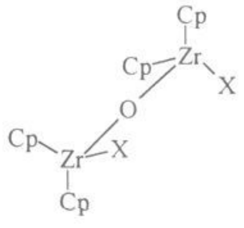
^{17}O NMR spectra have been reported for [$(MHCp^*_2)O$] (M = Hf, δ = 503, M = Zr, δ = 581 ppm) and [{Cp^*_2(X)Zr—O—Zr(H)Cp^*_2] (X = OH, δ = 532, X = Cl, δ = 576 ppm).[55]

The complexes [{Zr(OR)Cp_2}$_2$O] (R = 3- or 4-ClC_6H_4, *o*-, *m*-, or *p*-Tol, Ph) have been separated by thin-layer chromatography.[319]

3. Structural Data

Crystal structures of several homodinuclear complexes have been determined: [$(ZrRCp_2)_2O$] [(before 1980) R = Cl;[320] SPh;[321] Me,[322] (after 1980) R = *o*-Tol;[302] 4-Cl-phenoxy; Zr—O—Zr 161.9(9)°;[323] *o*- and *p*-Tol;[324] OPh, Zr—O—Zr 163.4°;[325] Me, Zr—O 1.948(1) Å, Zr—O—Zr 174.1(3)°;[309] Br;[326] O—C(Ph)=Mo$(CO)_5$ (**84**, M = Mo), Zr—O 1.958(1) Å, Zr—O—Zr 180°[308]] and for **82** [X = Cl, no Y, Zr—O 1.943(1) Å, Zr—O—Zr 156.0(1)°;[307] X = Cl, Y = $SiMe_2$, Zr—O 1.944(2) Å, Zr—O—Zr 178.6(1)°;[305] X = Cl, Y = CH_2, Zr—O 1.938(5) Å, Zr—O—Zr 174.3(2)°;[305] X = Cl, Y = $(SiMe_2)_2$, Zr—O 1.949(3), 1.946(3) Å, Zr—O—Zr 169.8(2)°;[297] X = Cl, Y = $(SiMe_2)_3$, Zr—O 1.9561(8) Å, Zr—O—Zr 165.2(3)° [297]). Structural data are also available for the heterodinuclear complex [Cp_2(Cl)-Zr—O—W$(CO)_3$Cp] (Zr—O—W 175.7°).[234]

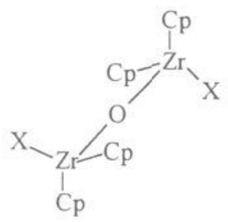
The relatively short Zr—O bond lengths, typically ca. 1.95 Å, indicate the presence of partial double-bond character. Thus, while the conformers **88** and **89** should be sterically favored (eq 33), structures are encountered which show a geometry between the extremes **88** and **90**. In **90**, π-interaction of the bridging oxygen lone pairs with the single available metallocene acceptor orbital stabilizes a linear heteroallene-type structure with an angle (X—Zr··Zr—X) of ca. 90°. The only structural exception is the complex **84** (M = Mo), which has a *trans* arrangement of the voluminous $Mo(CO)_5$−carbene units at the Zr—O—Zr bridge.[308] This antiperiplanar conformation **89** is unique among the family of early transition metal oxo-bridged complexes.



(gauche)

X-Zr...Zr-X = 60°

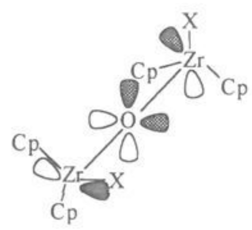
88



(antiperiplanar)

X-Zr...Zr-X = 180°

89



(perpendicular)

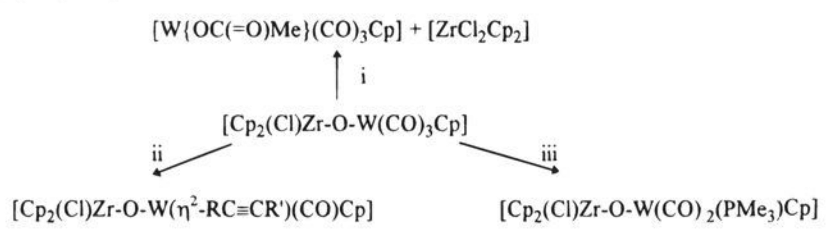
X-Zr...Zr-X = 90°

90

(33)

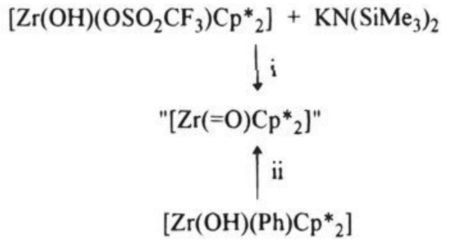
The crystal structure of [{Zr(μ-O)Cp_2}$_3$] shows a six-membered, nearly planar ring with Zr—O 1.959(3) Å, O—Zr—O 142.5(2)°.[313]

Scheme 24[a]



[a] (i) MeCOCl; (ii) +RC≡CR′ (R = Bu^t, R′ = H; R = R′ = Ph), −2CO; (iii) +PMe_3, −CO.

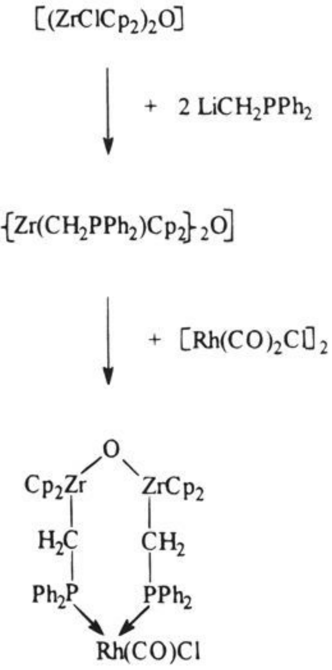
Scheme 25[a]



[a] (i) −$HN(SiMe_3)_2$, −$KOSO_2CF_3$, room temperature; (ii) 160 °C, −C_6H_6.

4. Chemical Properties

Introduction of a functionalized alkyl ligand in oxo-bridged zirconocene complexes and further reaction with [$Rh(CO)_2Cl$] have been studied (eq 34).[327]



(34)

Reactions of [Cp_2(Cl)Zr—O—W$(CO)_3$Cp] with acetyl chloride, alkynes, and PMe_3 have been carried out (Scheme 24).[234] As expected, MeLi reacts with [Cp_2(Cl)Zr—O—W$(CO)_2$(PMe_3)Cp] with substitution of the chloro ligand. The products are thermally more stable than the starting material.[234]

The oxo bridge is cleaved by protic reagents. Thus, [$(ZrRCp_2)_2O$] reacts with acids HX to yield [ZrR(X)Cp_2] (R = Cl, Br, OPh, X = Cl; R = Cl, X = F; R = Br, X = NO_3).[263]

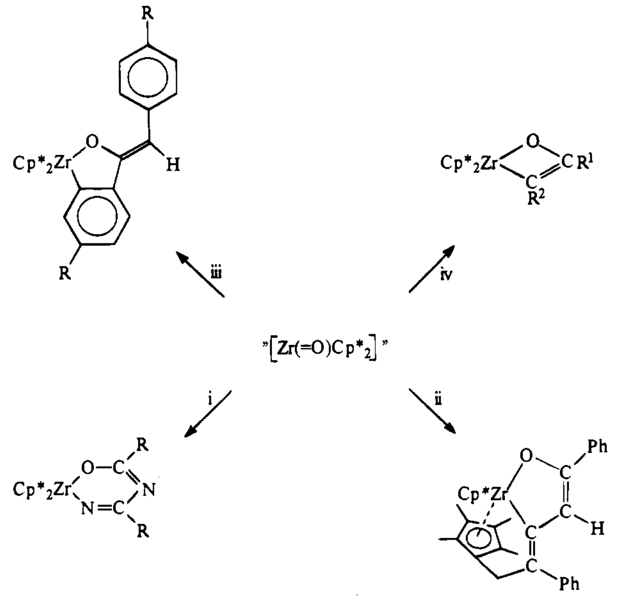
G. Zirconocene Oxide [Zr(=O)Cp^*_2]; Generation and Trapping

Unstable [Zr(=O)Cp^*_2] was generated (Scheme 25) and trapped (Scheme 26).[328–330]

Trapping with alkynes at 160 °C gives products that result from rearrangement or decomposition of the room-temperature product,[330] whereas with arylnitriles the same product is obtained at both temperatures (Scheme 26).

Benzene elimination was also carried out in the presence of donor ligands such as pyridine, 4-*tert*-

Scheme 26[a]



[a] (i) RCN (R = Ph, Bu^t), room temperature or 160 °C; (ii) PhC≡C–C≡CPh, 160 °C; (iii) 160 °C, $R^1C{\equiv}CR^2$ (R = H or Me; $R^1 = R^2$ = Ph; $R^1 = R^2$ = Tol); (iv) $R^1C{\equiv}CR^2$ ($R^1 = R^2$ = Ph; R^1 = Me, R^2 = Ph), room temperature.

butylpyridine, pyridine *N*-oxide, 4-(dimethylamino)pyridine, and triphenylphosphine oxide. Monitoring by ^1H NMR provided evidence that a triphenylphosphine adduct had formed; however, pure products could not be isolated from these reactions.[329] This is in contrast to zirconocene sulfide (cf. section VI.C) and zirconocene imide (cf. section III.C), which do form stable adducts with donor ligands.

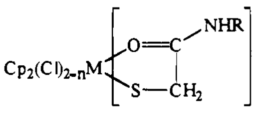
VI. Metallocene(IV) Complexes with S-, Se-, and Te-Centered Anionic Ligands

A. Metallocene(IV) Thiolates, Selenates, and Tellurates

1. Synthesis, Spectroscopic, and Chemical Properties

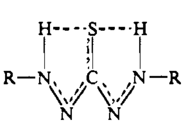
Several of the methods used for the preparation of metallocene(IV) alkoxides and aryloxides are suitable for the synthesis of the corresponding thiolates and selenates. The following synthetic routes have been employed: (a) the triethylamine method, (b) salt elimination, (c) insertion of chalcogens into M–C bonds, (d) oxidative addition of diphenyl dichalcogenides, (e) thermal rearrangement of α-zirconocenyl thioethers, (f) solvolysis, and (g) hydrozirconation of thioketones.

a. The Triethylamine Method. This was used earlier for the preparation of $[Zr(EPh)_2Cp_2]$ (E = S, Se)[331] and $[M(SH)_2Cp_2]$ (M = Ti, Zr)[332] and has been employed for the synthesis of the thiolatoacetamide complexes **91** from $[MCl_2Cp_2]$ and $RHNC(=O)CH_2SH$ (*n* = 1, 2, M = Hf,[333] M = Zr,[334] R = Ph, *o*-, *m*-, or *p*-Tol, nap, 3,5-$Me_2C_6H_3$). The products were obtained in 70–75% yield. Spectroscopic data (^1H NMR, IR) suggest that the thiolatoacetamides behave as monofunctional bidentate (O,S) chelating ligands. The electronic spectra show a fairly intense band between 247 and 294 nm which was assigned to a charge-transfer band. The complexes are gray, yellow, orange, or brown and extremely sensitive to hydrolysis.[333,334]



91

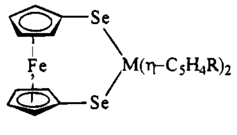
The same preparative method was employed for the synthesis of zirconocene dithizonato complexes. Depending on the stoichiometry of the starting materials [zirconocene dichloride/1,5-diarylthiocarbazone (**92**, R = Ph, *o*- or *p*-Tol, 2- or 4-ClC_6H_4)/triethylamine] the monosubstituted (1/1/1), disubstituted (1/2/2), or a polymeric (1/1/2) complex was obtained in 60–76% yield.[335] The complexes are diamagnetic and are nonelectrolytes in nitrobenzene. The electronic spectra of the red, brown, or black complexes show a single band in the range 410–430 nm, which was assigned to a charge-transfer transition.[335]



92

$[ZrCl_2Cp_2]$ reacts with S-containing Schiff bases R=NN=C(SH)SMe [R = PhCH, PhCMe, Ph_2C, C_5H_8, C_6H_{10}, $C_6H_4(OH)CH$, $C_{10}H_6$, (OH)CH, $MeC_6H_4(OH)CMe$, MeCC(OH)CHCR′ (R′ = Me, Ph)] in the presence of NEt_3 to yield the corresponding mono- and disubstituted complexes.[336] Similarly, $[ZrCl_2Cp_2]$ reacts with thiosemicarbazones in THF in the presence of NEt_3 or $BuNH_2$ to give $[ZrCl(L)Cp_2]$ or $[ZrL_3Cp]$ (L = semicarbazide), depending on the stoichiometry employed.[337] On the basis of spectral data, an S,N-chelating ligand was proposed.[337] The electronic and IR spectra of these complexes have been reported.[336,337]

The triethylamine method was also employed in the synthesis of the metalladiselenaferrocenophanes **93** (M = Zr, Hf, R = Bu^t; M = Zr, R = H) from $[Fe(\eta\text{-}C_5H_4SeH)_2]$ and the appropriate metallocene dichloride in boiling toluene in the presence of NEt_3 in 43–60% yield.[338] At ambient temperature these complexes appear to be nonfluxional in solution (^1H NMR), being locked in a staggered conformation of the ferrocene moiety.[338]



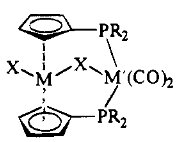
93

The reaction of $[MCl_2Cp_2]$ (M = Ti, Zr) with substituted thiophenols RSH (R = 4-FC_6H_4, 2,3,5,6-F_4C_6H, C_6F_5) in the absence or presence of a base (NEt_3 or $NaNH_2$) gave the mono- or disubstituted product, depending on the stoichiometry.[339] Often, mixtures of both compounds were obtained. The nonlinear optical properties have been studied.[339]

b. Salt Elimination. While the triethylamine method affords titanocene[340] and zirconocene thiolates $[Zr(EPh)_2Cp_2]$ (E = S, Se) and $[Zr(\eta^2\text{-}1,2\text{-}S_2R)Cp_2]$ (R = C_6H_4, 4-MeC_6H_3, C(CN)=C(CN))[331] in good yield, it has proven to be unsuitable for the preparation of hafnocene thiolates, the disubstituted product being obtained along with the starting materials and the monosubstituted complex.[341] An improved synthesis is the reaction of hafnocene dichloride with lithium thiolates in benzene at room temperature, which gave the yellow complexes $[Hf(SR)_2Cp_2]$ (R = Ph, *o*- or *p*-Tol, 4-$NH_2C_6H_4$) in 69–87% yield.[341] This method is also applicable to other systems. Thus, the reaction of metallocene dichlorides with lithium selenates, prepared in situ from selenium and LiR′[342] or from diselenide and $LiBEt_3H$,[343] gave the bisselenato complexes $[M(SeR')_2(\eta\text{-}C_5H_4R)_2]$ in 40–70% yield (M = Zr, Hf, R = H, Bu^t, R′ = Ph;[342] M = Zr, R = Me, R′ = Bz, Ph;[343] M = Zr, Hf, R = Bu^t, R′ = *p*-Tol; M = Hf, R = H, R′ = *p*-Tol;[344] M = Ti, Zr, Hf, R = H, Bu^t, R′ = Ph, *p*-Tol[345]). As MeSeLi is not accessible by the reaction of MeLi with selenium, the methyl selenates were prepared via insertion of Se into a M–C bond (vide infra).[342] The complexes are air stable for several hours or days, with the Hf complexes being more stable than those of Zr.[342] The dithiolato complexes $[Zr(SR)_2(\eta\text{-}C_5H_4R')_2]$ (R = Bz, R′ = Me, Bu^t) are prepared accordingly from zirconocene dichloride and a mixture of dibenzyl disulfide with $LiBEt_3H$ in 89–94% yield.[343]

Reaction of the metallocene dichlorides with equimolar amounts of lithium phenylselenate (from PhSeH and BuLi) gave the monoselenato complexes $[MCl(SePh)Cp_2]$ (M = Ti, Zr, Hf) in 34–76% yield.[346] The zirconium and hafnium complexes are yellow and air sensitive. The products were characterized by ^1H NMR, IR, and mass spectroscopy. The chemical shift of the cyclopentadienyl ligands decreases in the following order Ti > Zr > Hf.[346]

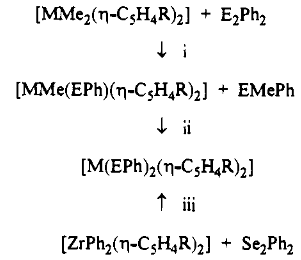
Salt elimination was also employed in the synthesis of **94** (X = SMe, R = Ph, *p*-Tol, M′ = Mo, W, M = Ti, Zr) (^{31}P δ = 7–26 ppm) from the chloro derivatives **94** (X = Cl) and NaSMe (57–69% yield).[347]



94

Phosphine sulfides were introduced into metallocene(IV) complexes by the reaction of $[MCl_2Cp_2]$ with $LiSPR_2$ (M = Zr, Hf, R = Cy, Ph).[135] Yields range from 65 to 75%. Alternatively, these complexes were obtained from the reaction of the appropriate metallocene bisphosphido complex and $HSPR_2$ or elemental sulfur (cf. section IV.A.4).[135] When the reaction mixture was stirred for 1–2 days, the final product was the metallocene sulfide $[\{M(\mu\text{-}S)Cp_2\}_2]$ (50–60% yield) (cf. section VI.B.1).[135] If lithium phosphine selenide is used in the reaction, the corresponding metallocene selenides $[\{M(\mu\text{-}Se)Cp_2\}_2]$ are formed immediately in over 90% yield.[135] The phosphine sulfide complexes show a singlet in the ^{31}P NMR spectrum (25–26 ppm, M = Zr; 63.5–64.5 ppm, M = Hf).[135]

Scheme 27[a]



[a] (i) Heptane; (ii) UV; (iii) UV, E = Se.

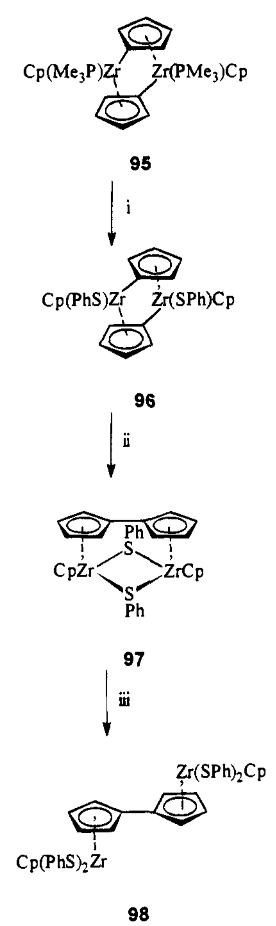
c. Insertion of Chalcogens into M–C Bonds. Chalcogens readily insert into zirconium– and hafnium–methyl bonds to give $[M(EMe)_2(\eta\text{-}C_5H_4R)_2]$ (M = Zr, Hf, R = H, Bu^t, E = Se;[342,345] M = Zr, R = H, E = S, Te[343]). The rate of insertion decreases in the sequence S > Se > Te, as do the yields (S, 47%; Se, 31%; Te, 19%). The methylselenato complexes decompose in days when exposed to air and are very sensitive in benzene solution.[342] The complexes $[M(SeR')_2(\eta\text{-}C_5H_4R)_2]$ (M = Zr, Hf, R = H, R′ = Ph; M = Zr, Hf, R = H, Bu^t, R′ = Me) exhibit parent ion peaks in the mass spectrum.[342,345] For the Zr derivatives (R = H, Bu^t, R′ = Me, Ph) fragmentation with loss of R′ is observed, while for the Hf complexes loss of SeR′ is favored.[342] In the IR spectrum no ν(M–Se) mode was assignable.[342]

$[HfPh_2(\eta\text{-}C_5H_4Bu^t)_2]$ cleanly inserts Se with formation of $[Hf(SePh)_2(\eta\text{-}C_5H_4Bu^t)_2]$, while $[HfPh_2Cp_2]$ failed to give a clean reaction product.[345] $[ZrPh_2(\eta\text{-}C_5H_4R)_2]$ (R = H,[345] Me[343]) inserts Se to give $[Zr(SePh)_2(\eta\text{-}C_5H_4R)_2]$, while $[ZrPh_2(\eta\text{-}C_5H_4Bu^t)_2]$ gives the metallacycle $[Zr(1,2\text{-}Se_2C_6H_4)(\eta\text{-}C_5H_4Bu^t)_2]$ (cf. section VI.A.2).[345] The reaction mixtures (R = H, Me) also contain the four-membered metallacyclic compounds.[343] This side reaction considerably restricts the use of this reaction for the preparation of metallocene chalcogenato complexes.[343]

d. Oxidative Addition of Diphenyl Dichalcogenides. The reaction of dimethylmetallocenes with diphenyl dichalcogenides in the dark yielded the monochalcogenato complexes shown in Scheme 27 (M = Zr, R = H, Bu^t, E = Se; M = Zr, R = H, E = S;[348] M = Zr, R = Bu^t; M = Hf, R = H[345]). The corresponding bischalcogenato complexes are formed on UV irradiation of the solutions or by employing two moles of E_2Ph_2.[348] The reaction was much slower if the *tert*-butylcyclopentadienyl derivatives were used or when Se_2Ph_2 was employed in the reaction. Diphenylzirconocenes did not react at room temperature in the dark. Upon irradiation, the disubstituted product is formed exclusively (Scheme 27).[348] Homolytic S_H2 substitution at the metal center was proposed as the mechanism.[348] Similarly, irradiation of $[MR'_2(\eta\text{-}C_5H_4R)_2]$ (M = Ti, Zr, Hf, R = H, R′ = Ph; M = Zr, Hf, R = Bu^t, R′ = Ph; M = Hf, R = H, Bu^t, R′ = *p*-Tol;[49] M = Zr, R = Bu^t, H, R′ = Ph[185]) in the presence of Se_2Ph_2 gives $[M(SePh)_2(\eta\text{-}C_5H_4R)_2]$ and R′–R′.[345]

Oxidation of **95** with Ph_2S_2 afforded the thermally unstable zirconium(III) complex **96**, which undergoes reductive coupling of the two bridging η^1,η^5-C_5H_4

Scheme 28[a]

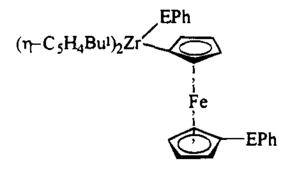


[a] (i) S_2Ph_2, $-2PMe_3$; (ii) Δ; (iii) S_2Ph_2.

rings to give a *cis*-fulvalenezirconium(III) complex **97** in boiling THF.[306,83] Further oxidation of **97** with Ph_2S_2 gave the bright yellow zirconium(IV) complex **98** (Scheme 28).[306,83]

Similarly, oxidative addition of disulfides (S_2R_2, R = Et, Ph) to $[Zr(CO)_2Cp_2]$ gives $[Zr(SR)_2Cp_2]$ in 57 and 84% yield, respectively.[349] Reaction of $[Zr(SPh)_2Cp_2]$ with the dicarbonyl complex gave the red, dimeric zirconocene(III) complex $[\{Zr(\mu\text{-}SPh)Cp_2\}_2]$ in 64% yield.[349]

Irradiation of **42** (R = Bu^t) in the presence of E_2Ph_2 (E = S, Se) yields **99**.[185]



99

With protic reagents $[Zr(C_2H_4)(PMe_3)Cp_2]$ undergoes protonation of the ethylene ligand. Thus, ethanedithiol yields $[Cp_2(Et)Zr(\mu\text{-}SCH_2CH_2S)Zr(Et)Cp_2]$[288] and Bu^tSH gives $[ZrEt(SBu^t)Cp_2]$.[206] Reaction of the latter with HX (X = HC(=O)O, ac) or ROH (R = Me, Et, Ph) gives $[ZrEt(X)Cp_2]$ and $[ZrEt(OR)Cp_2]$, respectively.[206]

The electronic structures of the complexes $[M(ER)_2(\eta\text{-}C_5H_4R')_2]$ (M = Zr, E = S, R = Ph, R′ = Bu^t; M = Zr, Hf, E = Se, R = Ph, R′ = H, Bu^t; M = Zr, E = Se, R = *p*-Tol, Me, R′ = H; M = Zr, Hf, E = Se, R = *p*-Tol, R′ = Bu^t, M = Zr, $(ER)_2$ = 1,2-$Se_2C_6H_4$, R′ = Bu^t) and $[ZrMe(SePh)(\eta\text{-}C_5H_4Bu^t)_2]$ as well as some titanocene analogues have been determined by He(I) and He(II) spectroscopy.[350] The analysis allowed the structures to be established, especially the conformation of the aryl groups with respect to the other ligands, as well as the influence of the metal atoms on the energy of the HOMO.[350]

^{77}Se and ^{13}C NMR data are available for $[M(SeR)_2(\eta\text{-}C_5H_4R')_2]$ (M = Zr, Hf, R = Ph, *p*-Tol, R′ = H, Bu^t) as well as their titanium analogues.[344] In the ^{77}Se NMR, a shielding effect is observed on going from Ti (δ = 839–852 ppm) to Zr (δ = 664–694 ppm) and Hf (δ = 540–557 ppm). Substitution of the aryl ligand by methyl led to a pronounced up-field shift of the ^{77}Se resonance in $[Zr(SeMe)_2Cp_2]$ (267.2 ppm).[344]

e. Thermal Rearrangement of α-Zirconocenyl Thioethers. Zirconocene thiolates $[Zr\{CHR'(SiMe_3)\}(SR)Cp_2]$ were obtained by thermal rearrangement of α-zirconocenyl thioethers $[Zr\{CH(SR)(SiMe_3)\}(R')Cp_2]$ in toluene (R = Ph, R′ = Ph, *p*-Tol, 4-$MeOC_6H_4$, 4-ClC_6H_4;[351] R = Me, R′ = Ph[351,352]) in 58–83% yield. The reaction followed first-order kinetics. Labeling studies showed this rearrangement to be intramolecular.[351] No thermal rearrangement was observed if R = R′ = Me, R = Me, R′ = Bz,[351,352] or R = Me, R′ = Cl.[352]

Similarly, thermolysis of $[Zr\{CH(SPh)Ph\}_2Cp_2]$ in toluene afforded $[Zr(SPh)_2Cp_2]$ and stilbene in over 90% yield.[353] The reaction followed first-order kinetics. The proposed mechanism involves a β-metal thiolate elimination.[353]

f. Solvolysis. Reactions of metal alkyls or amides with acidic proton sources are known to result in M–C or M–N bond cleavage and formation of a metal–heteroatom bond. Thus, the complexes $[M(SR)_2Cp_2]$ (M = Zr, R = Ph;[218] M = Hf, R = Bu^t [35]) have been obtained by solvolysis of $[ZrCp_4]$ and $[Hf(NMe_2)_2Cp_2]$, respectively, with the appropriate thiol. Similarly, the reaction of dimethylzirconocene with alkyl thiols in the presence of trimethylphosphine gave $[ZrMe(SCH_2R)Cp_2]$ (R = Me, Ph;[354,355] 4-$CF_3C_6H_4$, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$[354]) in ca. 90% yield, although the products could not be obtained pure.[354] Heating the reaction mixtures in benzene for several hours gave the corresponding zirconocene thioaldehydes $[Zr(\eta^2\text{-}SCHR)(PMe_3)Cp_2]$.[354,355] Dibenzyl zirconocene reacts with benzenethiol with formation of $[Zr(SPh)_2Cp_2]$ in 77% yield. In the presence of traces of di-*tert*-butyl hyponitrite, a 50% increase in the reaction rate was observed. The effect was not observed when diphenyl disulfide was used instead of the thiol.[356]

When alkylenedithiols $HS(CH_2)_nSH$ (n = 2–4), *o*- or *m*-$(HSCH_2)_2C_6H_4$ were reacted with dimethylzirconocene dimeric complexes $[Cp_2Zr(\mu\text{-}SRS)_2ZrCp_2]$ (R = $(CH_2)_n$, n = 2–4; *o*- or *m*-$CH_2C_6H_4CH_2$) were obtained in 40–55% yield.[357,358] Similar results have been reported for the analogous reaction with diols (cf. section V.A.1).[180] Alternatively, the same products were obtained by reacting *S*-(trimethylsilyl)alkylenedithiols, $HS(CH_2)_nSSiMe_3$ (n = 2, 3) with dimethylzirconocene or zirconocene hydride chloride in 60–67% and 50–55% yield, respectively.[358] The molecular structures of $[Cp_2Zr(\mu\text{-}SRS)_2ZrCp_2]$ [R =

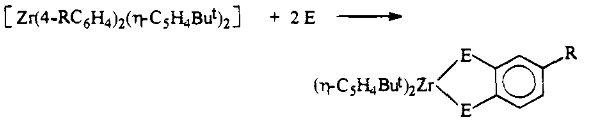
$(CH_2)_2$, Zr—S 2.56(1), 2.676(8) Å;[358] R = $(CH_2)_3$, Zr—S 2.480(2) to 2.518(2) Å[357,358]] were determined. These compounds [R = $(CH_2)_n$, n = 2 or 3] act as macrocyclic metalloligands. Thus, the reaction with $AgBPh_4$ led to encapsulation of the silver ion (30–45% yield). The structures of the resulting cationic complexes have been determined [R = $(CH_2)_2$, Zr—S 2.560(5) to 2.617(5) Å, Ag—S 2.479(5) to 2.514(5) Å;[358] R = $(CH_2)_3$, Zr—S 2.550(5) to 2.559(5) Å, Ag—S 2.658(5) to 2.599(5) Å[357,358]].

g. Hydrozirconation of Thioketones. Aromatic and aliphatic thioketones, $R_2C{=}S$ (4,4′-dimethoxythiobenzophenone, 4,4′-dimethylthiobenzophenone, 4-methoxythiobenzophenone, thiobenzophenone, 4,4′-bis(dimethylamino)thiobenzophenone, thiocamphor, adamantanethione, 3-thioxoandrosta-1,4-dien-17-one), undergo hydrozirconation at room temperature with $[\{ZrCl(H)Cp_2\}_n]$ to give yellow $[ZrCl(SCHR_2)Cp_2]$.[359] The products were generated in situ for use in organic synthesis.[359]

2. Dichalcogenophenylene Metallocenes

Related complexes, reported in 1968, include $[Zr(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)Cp_2]$ and $[Zr(1,2\text{-}S_2C_6H_4)Cp_2]$[331] and the enedithiolates $[Zr\{SC(R){=}C(R)S\}Cp_2]$ (R = CN,[331] H[360,361]).

a. Synthesis. Sulfur and selenium combine with diarylzirconocenes in boiling heptane to give the corresponding dichalcogenophenylene zirconocenes (eq 35; E = Se, R = H, Me;[344,362] E = S, Se, R = H, OMe; E = Te, R = H;[363] E = S, Se, R = NMe_2, Br[364]) in 64–80% yield. With tellurium, the reaction proceeded only at lower temperature (boiling hexane for 120 h) in 60% yield.[363] It was suggested that upon heating (aryne)metallocenes are generated and undergo insertion of two chalcogen atoms. Metallacycles were not obtained for zirconocene derivatives with unsubstituted cyclopentadienyl ligands nor for hafnocene derivatives.[363]



(35)

100

A more general route to dichalcogenophenylene metallocenes $[M(1,2\text{-}E_2C_6H_4)(\eta\text{-}C_5H_4R)_2]$ is the reaction of metallocene dichlorides with dipotassium or dilithium benzene-*o*-dichalcogenate (M = Zr, Hf, R = H, E = Se;[363,365] M = Hf, R = Bu^t, E = Se;[363] M = Hf, R = H, E = Te,[366] S[341]). $[Hf(1,2\text{-}S_2\text{-}4\text{-}MeC_6H_3)Cp_2]$ was prepared accordingly.[341] These complexes are more air stable than the corresponding dithiolato complexes. The related *cis*-1,2-enedithiolato complex $[Hf\{S_2C_2(CN)_2\}Cp_2]$ was obtained by the same method in 78% yield.[341]

The mixed *o*-thiatelluraphenylene zirconocene complexes, $[Zr(1\text{-}S\text{-}2\text{-}TeC_6H_4)(\eta\text{-}C_5H_4R)_2]$ (R = H, Bu^t) were obtained from zirconocene dichloride and dilithium *o*-benzenethiatelluride as violet-brown crystals in 33–46% yield.[367] Accordingly, the dilithium salt of 2-aminobenzenethiol reacts with $[MCl_2Cp_2]$ (M = Ti, Zr, Hf) to give the corresponding N,S chelate complexes in 51–72% yield.[43] The Ti derivative is dark red, and the Zr and Hf complexes are yellow or orange. The Ti complex shows no dynamic behavior in the ^1H NMR while the Hf complex exhibits rapid ring inversion at room temperature (cf. section III.A.1).[43]

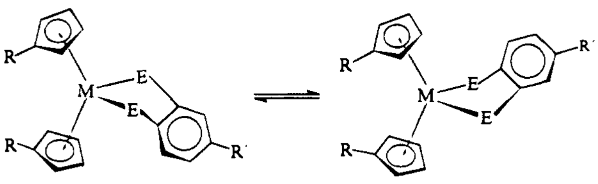
Table 4. Activation Parameters for $[M(1,2\text{-}E_2\text{-}4\text{-}R'C_6H_3)(\eta\text{-}C_5H_4R)_2]$

M	E	R	R′	$\Delta G^\ddagger$ (kJ/mol)	T (°C)	ref
Zr	S	H	H or Me		<−80	331
Hf	S	H	H	44.8	−64	341
Hf	S	H	Me	46.8	−54	341
Zr	Se	H	H		<−80	365
Hf	Se	H	H		−75	365
Hf	Te	H	H	48	−50	366
Zr	S	Bu^t	H	44	−45(Cp)	363
Zr	Se	Bu^t	H	48	−35(Cp)	363
Zr	Te	Bu^t	H	51	−30(Cp)	363
				49	−40(Bu^t)	363
Zr	S	Bu^t	OMe	48	−30(Cp)	363
Zr	Se	Bu^t	OMe	49	−30(Cp)	363
				49	−50(Bu^t)	363

When metallocene dichlorides $[MCl_2(\eta\text{-}C_5H_4R)_2]$ were reacted with 1,2,4,5-tetramercaptobenzene in the presence of triethylamine (R = H) or with 1,2,4,5-tetrasodium tetramercaptobenzene (R = H, $SiMe_3$) the dimeric chelate complexes $[\{(\eta\text{-}C_5H_4R)_2Zr\}_2(\mu\text{-}1,2,4,5\text{-}S_4C_6H_2)]$ (M = Ti, Zr, Hf, R = H,[368] $SiMe_3$[369]) were obtained in 35–67% yield.

b. Spectroscopic Properties. ^{77}Se NMR data are available for **100** [E = Se^1, Se^2, (R = H) 562.9 ppm; (R = Me) 574.5 (Se^1), 568.8 ppm (Se^2)].[344,362]

Variable-temperature ^1H NMR indicates that the five-membered ME_2C_2 chelate rings undergo rapid inversion at room temperature (eq 36). Activation parameters of zirconocene and hafnocene derivatives are given in Table 4. Related titanocene complexes have also been studied.[365,377,378] There is no significant correlation between the activation parameters and the central atom or the coordinating chalcogen atom. The maleonitriledithiolato complex $[Hf\{S_2C_2(CN)_2\}Cp_2]$ shows only one resonance for the Cp protons even at −90 °C.[341]



(36)

Negative chemical ionization (NCI) mass spectra have been recorded for $[Zr(EPh)_2(\eta\text{-}C_5H_4Bu^t)_2]$ (E = Se, Te), which show very little fragmentation.[370] Complexes $[\{(\eta\text{-}C_5H_4R)_2Zr\}_2(\mu\text{-}1,2,4,5\text{-}S_4C_6H_2)]$ (R = H) are insoluble in common organic solvents, but molecular ions were observed in the mass spectrum.[368] For the more soluble derivatives (R = $SiMe_3$, M = Ti,[368] Zr, Hf[369]) the presence of two conformations (chair and boat) is indicated by variable-temperature ^1H NMR. Thus, both conformations are present in solution at room temperature due to rapid inversion of the MS_2C_2 chelate rings, while only one conformation is present at low temperature (chair or boat).

c. Structural Data. A crystal structure determination of $[Zr(1,2\text{-}Se_2C_6H_4)(\eta\text{-}C_5H_4Bu^t)_2]$ confirmed the "envelope" conformation deduced from ^1H NMR studies [Zr—Se 2.670(1), 2.639(1) Å, Se—Zr—Se 81.1(1)°].[362] The dihedral angle between the phenyl—Se—Se and Zr—Se—Se planes of 56.1° is comparable to that found in $[Ti(1,2\text{-}S_2C_6H_4)Cp_2]$[371] (46°), the ethylene-1,2-dithiolato complex $[\overline{Ti\{SC(H)=C(H)S}\}Cp_2]$[372] (46.1°) and the tetrathiolato complex $[Cp_2Ti(S_2C=CS_2)TiCp_2]$[373] (46°), while comparable molybdocene and tungstocene complexes show much smaller angles (2.6–9°).[374–376]

The molecular structure of $[Zr(1\text{-}S\text{-}2\text{-}TeC_6H_4)(\eta\text{-}C_5H_4Bu^t)_2]$ (dihedral angle 53.7°)[367] is closely related to that of the *o*-diselenaphenylene zirconocene complex. However, the disorder of the chalcogen atoms in the former prevents an accurate comparison.

The molecular structure of $[\{(\eta\text{-}C_5H_4R)_2Zr\}_2(\mu\text{-}1,2,4,5\text{-}S_4C_6H_2)]$ (M = Ti, Hf, R = $SiMe_3$) shows the presence of the chair conformation in the solid state.[369] The dihedral angle (MS_2/S_2C_2) of 47° (M = Ti) and 52° (M = Hf) is comparable to those found in dichalcogenophenylene metallocene complexes.[369]

B. Dimeric Chalcogenido-Bridged Metallocene(IV) Complexes

1. Synthesis

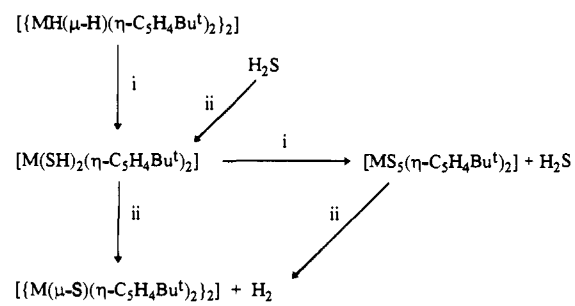
Several routes have been employed for the synthesis of chalcogenido-bridged bimetallic complexes: (a) classical metathetical reactions of metallocene dichlorides and chalcogenides, (b and c) reaction of a highly reactive organometallic species with elemental chalcogen, (d) replacement of chalcogen-containing ligands by chalcogen atoms, and (e) photochemical or thermal synthesis.

a. From Metallocene Dichlorides and Chalcogenide Anions. The reaction of metallocene dichlorides with chalcogenide anions in THF (18 h to 6 days) provides a facile route to chalcogenido-bridged complexes $[\{M(\mu\text{-}E)(\eta\text{-}C_5H_4R)_2\}_2]$ (M = Zr, Hf, R = H, Bu^t, E = S, Se;[379,301] M = Zr, Hf, R = Me, E = S, Se[379]). The required anhydrous nucleophilic species, E^{2-}, can be generated by reduction of the chalcogen with sodium metal or lithium triethylborohydride.[379,301] The rate of reaction is sensitive to steric hindrance, the slowest reaction being observed when R = Bu^t. The yield is 35–78% (except for M = Zr, Hf, R = H, E = Se, 5 and 13% yield). The lower yield for the unsubstituted selenido-bridged complexes was explained in terms of lower solubility and higher sensitivity toward hydrolysis.[379]

When metallocene dichloride was reacted with lithium phosphine selenides ($LiSePR_2$, R = Cy, Ph) the complexes $[\{M(\mu\text{-}Se)Cp_2\}_2]$ (M = Zr, Hf) were formed immediately, while the reaction with the corresponding lithium phosphine sulfides takes 1–2 days to give the corresponding sulfido-bridged complexes (via phosphine sulfido complexes, cf. section VI.A.1).[135]

b. From Metallocene Dihydrides. Dimeric metallocene dihydrides react with gray selenium or tellurium in toluene or THF for 1–3 days to afford exclusively the four-membered bimetallacyclic compounds $[\{M(\mu\text{-}E)(\eta\text{-}C_5H_4R)_2\}_2]$, in 40–79% yield (M = Zr, Hf, E = Se, R = Bu^t;[380,381] M = Zr, E = Se, R = H, Me;[380] M = Zr, Hf, E = Te, R = Bu^t [380]).

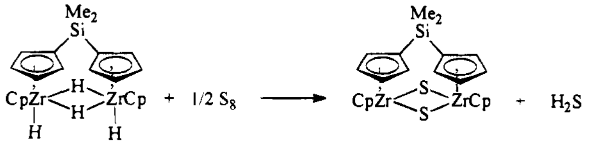
Scheme 29[a]



[a] (i) S; (ii) $[\{MH(\mu\text{-}H)(\eta\text{-}C_5H_4Bu^t)_2\}_2]$.

In the case of sulfur, the first step of the reaction involves the insertion of a sulfur atom into the metal—hydrogen bonds with formation of a bissulfanido complex, which can then react with either of the starting materials to give the sulfido-bridged bimetallic complex or the metallacyclohexasulfane (Scheme 29; M = Zr, Hf).[380,381] All of the reaction products (including H_2 and H_2S) were detected by ^1H NMR.[381] The bissulfanido complexes $[M(SH)_2(\eta\text{-}C_5H_4Bu^t)_2]$ (M = Zr, Hf) have been prepared independently from the corresponding metallocene dichlorides and hydrogen sulfide in the presence of triethylamine in toluene and shown to react with sulfur or metallocene dihydride as formulated in Scheme 29.[380] The metallocene dihydride reacts with the metallacyclohexasulfane complex to give the sulfido-bridged dimer, and with hydrogen sulfide the bissulfanido complex was obtained.[380] Thus, the sulfido-bridged species are only obtained when excess dihydrido complex is used. It was suggested that the difference in reactivity of S, Se, and Te is attributable to the increased solubility of sulfur in organic solvents.[380]

When the dinuclear zirconocenophane complex **101** was reacted with sulfur, only the sulfido-bridged product **102** was obtained in 39% yield (eq 37).[312] Alternatively, **102** was obtained on refluxing a solution of $[(ZrMe_2Cp)_2\{(\eta\text{-}C_5H_4)_2SiMe_2\}]$ and sulfur for 12 h.[312] The sulfido bridges in **102** resist cleavage with PMe_3, MeNC, and pyridine.[312]



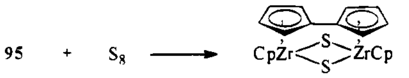
(37)

101 **102**

c. From Metallocene(II) Precursors. $[Zr(butadiene)(\eta\text{-}C_5H_4R)_2]$ (R = Bu^t, 1,1-dimethylpentyl) reacted with stoichiometric amounts of sulfur, gray selenium, or tellurium to give the complexes $[\{Zr(\mu\text{-}E)(\eta\text{-}C_5H_4Bu^t)_2\}_2]$ (E = S, Se[382] Te[300,383]) and $[\{Zr(\mu\text{-}Te)(\eta\text{-}C_5H_4R)_2\}_2]$ (R = 1,1-dimethylpentyl)[383] in 35–50% yield.

Oxidation of **95** with elemental sulfur resulted in reductive coupling of the two bridging $\eta^1,\eta^5\text{-}C_5H_4$ rings to give the *cis*-fulvalenezirconium(IV) complex **103** in 40% yield (eq 38).[306] The bright-red complex

103 was also obtained from the reaction of [$(ZrMe_2Cp)_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)$] or [$\{Zr(\mu\text{-}SPh)Cp\}_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)$] with sulfur.[306]



(38)

103

The reaction of [$Zr(CO)_2(\eta\text{-}C_5R_5)_2$] (R = H, Me) with H_2S or H_2Se in toluene at 80 °C over 3–8 days in a 1:1 ratio gave air-stable [$\{Zr(\mu\text{-}S)(\eta\text{-}C_5R_5)_2\}_2$] (79%, R = H; 46%, R = Me)[293] and [$\{Zr(\mu\text{-}Se)(\eta\text{-}C_5R_5)_2\}_2$] (50–62% yield, R = H, Me),[294] respectively, with liberation of CO and concomitant reduction of H_2S or H_2Se to H_2.

d. Replacement of Chalcogen-Containing Ligands by Chalcogen Atoms. The reaction of zirconocene diselenates or dithiolates with elemental sulfur or selenium gave the corresponding four-membered metallacyclic compounds in 55–100% yield as estimated by ^1H NMR (eq 39; E = Se, R = Bz, Ph, E′ = S; E = Se, R = Bz, E′ = Se; E = S, R = Bz, E′ = S).[343] The possibility that the products are formed via thermal decomposition of the starting materials can be excluded since the latter are stable for days in C_6D_6 below 50 °C.[343]

$$2\,[Zr(ER)_2(\eta\text{-}C_5H_4Me)_2] + 2\,E' \rightarrow [\{Zr(\mu\text{-}E')(\eta\text{-}C_5H_4Me)_2\}_2] + E_2R_2 \qquad (39)$$

e. Photochemical or Thermal Synthesis. The photochemical or thermal synthesis makes use of a photochemically or thermally generated low-valent metallocene unit. This method is, however, confined to cyclopentadienyl ligands which bear a bulky alkyl group (e.g. Bu^t). Photolysis of metallocene dialkyl or diaryl complexes in the presence of gray selenium or sulfur gave the chalcogenido-bridged dimeric complexes shown in eq 40 (M = Zr, Hf, R = Me, Ph, E = Se,[379,384] S;[379] M = Zr, R = Ph, E = Se;[344,345] M = Hf, R = *p*-Tol, E = Se[345]) in 60–70% yield. Biphenyl was obtained when diphenyl complexes were used as starting materials. The overall yield was lower when dimethylmetallocenes were used, and the byproducts were not characterized.[379,384] When the unsubstituted diphenylzirconocene was used, a complex mixture was obtained instead of the expected products. The selenido-bridged complexes (eq 40) were also formed by UV irradiation of a solution of equimolar amounts of diphenylmetallocene and [$\{M(SePh)_2(\eta\text{-}C_5H_4Bu^t)_2\}_2$].[384]

$$2[MR_2(\eta\text{-}C_5H_4Bu^t)_2] + 2E \xrightarrow{h\nu,\ \text{heptane}} [\{M(\mu\text{-}E)(\eta\text{-}C_5H_4Bu^t)_2\}_2] \qquad (40)$$

Thermally induced dimerization of metallocene dithiols [$M(SH)_2(\eta\text{-}C_5H_4R)_2$] with loss of hydrogen sulfide gives [$\{M(\mu\text{-}S)(\eta\text{-}C_5H_4R)_2\}_2$] and was observed to occur fairly readily when R = H (M = Zr, Hf),[385] while the reaction of the species with R = Bu^t needed more drastic conditions (boiling toluene, 30 h).[381]

Monitoring of the thermolysis of the cationic complex [$Zr(SBu^t)(THF)Cp_2$][BPh_4] in THF-d^8 at 97 °C by ^1H NMR showed the formation of [$\{Zr(\mu\text{-}S)Cp_2\}_2$] and products due to decomposition of [Bu^t][BPh_4].[386]

Thermolysis of [$Zr\{\eta^2\text{-}S_2CP(SiMe_3)_2\}(Cl)Cp_2$] gives [$\{Zr(\mu\text{-}S)Cp_2\}_2$].[134] The same product is obtained from [$Zr\{P(SiMe_3)_2\}_2Cp_2$] or [$ZrMe\{P(SiMe_3)_2\}Cp_2$] and elemental sulfur in low yield.[134]

2. Mixed Species

a. Mixed-Chalcogenido Ligands. UV irradiation of the oxo-bridged complex [$\{ZrMe(\eta\text{-}C_5H_4Bu^t)_2\}_2O$] in the presence of sulfur or gray selenium in toluene gave the mixed chalcogenide-bridged complexes [$\{ZrMe(\eta\text{-}C_5H_4Bu^t)_2\}_2(\mu\text{-}O)(\mu\text{-}E)$] (E = S,[301] Se[300,301]). The complexes display the characteristic IR band at 790 cm^{-1} associated with the Zr—O—Zr unit. In the ^1H NMR spectra the cyclopentadienyl signals are split into four resonances at ambient temperature.[301]

Controlled hydrolysis of [$\{Zr(\mu\text{-}Te)(\eta\text{-}C_5H_4Bu^t)_2\}_2$] with $CuSO_4{\cdot}5H_2O$ afforded the green complex [$\{Zr(\eta\text{-}C_5H_4Bu^t)_2\}_2(\mu\text{-}O)(\mu\text{-}Te)$] in 60% yield.[300] At ambient temperature four signals are observed for the methine protons and one for the Bu^t group. With decreasing temperature, these split into eight and two resonances, respectively, which is in accordance with the overall C_2 symmetry observed in the solid state (cf. section VI.B.4).[300] The activation energy for the hindered M—$C_5H_4Bu^t$ rotation was estimated to be $\Delta G^{\ddagger}(206\ K) \approx 40.2 \pm 1.5$ kJ mol^{-1}.[300] Similar dynamic NMR spectra were observed for the selenido analogue ($\Delta G^{\ddagger}(222\ K) \approx 46.1 \pm 1.5$ kJ mol^{-1}).[300]

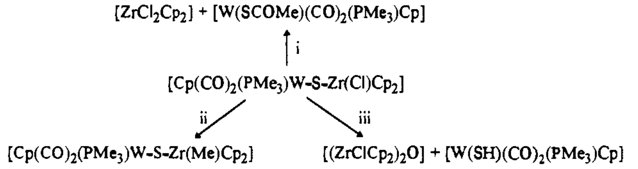
b. Heterobimetallic and Unsymmetrical Complexes. A facile synthesis of sulfido-bridged bimetallic species or unsymmetrically substituted complexes is shown in eq 41 (M = M′ = Zr, R = H; M = Hf, M′ = Zr, R = H, Bu^t; M = Zr, M′ = Hf, R = H, Bu^t).[343] The products are red, blue, or green, have high melting points (>210 °C), and are obtained in 48–66% yield. Replacement of the dihydride by a dimethyl complex was successful only for the preparation of the derivative with M = M′ = Zr and R = H.[343] For the other combinations, no reaction was observed at room temperature, and heating the mixture led to condensation and formation of the symmetrical complexes.[343]

$$2\,[M(SH)_2(\eta\text{-}C_5H_4Bu^t)_2] + [\{M'H(\mu\text{-}H)(\eta\text{-}C_5H_4R)_2\}_2] \longrightarrow [(\eta\text{-}C_5H_4Bu^t)_2M(\mu\text{-}S)_2M'(\eta\text{-}C_5H_4R)_2] \qquad (41)$$

The thermal stability of some derivatives (eq 41; M = M′ = Zr, R = H; M = Hf, M′ = Zr, R = H, Bu^t) has been studied. While the heterobimetallic complexes were practically unchanged in C_6D_6 at 190 °C (sealed NMR tube) after 2 days, disproportionation of the unsymmetrical biszirconocene derivative into the corresponding symmetrical complexes [[$\{Zr(\mu\text{-}S)(\eta\text{-}C_5H_4Bu^t)_2\}_2$], [$\{Zr(\mu\text{-}S)Cp_2\}_2$]] was observed under the same conditions (ratio 2:1:1).[343] The same equilibrium mixture (2:1:1, statistical distribution) was obtained, when equimolar amounts of the symmetrical complexes were heated in benzene.[343] The disproportionation and comproportionation are assumed to occur via breaking of metal—sulfur bonds, giving transient monomeric species with a M═S double bond, which dimerize to give the observed products.[343]

The tungsten—zirconium complex *cis*-[$Cp(CO)_2(PMe_3)W{-}S{-}Zr(Cl)Cp_2$], which contains a single unsupported M—S—M′ linkage, was prepared by introducing 1 equiv of propylene sulfide into a mixture of Li[$W(CO)_2(PMe_3)Cp$] and [$ZrCl_2Cp_2$]. One

Scheme 30^a



^{a} (i) MeCOCl; (ii) MeLi; (iii) 0.5 H_2O.

equivalent of propylene is evolved.[387] The heterodinuclear complex exhibits a chemical reactivity (Scheme 30), comparable to that of the oxo-bridged analogue (cf. Scheme 24).

3. Chemical and Spectroscopic Properties

The dimeric chalcogenido-bridged metallocenes are diamagnetic,[384] high melting[300,345,379,382,384] solids. Cryometric measurements have shown that the dimeric structure is retained in solution.[379] The selenido-bridged complexes are bright green,[345,379,382,384] the sulfido-bridged zirconocene complexes are green or blue,[379,382] and the hafnocene derivatives are red.[379,380] The tellurido-bridged complexes $[\{M(\mu\text{-Te})(\eta\text{-}C_5H_4Bu^t)_2\}_2]$ are red to deep violet (M = Zr)[300,380] or red (M = Hf).[380]

For most complexes the ^1H NMR pattern is indicative of cyclopentadienyl ligands in a symmetrical complex.[379,384] The cyclopentadienyl resonances are practically unchanged on cooling.[384] An exception is $[\{Zr(\mu\text{-Te})(\eta\text{-}C_5H_4Bu^t)_2\}_2]$, in which the two resonances for the methine CH groups broaden with decreasing temperature. However, a limiting low-temperature NMR spectrum could not be obtained, and the activation energy for the hindered $Zr-C_5H_4Bu^t$ rotation could not be determined.[300]

^{77}Se NMR data are available for $[\{Zr(\mu\text{-Se})(\eta\text{-}C_5H_4Bu^t)_2\}_2]$ (802.6 ppm).[344]

The mass spectra show the molecular ion peak of the dimeric complexes with the expected isotope distribution pattern.[345,379,384] Successive loss of Cp ligands and chalcogen are generally observed.

4. Structural Data

Structural data are available for several complexes (Table 5).

The symmetrically bridged complexes have an almost exactly square-planar M_2E_2 core (cf. Table 5). Both diagonal element—element distances are clearly beyond bonding range [e.g. Te···Te 4.006(1) Å, Zr···Zr 4.067(1) Å in $[\{Zr(\mu\text{-Te})(\eta\text{-}C_5H_4Bu^t)_2\}_2]$].[300] The presence of a $SiMe_2$ group bridging two cyclopentadienyl ligands has only a minor effect on the central Zr_2S_2 core (dihedral angle 4.1°).[312] The geometry of the Zr_2S_2 core of the fulvalene complex $[\{Zr(\mu\text{-S})Cp\}_2(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]$[306] is closely related to that of zirconocene sulfide.[134,293] However, the former shows considerable deviation from planarity (S—Zr—Zr′—S′ −144.81(5)°).[306] In contrast to the symmetrical dimeric complexes, $[\{Zr(\eta\text{-}C_5H_4Bu^t)_2\}_2(\mu\text{-O})(\mu\text{-Te})]$ exhibits a considerably distorted arrangement.[300]

The heterobimetallic complex *cis*-$[Cp(CO)_2(PMe_3)W-S-Zr(Cl)Cp_2]$ has completely different structural features due to the presence of only one sulfido bridge. Thus, the M—S—M′ angle of 132.42(4)° is large and the overall structure is similar to that observed for μ-oxo complexes (cf. section V.F.3).[387]

C. Zirconocene Sulfide $[Zr(=S)Cp^*_2]$; Generation and Trapping

The unstable zirconocene sulfide was generated and trapped as shown in Scheme 31.[328,329] The trapping products $[\overline{Zr(SCPh=C}Ph)Cp^*_2]$ [Zr—S 2.505(1) Å] and $[Zr(=S)\{4\text{-}Bu^t(NC_5H_4)\}Cp^*_2]$ (Zr—S 2.316 Å) were structurally characterized.

D. Metallocene(IV) Complexes with Polychalcogenido Ligands

1. Synthesis

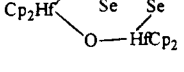
The complexes $[MS_5Cp_2]$ (M = Ti, Zr, Hf) have been known since 1966 (M = Ti) and 1980 (M = Zr, Hf). While the Ti and Zr compounds can be prepared from the reaction of $[M(SH)_2Cp_2]$ with the sulfur-transfer reagent benzimidazole, the highest yield of all three complexes (50–60%) was obtained by the reaction of metallocene dichloride with a $Li_2S_2/3S$ mixture.[332,385]

Pentasulfido complexes are formed during the synthesis of sulfido-bridged complexes when the starting materials are treated with excess sulfur (cf. section VI.B.1). Thus, $[MS_5(\eta\text{-}C_5H_4Bu^t)_2]$ (M = Zr, Hf) was formed when (i) $[MPh_2(\eta\text{-}C_5H_4Bu^t)_2]$ is photolyzed in the presence of excess sulfur,[379] (ii) when $[\{MH(\mu\text{-H})(\eta\text{-}C_5H_4Bu^t)_2\}_2]$ is treated with excess sulfur (cf. Scheme 29),[380,381] or (iii) when [Zr(butadiene)$(\eta\text{-}C_5H_4Bu^t)_2$] is reacted with excess sulfur (cf. section VI.B.1.c).[382] Alternatively, the pentasulfido complexes $[MS_5Cp_2]$ (M = Ti, Zr, Hf) (50–60% yield),[332] $[MS_5(\eta\text{-}C_5H_4Bu^t)_2]$ (M = Zr, Hf) (48–71% yield),[379] and $[ZrS_5\{(\eta\text{-}C_5H_4)_2SiMe_2\}]$ (14% yield)[388] are accessible by treatment of the appropriate metallocene dichloride with a mixture of $LiBEt_3H$ and sulfur (2:5). The pentasulfido complex $[ZrS_5(\eta\text{-}C_5H_4Bu^t)_2]$ reacts with the starting material (metallocene dihydride or butadiene complex) to give $[\{Zr(\mu\text{-S})(\eta\text{-}C_5H_4Bu^t)_2\}_2]$.[380–382]

The general route to pentasulfanes has been extended to the corresponding selenanes (eq 42; M = Ti, Zr, Hf; 50–72% yield).[385] Alternatively, Na_2Se_x (x ca. 5) was used and the same products were obtained in 40–89% yield.[389] The orange zirconocene and hafnocene derivative appeared to be light sensitive, and the latter tended to decompose upon recrystallization. The Ti compound is purple.[385]

$$[MCl_2Cp_2] + 2\,LiBEt_3H + 5\,Se \rightarrow [MSe_5Cp_2] \qquad (42)$$

With traces of moisture, the hafnocene derivative underwent hydrolysis to **104**, which has been structurally characterized [Hf—Se 2.675(5), 2.674(5) Å, Hf—O—Hf 167.4(1)°, Hf—Se—Se and Se—Se—Se 105.4(2)–107.7(3)°].[389]

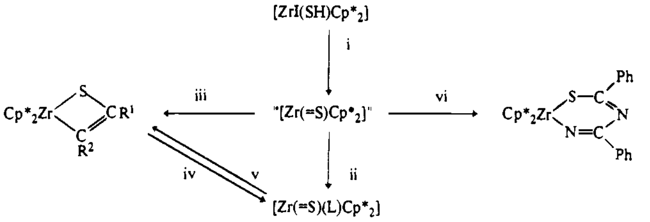


104

Table 5. Selected Structural Parameters for Chalcogenido-Bridged Dimetallic Complexes

compound	M—E (Å)	E—M—E (deg)	M—E—M (deg)	ref(s)
$[\{Zr(\mu\text{-}Te)(\eta\text{-}C_5H_4Bu^t)_2\}_2]$	2.855(1)	89.14(1)	90.86(1)	300,383
$[\{Zr(\mu\text{-}S)Cp_2\}_2]$	2.487(2), 2.480(2)	89.5(2)	90.5(2)	134
$[\{Zr(\mu\text{-}S)Cp_2\}_2]$	2.490(3), 2.482(3)	89.6(1)	90.4(1)	293
$[\{Zr(\mu\text{-}S)Cp\}_2(\eta^5{:}\eta^5\text{-}C_{10}H_8)]$	2.490(1)	87.85(1)	86.60(3)	306
$[\{Zr(\mu\text{-}S)Cp\}_2\{(\eta\text{-}C_5H_4)_2SiMe_2\}]$	2.488(1)	89.87(4)	90.06(4)	312
$[\{Zr(\eta\text{-}C_5H_4Bu^t)_2\}_2(\mu\text{-}O)(\mu\text{-}Te)]$	2.880(1) (E=Te) 1.967(7) (E=O)	84.4(3)	72.1(1) (E=Te) 119.2(2) (E=O)	300
cis-$[Cp(CO)_2(PMe_3)W{-}S{-}Zr(Cl)Cp_2]$	2.418(1)		132.42(4)	387

Scheme 31[a]



[a] (i) +$KN(SiMe_3)_2$, room temperature, −KI, −$HN(SiMe_3)_2$; (ii) L, L = py, 4-*tert*-butylpyridine; (iii) $EtC{\equiv}CEt$, $R^1 = R^2 = Et$; (iv) +L, L = py, 4-*tert*-butylpyridine, $-R^1C{\equiv}CR^2$, $R^1 = R^2 = Et$, $R^1 = R^2 = Ph$, $R^1 = R^2 = p$-Tol; (v) $+R^1C{\equiv}CR^2$, $R^1 = R^2 = Et$, $R^1 = R^2 = Ph$, $R^1 = R^2 = p$-Tol, 85 °C, −L, L = py, 4-*tert*-butylpyridine; (vi) PhCN.

Table 6. Activation Parameters for Pentachalcogenido and Trisulfido Metallocene(IV) Complexes

	$\Delta G^\ddagger$ (kJ mol^{-1})	ref(s)
	$[MS_5Cp_2]$	
M = Zr	(227 K) 48.6	385,332
M = Hf	(257 K) 58.0	385,332
	$[MS_5(\eta\text{-}C_5H_4Bu^t)_2]$	
M = Zr	(243 K) 51.6 (C_5H_4) (239 K) 52.7 (Bu^t)	379
M = Hf	(283 K) 61.2 (C_5H_4) (277 K) 61.3 (Bu^t()	379
	$[MSe_5Cp_2]$	
M = Zr	49.9	385
M = Hf	61.6	385
	$[MS_3Cp^*_2]$	
M = Zr	39.3	385,391
M = Hf	<30	385

While pentasulfido complexes with Cp ligands are only slightly soluble, substituents on the Cp ligand increase the solubility without altering the structural or chemical properties.[390] However, formation of $[MS_3Cp^*_2]$ was observed when the bis(pentamethylcyclopentadienyl)metal dichlorides were reacted with sulfur in the presence of $LiBEt_3H$ (M = Ti, Zr, Hf)[385] or with Li_2S_2/S_8 (1:3/8) in THF (M = Ti, Zr).[391] Yields of 55−76% were obtained for the Ti and Zr derivative, while that of the Hf compound was only 9%. The products are high melting solids, air stable in solution, and monomeric (molecular weight determination). The Ti derivative is black; the others are orange. The reagent $2LiBEt_3H/5S$ has been shown to contain the polysulfide ions S_x^{2-} ($x = 2-5$) in the ratio 2.6:1.4:1.0:4.6 (2:3:4:5) by reaction with benzyl chloride and ^1H NMR investigation of the resulting reaction products.[385]

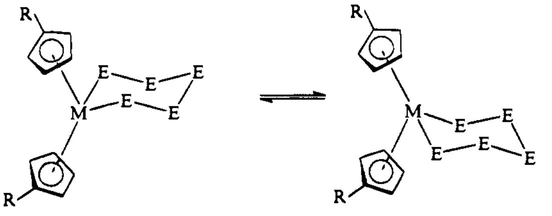
It was shown (^1H NMR monitored) that chalcogenido-bridged dimeric complexes react with excess chalcogen with formation of the corresponding pentachalcogenido complexes $[ZrS_5(\eta\text{-}C_5H_4R)_2]$ (E = S, R = H, Me, Bu^t; E = Se, R = H, Me; 49−100% yield).[343] The reaction rate depends strongly on the bulk of the cyclopentadienyl ligand. Thus, for R = Bu^t, E = S heating is required, and the selenium analogue did not react with elemental Se.[343] Reaction of $[\{Zr(\mu\text{-}Se)(\eta\text{-}C_5H_4Me)_2\}_2]$ with excess sulfur gave the corresponding zirconocene pentasulfide.[343]

The reaction of zirconocene dichloride with Na_2S_5 and $(NH_4)_2S_5$ is reported to give the polymeric products $[\{ZrS_3Cp\}_n]$ and $[\{Zr_2S_7Cp_2\}]$, respectively.[392] Also, treating $[Zr(SH)_2Cp_2]$ with sulfur gave the polymeric product $[\{ZrS_5Cp\}_n]$. The products do not contain $ZrCp_2$ groups.[392]

2. Spectroscopic Properties

a. Mass Spectra. The pentasulfido, pentaselenido, and trisulfido complexes show a molecular ion peak in the mass spectrum. While the first two show metastable ion peaks corresponding to loss of S_2 or Se_2, the trisulfido complexes do not.[385]

b. Variable-Temperature NMR Studies. It was shown earlier that the complexes $[MS_5Cp_2]$ undergo chair-to-chair ring flipping (eq 43).[332,393,394] Thus, at



(43)

low temperature two distinct peaks due to the axial and equatorial Cp groups were observed. The pentaselenido and trisulfido complexes show comparable temperature-dependent ^1H NMR spectra, suggesting that a ring inversion takes place in all the complexes.[385] Table 6 lists the free energy of activation for the ring inversion. The $\Delta G^\ddagger$ values are similar for the pentasulfido and -selenido complexes and follow the order Ti > Zr > Hf. Ring inversion is slow for the titanocene derivatives at room temperature, but rapid for the Zr and Hf analogues. The variable-temperature NMR results for the trisulfido complexes are consistent with the occurrence of two processes. Only one peak for the methyl protons is observed at room temperature, indicating rapid ring inversion. Cooling slows the exchange and two signals appear ($\Delta G^\ddagger$ in Table 6 are given for this process). At very low temperature further collapse occurs, which may be due to the slowing of the rotation of the Cp* rings.[385] For the alkylcyclopentadienyl-substituted pentasulfido complexes two coalescences were observed—one related to the Cp protons, and the other to the Bu^t groups.[379]

3. Structural Data

While the molecular structure of [TiS_5Cp_2] has been known since 1971[395] (two crystalline modifications were characterized by X-ray diffraction which show similar crystallographic data)[395,396] the structures of the Zr and Hf derivatives were reported in 1987.[397] The pentaselenido complexes have also been structurally characterized (Ti,[389,398] Zr, Hf[389]). Of the trisulfido complexes, only the Ti derivative was structurally characterized.[391]

The pentasulfido and -selenido complexes exhibit the chair conformation in the solid state. The M—S and M—Se bond lengths of the pentachalcogenido complexes increase in the order Ti < Hf < Zr [(M—S) 2.448(1) (Ti), 2.523(2) (Hf), 2.544(1) Å (Zr); (M—Se) 2.572(2) (Ti), 2.650(2) (Hf), 2.659(2) Å (Zr)]. The S—M—S and Se—M—Se bond angles increase in the same order [(S—M—S) 94.59(4) (Ti), 96.8(1) (Hf), 97.8(1)° (Zr); (Se—M—Se) 95.4(1) (Ti), 97.7(1) (Hf), 99.3(1)° (Zr)].

E. Metallocene(IV) Dithiocarbamato Complexes and Related Compounds

1. Synthesis

In general, dithiocarbamato complexes are obtained by treatment of metallocene dichloride with equimolar amounts of the potassium, sodium, or ammonium salts of dithiocarbamates in dichloromethane at elevated temperature for up to 20 h (eq 44, Table 7). The known derivatives [$Zr(\eta^2\text{-}S_2CNR'_2)(X)(\eta\text{-}C_5H_4R)_2$] (R = H, Me, X = Cl, R′ = Me, Et;[399] R = H, X = Me, R′ = Me, Et[400]) were prepared accordingly. The zirconocene silyl complexes [$MCl(SiMe_3)Cp_2$] (M = Zr, Hf) reacted with NaS_2CNEt_2 to give a silyl dithiocarbamato complex (cf. section II.D.3).[12] The monothiocarbamato complex [$ZrCl(SOCNMe_2)Cp_2$] was prepared according to eq 44 from zirconocene dichloride and the appropriate sodium salt.[278]

$$[MCl_2(\eta\text{-}C_5H_4R)_2] + \text{Na, K or } NH_4(S_2CNR'R'') \rightarrow [MCl(\eta^2\text{-}S_2CNR'R'')(\eta\text{-}C_5H_4R)_2] \quad (44)$$

Table 7. Abbreviations Used in Eq 44

M	R	R′	R″	ref(s)
Zr,Hf	H,Me	Bz	Bz	401
Zr	Me	H	Ph, o-, *m*-, *p*-Tol, 2-, 3-, 4-ClC_6H_4, 4-$MeOC_6H_4$, 2-, 4-$EtOC_6H_4$, 4-BrC_6H_4, 4-IC_6H_4	402
Zr[a]	H,Me	H	$P(=S)OEt_2$	403
Hf	H	H	cyclopentyl or cycloheptyl	404
Hf	H	Et	*m*-Tol	404
Zr	H	H	cyclopentyl or cyclohexyl	405
Zr	H	Et	*m*-Tol	405
Zr[a]	H,Me	H	$P(=O)(OEt)_2$	406
Zr	H	Cy	Me,Et,Pr^i	407
Zr	H	H	o-, *m*-, *p*-Tol, Ph, 2-, 3-, 4-ClC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$, 4-BrC_6H_4, 4-IC_6H_4	408
Zr	H	Me	Me	409, 410
Zr	H	Bz	Bz	411
Zr	H	NR′R″ = pyrrolidino, piperidino		412
Zr	*b*	Me	Me	413
Zr	*b*	Et	Et	413
Zr	*b*	Pr^i	Pr^i	413
Zr	*b*	H	Ph, *o*-, *m*-, *p*-Tol, 2-, 3-, 4-ClC_6H_4, 4-BrC_6H_4, 4-IC_6H_4, 4-$MeOC_6H_4$	414

[a] Also $Zr(\eta^5\text{-indenyl})_2$. [b] η^5-Fluorenyl instead of Cp.

Substituted dithiocarbamato complexes can be obtained by reacting the appropriate zirconocene derivative [$ZrCl(X)Cp_2$] with sodium dithiocarbamate. Thus, complexes [$Zr(\eta^2\text{-}S_2CNMe_2)(X)Cp_2$] (X = CH_2SiMe_3, CH_2CMe_2Ph, Bz, OPh, 4-pyridyloxy, 2,6-dimethylphenoxide) were prepared.[409] For the halide derivatives (X = Br, I) zirconocene dibromide and diiodide were used as starting materials. The methyl derivative (X = Me) was obtained by reaction of the chloro derivative with MeLi.[409]

The acid–base adduct, $HS_2CNH(NHPh)\cdot H_2NNHPh$, also reacted with [$ZrCl_2L_2$] (L = Cp, $\eta\text{-}C_5H_4Me$, η^5-indenyl, η^5-pyrrolyl) with formation of [$ZrCl\{\eta^2\text{-}S_2CNH(NHPh)\}L_2$], which contains a dithiocarbazato group.[415]

Insertion of CS_2 into the Zr—P bond of [$Zr\{P(SiMe_3)_2\}(X)Cp_2$] (X = Cl, Me) yielded [$Zr\{\eta^2\text{-}S_2CP(SiMe_3)_2\}(X)Cp_2$]. The ligand can be regarded as the P-analogue of a dithiocarbamato ligand (cf. section IV.A.4).[97]

[$ZrCl_2Cp_2$] reacts with dipotassium dithiooxalate (dto) to give [$(ZrClCp_2)_2(dto)$], in which each Zr is five-coordinate, bound to one S and one O of the dto ligand (cf. section V.C.5).[253]

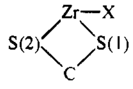
When the reaction shown in eq 44 was carried out with 3 equiv of sodium dithiocarbamate, elimination of cyclopentadienyl sodium occurred and tris(dithiocarbamato) complexes were formed.[404,405,412,416,417]

The related complexes [$Zr(\eta^2\text{-}S_2COR)_3Cp$] (R = Me, Et) have been prepared from [$ZrCl_2Cp_2$] and sodium alkyl xanthates.[418]

2. Structural Data

Crystal structures have been determined for [$Zr(\eta^2\text{-}S_2CNR_2)(X)Cp_2$] (X = Cl, R = Et;[410] X = OPh, R = Me;[419] X = Cl, R = Bz;[401,411] X = $SiMe_3$, R = Et[12]), the related [$ZrCl\{\eta^2\text{-}S_2CP(SiMe_3)_2\}Cp_2$],[97] and the monothiocarbamato complex [$ZrCl(SOCNMe_2)Cp_2$].[278]

For the dithiocarbamato complexes, the endocyclic parameters of the ZrS_2X fragment **105** are very similar. The Zr—S(1) bond which faces the X group is always slightly shorter than Zr—S(2) [Zr—S(1) 2.635(2)–2.670(1) Å, Zr—S(2) 2.713(1)–2.789(4) Å]. The C—S(1) bond is always slightly longer than C—S(2) [C—S(1) 1.713(5)–1.721(11) Å; 1.68(3) in the P-analogue; C—S(2) 1.694(11)–1.708(2) Å, 1.64(3) in the P-analogue]. However, both indicate C—S double-bond character. The S(1)—Zr—S(2) angles range from 63.4(2) to 64.61(1)°, the S(1)—C—S(2) angles from 113.78(9) to 114.7(2)° [117(1)° in the P-analogue]. The X—Zr—S(1) and X—Zr—S(2) bond angles lie in the range of 69.66(1) to 75.6(3)° and 134.06(2) to 139.3(3)°, respectively. The C—N bond lengths range from 1.317(6) to 1.334(5) Å and indicate some multiple-bond character. Accordingly, the coordination of the N atom is trigonal planar and the atoms Zr, X, S(1), S(2), C (**105**), and the NC_2 fragment are nearly coplanar and lie in a quasi-mirror plane. However, the P—C bond length in the P-analogue [1.87(2) Å] indicates a single bond and the PSi_2 plane is roughly orthogonal to the ZrS_2CP plane.



105

In [ZrCl(SOCNMe$_2$)Cp$_2$] [Zr—S 2.641(2) Å] the O and S atoms of the bidentate SOCNMe$_2$ ligand are coplanar with the Zr and Cl atoms. The bidentate ligand is oriented so as to place the smaller O atom in the sterically more congested, lateral coordination site and the larger S atom in the less congested interior site adjacent to the Cl atom. The Zr—O bond [2.249(4) Å] is long, indicating considerable crowding.[278]

3. Spectroscopic Properties

The alkyl- and aryldithiocarbamato complexes of Hf and Zr are generally white; they are air stable as solids but moisture sensitive in solution. Some complexes have been shown to be monomeric nonelectrolytes (molecular weight determination and measurement of the electric conductivity in nitrobenzene).[402–408,413] Measurement of the magnetic susceptibility of some complexes showed them to be diamagnetic.[403,406,408] IR and ^1H NMR spectra have been reported for most complexes.[401–409,415]

a. IR Spectra. The IR spectra unambiguously show the η^2-bonding mode of the dithiocarbamato ligand. One medium to strong band in the range 960–1020 cm^{-1} [ν(C—S)] indicates the presence of a four-membered ZrS_2C ring. The strong thioureide band [ν(C—N)] in the range 1495–1525 cm^{-1} is characteristic for dithiocarbamato complexes. This absorption lies between that for ν(C—N) (1200–1350 cm^{-1}) and ν(C=N) (1640–1690 cm^{-1}), thus indicating some double-bond character. A medium intensity absorption in the region of 320–370 cm^{-1} was assigned to ν(Zr—S). ν(Zr–Cl) lies in the range 360–390 cm^{-1}.

The *O*,*O*-diethylphosphonothiol and the *O*,*O*-diethylphosphonodithiocarbamato derivatives are white, yellow, or brown and decompose in air. The ν(C—N) mode of these complexes is shifted to lower wavenumbers (1355–1375 cm^{-1}) compared to complexes with alkyl or aryl dithiocarbamato ligands, while the range of ν(C—S) is the same for both.[403,406]

In the monothiocarbamato complex [ZrCl(SOCNMe$_2$)Cp$_2$] the ν(CN) and ν(CO) modes are observed at 1568, ν(CS) at 939, and ν(ZrO) and ν(ZrS) at 559 and 333 cm^{-1}, respectively.[278]

b. ^1H NMR. In ^1H NMR spectra one signal is observed for the cyclopentadienyl ligands (5.9–6.6 ppm). The chemical shift decreases in the following order Ti > Zr > Hf for [MCl(η^2-S$_2$CNBz$_2$)(η-C$_5$H$_4$R)$_2$] (M = Ti, Zr, Hf, R = H, Me).[401] The peak for the N—H proton is broad and was observed in the range of 4.7 to 5.2 ppm.[403,405,406,408]

A five-coordinate trigonal-bipyramidal structure with two cyclopentadienyl ligands in axial position has been proposed on the basis of a single resonance for the cyclopentadienyl and for the dithiocarbamato protons in the ^1H NMR spectra at 30 °C.[399] This geometry is unprecedented and unlikely for steric reasons, and it was shown that the complexes are fluxional at 30 °C leading to the observance of single resonances.[409,410] The fluxionality of [Zr(η^2-S$_2$CNMe$_2$)(X)Cp$_2$] (X = Cl,[409,410] Br, I, Me, Bz, OPh, CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, 4-pyridyloxy, 2,6-dimethylphenoxide[409]) and the *N*,*N*-dimethylthiocarbamates [Zr(SOCNMe$_2$)(X)Cp$_2$] (X = Cl, 4-pyridyloxy) has been studied. At low temperature these complexes exhibit two signals for the inequivalent methyl groups. The complexes show similar exchange rates and activation parameters ($\Delta G^{\ddagger}$(298 K) = 50–80 kJ mol^{-1}). The kinetic data are also similar to those of organic dithiocarbamates. Thus, an exchange mechanism involving rotation about the C—N bond was assumed. Preliminary rupture of one Zr—S bond was not ruled out.[409,410,413,414]

c. Electronic Spectra. The electronic spectra of dithiocarbamato complexes exhibit a single band in the region of 360–412 nm, which was assigned to a charge-transfer transition.[402,403,405,406,408,413,414]

VII. Metallocene(IV) Complexes with Zr—M or Hf—M Bonds (M = Transition Metal)

A. Synthesis

A widely used route to complexes with metallocene—transition metal bonds is nucleophilic attack of a metal complex anion on a metallocene halide (eq 45, X = Cl, Me, OBu^t, R = H, M = Ru, Fe;[420] X = Me, Cl, octyl, R = H, M = Fe;[421] X = OBu^t, R = PPh$_2$, M = Fe,[422] yields range from 58 to 83%). The derivatives X = Me, OBu^t, R = H, M = Ru were also obtained from the reaction of the corresponding chloro complex with MeLi or KOBu^t, respectively.[420]

$$[ZrCl(X)Cp(\eta\text{-}C_5H_4R)] + M'[M(CO)_2Cp] \rightarrow [Cp(\eta\text{-}C_5H_4R)(X)Zr\text{-}M(CO)_2Cp] + M'Cl \quad (45)$$

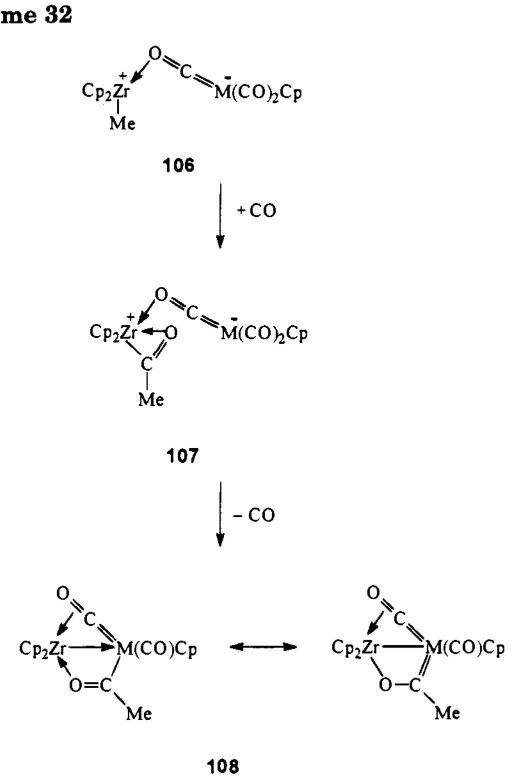
$$(M' = Na, K)$$

Reactions with carbonyl complexes can result in M—M′ or M—O—C—M′ linkage, whereby the bonding mode is determined by steric effects. Thus, the low steric requirements of the M(CO)$_2$Cp fragments (M = Fe, Ru) allow M—M′ bond formation,[420–422] whereas with the more crowded M(CO)$_3$Cp$^-$ anion, Zr—O bonding to give **106** is favored (M = Mo,[423–426] W[426]). However, treatment of **106** with CO gives an η^2-acetyl complex **107**, which slowly loses CO to form the metal—metal bonded complex **108** (Scheme 32).[423,425,426]

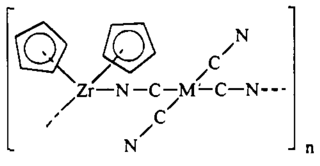
The metallacycle [Zr{C(SiMe$_3$)=CPhCPh=C(SiMe$_3$)}Cp$_2$] reacts with [WH(CO)$_3$Cp] at 70 °C in toluene to give the adduct [Cp$_2$Zr{C(SiMe$_3$)=CHPh}{OC—W(CO)$_2$Cp}] in 36% yield.[202] The bridging CO ligand shows spectroscopic features (ν(CO) 1573 cm^{-1})[202] very similar to those of the analogous bimetallic complexes [Cp$_2$(Me)Zr←O≡C—M(CO)$_2$Cp] [ν(CO) 1540 (M = Cr), 1590 (M = Mo), 1540 (M = W)].[423,427]

Reaction of metallocene diiodide with (NBu$_4$)$_2$[M(CN)$_4$] (M = Pd, Pt) gives polymeric cyano-bridged species (**109**, M = Zr, Hf, M′ = Pd, Pt) without metal—metal bonding in 95–98% yield.[428] The reaction of [ZrCl$_2$Cp$_2$] with potassium hexacyanoferrate-

Scheme 32

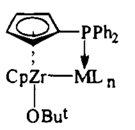


(II) is reported to produce two bimetallic complexes with Zr—Fe bonds.[429]



109

When $[ZrCl(OBu^t)Cp(\eta\text{-}C_5H_4PPh_2)]$ was reacted with $K[Fe(CO)_2Cp]$, the Zr—Fe bonded product shown in eq 45 was obtained in 50% yield.[422] On irradiation, decarbonylation occurred with formation of **110** $[ML_n = Fe(CO)Cp]$ in 84% yield. Irradiating a mixture of the zirconocene alkoxide chloride and $Na[Co(CO)_4]$ for 3 days gave 110 $[ML_n = Co(CO)_3]$ directly in 16% yield.[422]



110

Reaction of $[ZrI_2Cp_2]$ with 2 equiv of $K[Ru(CO)_2Cp]$ gave the orange disubstitution product $[Cp_2Zr\{Ru(CO)_2Cp\}_2]$ in 90% yield.[231] The monosubstituted product was observed as an intermediate by ^1H NMR.[231] The corresponding reaction with $[ZrCl_2Cp_2]$ was much slower, and significant amounts of $[Ru(CO)_2Cp]_2$ were formed.[231] However, the Fe analogue $[Cp_2ZrCl\{Fe(CO)_2Cp\}]$ was obtained by reacting $[ZrCl_2Cp_2]$ with $Na[Fe(CO)_2Cp]$.[421] The more soluble alkyl derivatives $[Cp_2ZrR\{Fe(CO)_2Cp\}]$ (R = Me, octyl) have been prepared analogously.[421] The Fe complex is not accessible via the reaction of $[ZrI_2Cp_2]$ with 2 equiv of $K[Fe(CO)_2Cp]$, which yielded $[Fe(CO)_2Cp]_2$ and unidentified Zr products. Variable-temperature ^1H NMR studies indicated that the monosubstituted product is formed in 100% yield at −78 °C; at −20 °C 33% of the disubstituted compound is formed. Both decompose above −20 °C.[231] Reaction of $[ZrI_2Cp^*_2]$ with 2 equiv of $Na[Fe(CO)_2Cp]$ or of $[\{Zr(N_2)Cp^*_2\}_2(N_2)]$ with $[\{Fe(CO)_2Cp\}_2]$ gave compound **65** (cf. section V.B.).[231,232] The isostructural Ru compound has also been prepared.[231] The formation of these compounds instead of complexes with a direct Zr—Fe or Zr—Ru bond is probably due to a combination of the steric and electronic effects of the Cp* ligand.

Scheme 33[a]

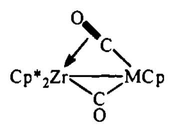
$$\begin{array}{c} [ZrR(X)Cp_2] + K[ReH_6(PPh_2R')_2] \\ \downarrow \text{i} \\ [Cp_2(R)Zr(\mu\text{-}H)_n\{ReH_{6-n}(PPh_2R')_2\}] \ (n > 1) \\ \uparrow \text{ii} \\ [ZrR(X)Cp_2] + [ReH_7(PPh_2R')_2] \end{array}$$

[a] (i) −KCl (R = OPr^i, H, Me, X = Cl, R′ = Me), ref 434; (ii) $-Me_2NH$ (R = Cl, NMe_2, X = NMe_2, R′ = Ph), ref 79.

When the dianion $Fe(CO)_4^{2-}$ was reacted with $[ZrR(X)Cp_2]$ (R = Me, X = Cl; R = octyl, X = BF_4) the disubstituted $Fe(CO)_4$ complexes *cis*-$[Fe(CO)_4(ZrRCp_2)_2]$ were obtained.[430] The reaction of $Na_2[Fe(CO)_4]$ with hafnocene dichloride or diiodide gave the dark-brown dimeric complex $[Cp_2Hf\{Fe(CO)_4\}]_2$, which contains a four-membered Hf—Fe—Hf—Fe ring.[431]

Zirconocene dihydride or the dinitrogen complex react with cyclopentadienylmetal dicarbonyl with formation of metal—metal bonded carbonyl-bridged species **111** (eq 46, M = Co, 95% yield;[432] M = Rh, 44% yield;[433] M = RuH, 59% yield[433]). No reaction was observed with $[MH(CO)(PMe_3)Cp]$ (M = Fe, Ru) (7 weeks at room temperature).[433] In the reaction of zirconocene dihydride with $[Rh(CO)_2Cp]$, formation of an intermediate zirconoxycarbene complex $[Cp^*_2(X)Zr\{OC(H){=}Rh(CO)Cp\}]$ (X = H) was observed by NMR. This complex (X = Cl) was the exclusive product when zirconocene hydride chloride was used as starting material because elimination of H_2 is then prevented.[433]

$[ZrH_2Cp^*_2]$ or 1/2 $[\{Zr(N_2)Cp^*_2\}_2(N_2)]$ + $[M(CO)_2Cp]$ ⟶



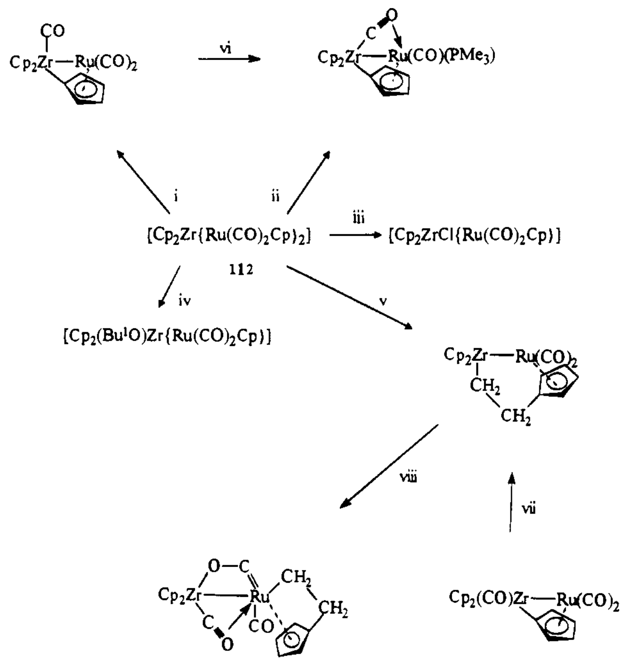
+ H_2 or 3/2 N_2 (46)

111

Hydrido-bridged complexes with a Zr—M bond were obtained in 70% yield as shown in eq 47 (R = Cl, H,[434] R = H[435]) and Scheme 33.[434] All Re-bound hydride ligands appear equivalent at 25 and −85 °C in the ^1H NMR,[434,79] but the low-energy stretching bands (1710, 1565 cm^{-1}) in the IR suggest the presence of hydride bridges.[434]

$$[ZrCl(R)Cp_2] + K[OsH_3(PMe_2Ph)_3] \rightarrow [Cp_2(R)Zr(\mu\text{-}H)_3Os(PMe_2Ph)_3] + KCl \quad (47)$$

Scheme 34^a



^{a} (i) +CO, −[RuH(CO)$_2$Cp], ref 436; (ii) +PMe$_3$, −[RuH(CO)$_2$Cp], ref 436; (iii) [ZrCl$_2$Cp$_2$], ref 231; (iv) [Cp$_2$(Bu^{t}O)Zr{Fe(CO)$_2$Cp}], −[Fe(CO)$_2$Cp]$_2$ (possibly resulting from decomposition of [Cp$_2$Zr{Ru(CO)$_2$Cp}{Fe(CO)$_2$Cp}]), ref 231; (v) +CH$_2$=CH$_2$, −[RuH(CO)$_2$Cp], ref 436; (vi) +PMe$_3$, ref 436; (vii) H$_2$C=CH$_2$, ref 436; (viii) CO, ref 437.

B. Chemical Properties

The trimetallic complex **112** reacts with CO, PMe$_3$, or ethylene to give dimetallic complexes (Scheme 34).[436] Also, the Ru(CO)$_2$Cp groups exchange with the chloro or Fe(CO)$_2$Cp ligands of [ZrCl$_2$Cp$_2$] or [Cp$_2$(Bu^{t}O)Zr−Fe(CO)$_2$Cp] (Scheme 34).[231]

Reaction of the dimetallic carbonyl-bridged species 111 (M = Co, Rh, RuH) with CO gives zirconocene dicarbonyl and the corresponding cyclopentadienyl transition metal carbonyl (eq 48).[433]

$$111 + CO \rightarrow [M(CO)_2Cp] + [Zr(CO)_2Cp^*_2] \qquad (48)$$

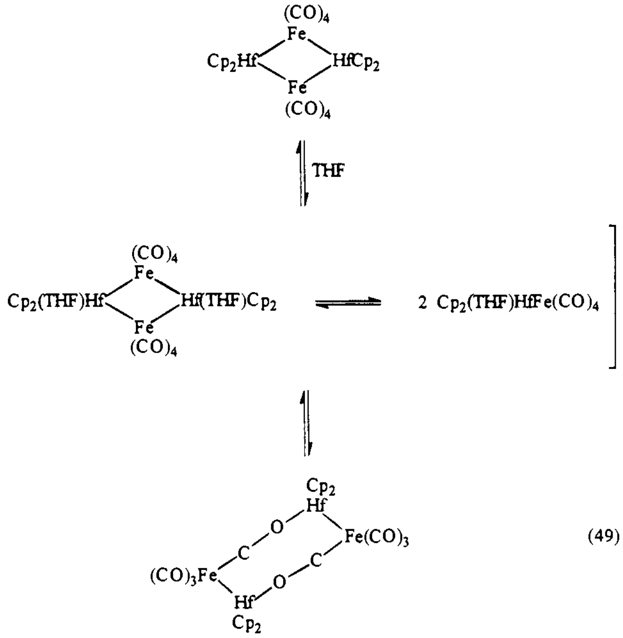
The complexes [Cp$_2$(R)Zr(μ-H)$_n${ReH$_{6-n}$(PPh$_2$R′)$_2$}] (n > 1) (R = Cl, R′ = Ph; R = H, R′ = Me) and [Cp$_2$(H)Zr(μ-H)$_3$Os(PMe$_2$Ph)$_3$] failed to react with CO.[79] CO$_2$ inserts into the terminal Zr−H bond, yielding the corresponding formato complexes.[79]

The dimeric hafnocene−iron tetracarbonyl complex reacts rapidly with HCl to give hafnocene dichloride and Fe$_3$(CO)$_{12}$. On dissolution in THF, isomerization to an isocarbonyl complex is observed (eq 49).[431]

[Cp$_2$ZrMe{Ru(CO)$_2$Cp}], although thermally stable, is rapidly hydrolyzed on exposure to air with cleavage of the metal−metal bonds and formation of [(ZrMeCp$_2$)$_2$O] and [RuH(CO)$_2$Cp].[420]

C. Spectroscopic Properties

The two ν(CO) bands of the Zr−Fe- and Zr−Ru-bonded compounds are ca. 30 and ca. 120 cm^{-1} higher in energy than the corresponding bands of K[M(CO)$_2$Cp] (M = Fe,[231,421] Ru[231]), as expected for compounds with a Zr−M bond. The ^{13}C NMR spectra of [Cp$_2$ZrX{Ru(CO)$_2$Cp}] (X = Cl, Me, OBu^t)[420] show one CO signal, whereas [Cp$_2$Zr{Ru(CO)$_2$Cp}$_2$] exhibits two CO signals at −60 °C and a single broad peak at 51 °C.[231] The temperature-dependent dynamic process ($\Delta G^\ddagger$ = 56.2 ± 2.0 kJ mol^{-1}) probably involves rotation about the Zr−Ru bonds. The two resonances at low temperature are consistent with the solid-state structure (cf. section VII.D), which has two sets of equivalent CO ligands.[231]



(49)

The Zr−Fe and Zr−Ru bonded complexes exhibit a parent ion peak in the mass spectrum.[420,421]

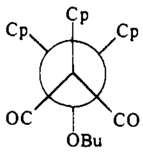
In [Cp$_2$Hf{Fe(CO)$_4$}]$_2$[431] and *cis*-[Fe(CO)$_4$(ZrRCp$_2$)$_2$] (R = Me, octyl)[430] four terminal CO bands are observed, consistent with the local C_{2v} symmetry of the Fe(CO)$_4$ fragment. The shift of ν(CO) from 1788 cm^{-1} in Fe(CO)$_4$$^{2-}$ to 1940−2040 cm^{-1} in the Hf−Fe-bonded complex indicates removal of electron density from Fe, as is expected for a neutral M−M′ bonded complex. In the Raman spectrum the intense peaks at 184 and 138 cm^{-1} were assigned to ν(Hf−Fe) modes, the presence of two bands indicating a dimeric molecule.[431] The complexes [Cp$_2$ZrX{Fe(CO)$_2$Cp}] exhibit the ν(Zr−Fe) band at 187 (X = Me) and 181 cm^{-1} (X = Cl), respectively.[421]

The carbonyl-bridged complexes 111 (M = Rh,[433] RuH,[433] Co[432]) exhibit absorptions at 1670−1700 and 1710−1750 cm^{-1} for the two bridging carbonyl groups.

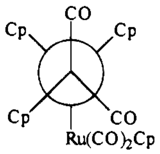
D. Structural Data

The zirconocene−ruthenium complexes [Cp$_2$Zr(OBu^t){Ru(CO)$_2$Cp}][420] and [Cp$_2$Zr{Ru(CO)$_2$Cp}$_2$][231] contain direct, unbridged zirconium to late transition metal bonds. In the former, the OBu^t and Ru(CO)$_2$Cp groups reside in a crystallographically imposed mirror plane so that the ruthenium substituents are staggered with respect to those of the zirconium center **113**. In [Cp$_2$Zr{Ru(CO)$_2$Cp}$_2$], a staggered conformation **114** is associated with each Zr−Ru bond, with the overall molecular symmetry approximating to C_2.

In the other complexes, the two metal atoms are also bridged by carbonyl, hydride, or cyclopentadienyl ligands. Table 8 summarizes the structurally characterized complexes as well as the observed M−M′ distances.



113



114

According to MO calculations performed on the model complex $[Cp_2ZrI\{Ru(CO)_2Cp\}]$ the metal–metal bonding is best described as a dative donor–acceptor bond. The formally anionic $Ru(CO)_2Cp$ fragment donates electron density from a filled $4d_{z^2}$ and $4d_{xz}$ orbital of Ru to a formally empty corresponding orbital of the Zr(IV) center.[438]

VIII. Metallocene(IV) Complexes with Pseudohalide or Oxoanion Bonds

A. Metallocene Complexes with Azido, Triazenido, Sulfur Diimido, Thionylimido, Isocyanato, and Thiocyanato Ligands

While the reaction of trimethylsilyl azide with zirconocene dichloride was unsuccessful,[439] dimethylzirconocene reacts to give tetramethylsilane and white, air-sensitive $[ZrMe(N_3)Cp_2]$.[440] The IR spectrum shows the ν_{as} and ν_s (N_3) modes at 2080 and 1270 cm^{-1}, respectively. The bisazide, $[Zr(N_3)_2Cp_2]$, was first obtained from sodium azide and zirconocene dichloride in the strict absence of water.[441] A different synthetic approach is the reaction of $[Zr(OCHMeCH_2Cl)_2Cp_2]$ with trimethylsilyl azide.[442]

Early transition metal complexes are known to catalyze the reaction of epoxides with trimethylsilyl azide. When an azido complex is used as precursor, the reaction follows an overall second-order law.[442] Thus, $[Zr(N_3)_2Cp_2]$ readily inserts propylene oxide or styrene oxide into the Zr–N bonds by α- or β-opening of the epoxide ring with formation of the corresponding alkoxides. With cyclohexene oxide, only one molecule of epoxide was inserted.[442]

Interaction of phenyl azide with $[ZrR_2Cp_2]$ (R = Me, Ph) gives the highly air sensitive yellow (R = Me) or orange (R = Ph) 1,3-triazenido complexes $[ZrR\{N(R)NNPh\}Cp_2]$ with a bidentate triazenido group.[440] Analogously, $[HfH_2Cp^*_2]$ reacts smoothly with RN_3 (R = Ph, *p*-Tol) to give moderately stable $[HfH\{N(H)NNR\}Cp^*_2]$, which upon thermolysis at 80 °C loses N_2 to form an arylamido complex.[57]

The reaction of $[MCl_2Cp(\eta\text{-}C_5R_5)]$ (M = Zr, R = H, Me; M = Hf, R = Me) with $Me_3SnNSNSnMe_3$ yields the sulfur diimido complexes $[Cp(\eta\text{-}C_5R_5)M(NSN)_2MCp(\eta\text{-}C_5R_5)]$ as thermally- and air-stable yellow solids in 62–84% yield.[443] However, the reaction of titanocene dichloride led to undefined products.[443] The unsymmetrically substituted compounds (R = Me) exist as two different isomers with identical cyclopentadienyl groups located on the same or on opposite sides of the $M(NSN)_2M$ metallacycle, as deduced from ^1H NMR spectra.[443] In the IR spectra, strong absorptions between 1195 and 1120 cm^{-1} as well as 1100 and 1200 cm^{-1} were assigned to the ν(NSN) modes.[443]

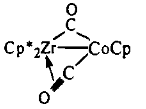
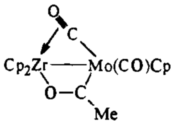
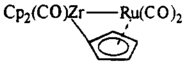
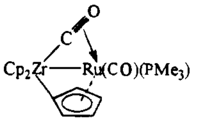
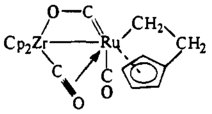
Thionylimido complexes $[M(NSO)_2(\eta\text{-}C_5R_5)(\eta\text{-}C_5R'_5)]$ (M = Ti, R = R′ = H; M = Zr, R = H, R′ = Me; M = Zr, Hf, R = R′ = Me) are available by salt elimination.[444] Several other routes to the titanocene derivative are known.[444] The complexes are pale to deep yellow and only slightly sensitive to air. Parent ion peaks are observed in the mass spectrum. In the IR spectra three absorptions (ca. 1250, 1080, 520 cm^{-1}) which are characteristic of the NSO ligand are observed.[444] The crystal structure of $[Zr(NSO)_2CpCp^*]$ [Zr–N 2.121(4), N–S 1.469(4), S–O 1.435(4) Å, N–Zr–N 97.1(2), Zr–N–S 159.8(2), N–S–O 120.0(2)°] reveals a pseudo-tetrahedral coordination of Zr with two N-bonded NSO ligands forming a nearly planar $Zr(NSO)_2$ unit. The long Zr–N bonds indicate little multiple bonding.[444] The overall structure is comparable to that of the titanocene analogue.[445] The titanocene derivative reacts with $LiN(SiMe_3)_2$ with elimination of $Li(OSiMe_3)$ and formation of $[Ti\{NSN(SiMe_3)\}_2Cp_2]$.[445]

The dithiocyanato complexes $[M(SCN)_2(\eta\text{-}C_5H_4R)_2]$ (M = Ti, Zr, Hf; R = Me, Et, Pr, Bu;[446] R = allyl, crotyl, 2-cyclopenten-1-yl, 3-methyl- or 3-ethyl-cyclopenten-1-yl, 2-cyclohexen-1-yl;[447] R = substituted 2-cyclopenten-1-yl;[448] R = ER'_3, E = C, Si, Ge, R′ = alkyl[449]) were prepared by reacting the appropriate metallocene dichloride with potassium thiocyanate.

The corresponding metallocene diisocyanato complexes $[M(NCO)_2Cp_2]$ (M = Ti, Zr, Hf) have been known since 1970;[450] however, it was only in 1979 that the N-bonding mode of the ligand was unambiguously confirmed by an X-ray crystal structure determination of the Zr complex.[451]

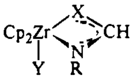
The reaction of zirconocene hydride chloride with the heterocumulenes RNCS (R = Ph, β-nap) gave the metallacyclic compounds **115** (X = S, Y = Cl) and **116** (R = Ph, β-nap).[452] When zirconocene dihydride is reacted with the corresponding isocyanates RNCO (R

Table 8. Metal–Metal Distances in Complexes with M–M′ Bonds

compound	M–M′ (Å)	ref
$[Cp_2Zr\{Ru(CO)_2Cp\}_2]$	Zr–Ru 2.938(1), 2.948(1)	231
$[Cp_2Zr(OBu^t)\{Ru(CO)_2Cp\}]$	Zr–Ru 2.910(1)	420
$[Cp_2ZrCl(\mu\text{-}H)_3Os(PMe_2Ph)_3]^a$	Zr–Os 2.805(1)	434
$[Cp_2(Cl)Zr(\mu\text{-}H)_n\{ReH_{6-n}(PPh_3)_2\}]^b$	Zr–Re 2.975(3)	79
	Zr–Co 2.926(1)	432
	Zr–Mo 3.297(1)	423
	Zr–Ru 3.064(1)	436
	Zr–Ru 3.080(1)	436
	Zr–Ru 3.007(1)	437

[a] *fac*-OsH_3P_3 unit. [b] Hydrides not located.

= Ph, α-nap) complex **115** (X = O, Y = H) is obtained.[453]



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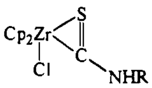

116

B. Metallocene Complexes with Nitrato, Nitro, Nitrito, and Related Ligands

In general, metallocene nitrates are obtained from the reaction of metallocene complexes with nitric acid. Thus, $[ZrCl(NO_3)Cp_2]$ is obtained from $[ZrCl_2Cp_2]$ and HNO_3.[454] The corresponding bromide $[ZrBr(NO_3)Cp_2]$ is obtained from the reaction of $[ZrBr(X)Cp_2]$ (X = OPh, Br)[455] or $[(ZrBrCp_2)_2O]$[454,455] with HNO_3 or by comproportionation of zirconocene dibromide and zirconocene dinitrate. IR and Raman spectra indicate that zirconocene bromide nitrate is a dimer with covalently bound NO_3 bridging ligands.[455] However, the X-ray structure of $[ZrCl(NO_3)Cp_2]$ revealed a monomeric molecule with η^2-bonded nitrato ligands (Zr—O 2.15(3), 2.54(3) Å).[454] The analogous Hf complex $[HfBr(NO_3)Cp_2]$ is available from $[(HfBrCp_2)_2O]$ and HNO_3.[456]

If dilute HNO_3 is employed, hydrolysis occurs with formation of metallocene hydroxide nitrates. Thus, $[ZrCl_2Cp_2]$ reacts with nitric acid in $CHCl_3$ with cleavage of a Zr—Cp bond and formation of $[\{Zr(NO_3)_2(\mu\text{-}OH)Cp\}_2]\cdot 2THF$.[457] The same product is obtained on hydrolysis of $[Zr(NO_3)_2Cp_2]$.[458] The crystal structure shows bidentate nitrato ligands [Zr—O 2.274(4) to 2.320(4) Å, O—Zr—O 55.6(2), 55.9(2)°] and bridging hydroxo groups [Zr—O 2.167(3), 2.090(4) Å].[457] $[HfCp_4]$ reacts with HNO_3 to yield the corresponding hafnocene complex.[456] However, $[ZrCp_4]$ reacts with HNO_3 to afford $[Zr(NO_3)(OH)Cp_2\cdot H_2O]$, which hydrolyzes to $[Zr(NO_3)(OH)_2Cp\cdot H_2O]_4$.[458] The IR spectra of solid $[Zr(NO_3)(OH)Cp_2\cdot H_2O]$ and $[Zr(NO_3)(OH)_2Cp\cdot H_2O]_4$ show a strong absorption band at 1385 cm^{-1}, characteristic of the NO_3^- ion. The latter complex also shows bands at 1564 and 1278 cm^{-1}, which are characteristic of a covalently bonded nitrato group. In solution, only bands due to covalently bonded nitrate are present for both complexes.[458] IR and Raman spectra of $[Zr(NO_3)_2Cp_2]$ are different in solution and in the solid state. Molecular weight measurements in THF showed the complex to be trimeric.[458]

The reaction of $[ZrL_2Cp_2]$ and $[ZrL(X)Cp_2]$ (LH = Ac_2CH_2, Bz_2CH_2, X = Cl, Br) with HNO_3 was studied. With $[ZrL_2Cp_2]$ at −35 °C $[ZrL_2(NO_3)Cp_2]$ was obtained, which reacts further at 20 °C to give $[ZrL(NO_3)_2Cp]$. $[ZrL(X)Cp_2]$ gives $[Zr(NO_3)(X)Cp_2]$ at −35 °C.[459]

$[ZrCl_2L_2]$ (L = Cp, η-indenyl) reacts with $NaNO_2$ in refluxing THF to give $[Zr(NO_2)_2L_2]$. Use of $AgNO_2$ yields the nitrito complex $[Zr(ONO)_2L_2]$.[460]

The nitronato complexes $[Zr(O_2N{=}CMeR)(X)Cp_2]$ (X = Cl, R = Me, H; X = CH_2CMe_2Ph, R = Me) were prepared from $Li(O_2N{=}CMeR)$ and the appropriate zirconocene chloride derivative. Their IR spectra suggest a symmetrical chelating mode of coordination for the alkanenitronato ligand (ν(CN) mode 1638–1651 cm^{-1}), which was established unambiguously by X-ray analysis of the derivative with X = Cl, R = Me [Zr—O 2.218(2), 2.230(2) Å, O—Zr—O 59.1(1)°].[290]

The reaction of diphenylzirconocene with NO in benzene gives $[ZrPh\{ON(Ph)NO\}Cp_2]$.[461] The chloro derivative $[ZrCl\{ON(R)NO\}Cp_2]$ (R = Ph, *p*-Tol) is obtained from zirconocene dichloride and $Ag\{ON(R)NO\}$, whereas with $NH_4\{ON(p\text{-}Tol)NO\}$ only $[Zr\{ON(p\text{-}Tol)NO\}_4]$ was formed.[461] The complexes are white. IR spectra indicate the presence of a Zr{ON(R)NO} chelate ring (three strong absorptions between 1170 and 1365 cm^{-1}, one between 920 and 945 cm^{-1}).[461] The corresponding *N*-methyl-*N*-nitrosohydroxylaminato complexes were reported in 1972. Thus, $[ZrMe(X)Cp_2]$ (X = Cl, Me) reacts with NO to give $[Zr\{ON(Me)NO\}(X)Cp_2]$.[462]

Di-*tert*-butyl nitroxide readily substitutes $[MR_2Cp_2]$ (M = Zr, R = Cl, Br, Me, CH_2R' with R′ = Ph, *o*-, *m*-, or *p*-Tol, 2- or 4-ClC_6H_4, 4-FC_6H_4, α- or β-nap; M = Hf, R = Bz) by displacement of an alkyl radical to give high yields of Bu^t_2NOR and $[M(ONBu^t_2)(R)Cp_2]$.[356]

C. Metallocene Complexes with Sulfato, Sulfonato, and Sulfone Ligands

$[Zr(HSO_4)_2Cp_2]$ was obtained from sulfuric acid and $[(ZrClCp_2)_2O]$.[463]

The reaction of zirconocene dichloride with AgO_3SCF_3 in THF gives $[Zr(O_3SCF_3)_2(THF)Cp_2]$, which has a five-coordinate bent metallocene structure, the THF group being symmetrically surrounded by CF_3SO_3 ligands [Zr—O(SO_3CF_3) 2.219(6), Zr—O(THF) 2.278(9), O—SO_2CF_3 1.455(7) Å].[464] This complex and its Ti analogue $[Ti(O_3SCF_3)_2Cp_2]$ proved to be efficient catalysts for Diels–Alder reactions (acceleration rates of 10^3 to $>10^5$).[465] The reaction of $[Zr(O_3SCF_3)_2(THF)Cp_2]$ with bipy or water gives the ionic compounds $[Zr(O_3SCF_3)(bipy)Cp_2]^+CF_3SO_3^-$ [466] and $[Zr(H_2O)_3Cp_2]^{2+}(CF_3SO_3^-)_2\cdot THF$,[467] respectively. Both products have been structurally characterized.[466,467]

The reaction of dimethylzirconocene with 1 or 2 equiv of $H_2C(SO_2CF_3)_2$ yields $[ZrMe\{HC(SO_2CF_3)_2\}Cp_2]$ and $[Zr\{HC(SO_2CF_3)_2\}_2Cp_2]$, respectively.[178] The methyl hafnocene analogue was prepared accordingly.[309] Analogously, the complexes $[ZrMe_{2-n}(X)_nCp_2]$ [n = 1 or 2, X = $PhC(SO_2CF_3)_2$, $N(SO_2CF_3)_2$, CF_3SO_3, $HC(SO_2)_2(CF_2)_3$; n = 2, X = $CH_2{=}CHCH_2C(SO_2CF_3)_2$] were prepared.[178] The complexes are nonelectrolytes in dichloromethane. In acetonitrile solvolysis occurs with formation of $[ZrMe(CH_3CN)_2Cp_2]^+$ (monosubstituted complex) and $[Zr(CH_3CN)_3Cp_2]^{2+}$ (disubstituted complex).[178] THF is polymerized by these compounds.[178] The X-ray analysis of $[Zr\{HC(SO_2CF_3)_2\}_2Cp_2]$ shows a bidentate [Zr—O 2.243(2), 2.259(2) Å] and a monodentate [Zr—O 2.237(2) Å] $CH(SO_2CF_3)$ ligand.[178] The two types of ligands interconvert rapidly on the NMR time scale. Thus, only one signal is observed for the mono- and disubstituted zirconocene complexes in the ^{19}F NMR (−77 to −80 ppm); this signal is invariant down to −100 °C for the monosubstituted complex, but a limiting low-temperature spectrum was obtained for the disubstituted compound, which exhibits four signals at

−94 °C.[178] Similar observations were made for the other mono- and disubstituted complexes.[178]

^{91}Zr NMR spectra of these complexes as well as some dialkyl, dichloro, and mixed zirconocene(IV) complexes and several monocyclopentadienyl substituted Zr(IV) derivatives have been reported.[178]

The complex $[ZrMe\{CH(SO_2CF_3)_2\}Cp_2]$ inserts CO into the Zr−Me bond to give the corresponding η^2-acetyl derivative. ^{19}F NMR spectra suggest the presence of a monodentate oxygen-bonded $CH(SO_2CF_2)_2$ ligand.[178]

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