

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

E. Hey-Hawkins

Institut für Anorganische Chemie, Universität Leipzig, Talstrasse 35, D-04103 Leipzig, Germany

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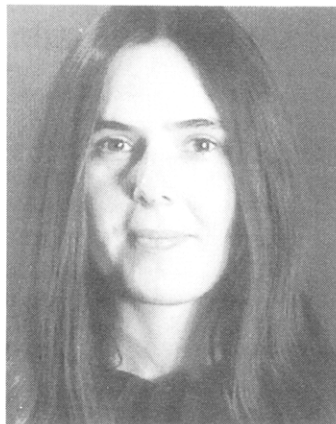
I. Scope of the Review

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(ER₃)Cp₂] (M = Zr, ER₃ = SiPh₃, GePh₃, SnMe₃, GeEt₃; M = Hf, ER₃ = SiPh₃, GePh₃), which were obtained by reaction of [MCl₂Cp₂] with LiER₃, NaER₃, or [Cd(GeEt₃)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(SiMe₃)₃ ligand was introduced by the reaction of [MCl₂Cp(η-C₅R₅)] with [Li(THF)₃E(SiMe₃)₃] to give [MCl{E(SiMe₃)₃}Cp(η-C₅R₅)] (62–71% yield,



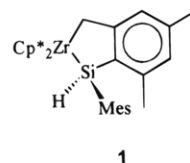
Evamarie Hey-Hawkins was born in Scherfede, Germany, in 1957. She received her Diplom and Dr. rer. nat. degrees in chemistry with Professor Dr. K. Dehnicke from the University of Marburg, Germany. She was a Visiting Scientist at the University of Sussex (1984–1985), the University of Western Australia (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.

$M = \text{Zr, Hf, R} = \text{H, E} = \text{Si};^6 M = \text{Zr, R} = \text{H, E} = \text{Ge};^7 M = \text{Zr}^8 \text{ or Hf},^9 R = \text{Me, E} = \text{Si}$). Analogously, reaction of $[\text{ZrCl}(\text{SiMe}_3)\text{Cp}_2]$ or $[\text{ZrCl}(\text{Cp})_2\text{O}]$ with $[\text{Li}(\text{THF})_3\text{Si}(\text{SiMe}_3)_3]$ yielded $[\text{Zr}(\text{SiMe}_3)\{\text{Si}(\text{SiMe}_3)_3\}\text{Cp}_2]$ and $[\text{Cp}_2(\text{Cl})\text{Zr}(\mu\text{-O})\text{Zr}\{\text{Si}(\text{SiMe}_3)_3\}\text{Cp}_2]$, respectively.⁶ Replacement of the second chloro ligand was not observed in the latter. Both chloro ligands of $[\text{ZrCl}_2\text{Cp}_2]$ are replaced on reaction with $[\text{Li}(\text{SiPh}_2)_5\text{-Li}]$ in THF; the product $[\text{Zr}\{\text{SiPh}_2(\text{SiPh}_2)_3\text{SiPh}_2\}\text{Cp}_2]$ was obtained in 4% yield.¹⁰

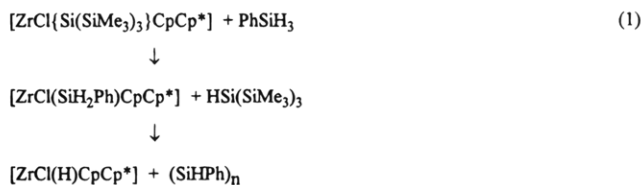
The previously reported $[\text{MCl}(\text{EPh}_3)\text{Cp}_2]$ ($M = \text{Zr, Hf, E} = \text{Si, Ge, Sn}$) were described as being difficult to purify due to their instability in solution at room temperature.² However, the analogous complexes $[\text{MCl}(\text{EPh}_3)\text{Cp}^*(\eta\text{-C}_5\text{R}_5)]$ ($\text{Cp}^* = \eta\text{-C}_5\text{Me}_5; M = \text{Zr, Hf, E} = \text{Si, Ge, Sn, R} = \text{H}; M = \text{Zr, E} = \text{Si, Ge, Sn, R} = \text{Me}; M = \text{Hf, E} = \text{Si, R} = \text{Me}$) have been obtained as stable, hydrocarbon-soluble materials by reacting metallocene dichlorides with LiEPh_3 in THF or by σ -bond metathesis of $[\text{ZrCl}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$ or $[\text{ZrCl}(\text{EPh}_3)\text{CpCp}^*]$ ($E = \text{Si, Ge}$) with Ph_3SnH in 60–78% yield.¹¹ Reaction of $[\text{ZrCl}_2\text{CpCp}^*]$ with LiSnPh_3 yielded only the aryl complex $[\text{ZrCl}(\text{Ph})\text{CpCp}^*]$.¹¹

Silylation of $[\text{MCl}_2\text{Cp}_2]$ with $[\text{Al}(\text{SiMe}_3)_3(\text{OEt}_2)]$ gave $[\text{MCl}(\text{SiMe}_3)\text{Cp}_2]$ as red ($M = \text{Zr}$) or orange ($M = \text{Hf}$) solids in 72–80% yield;¹² $[\text{ZrCl}(\text{X})\text{CpCp}^*]$ [$\text{X} = \text{Cl, Si}(\text{SiMe}_3)_3$] failed to react.⁸ The reaction of $[\text{ZrCl}_2\text{Cp}_2]$ with $[\text{Hg}(\text{SiMe}_3)_2]$ in benzene was earlier reported to give white solids, formulated as $[\text{Zr}(\text{SiMe}_3)(\text{X})\text{Cp}_2]$ ($\text{X} = \text{Cl, SiMe}_3$);¹³ however, the product with $\text{X} = \text{Cl}$ was later shown to be $[\text{ZrCl}(\text{OSiMe}_3)\text{Cp}_2]$,¹² which was obtained by reaction of $[\text{ZrCl}(\text{SiMe}_3)\text{Cp}_2]$ 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 $[\text{ZrMe}(\text{SiHMe}_2)\text{Cp}_2]$, which is unstable above 0 °C, and the thermally stable $[\text{ZrMe}(\text{SiHMe}_2)\text{Cp}^*_2]$.¹⁴ An attempt to replace both chlorine atoms in $[\text{ZrCl}_2\text{Cp}^*_2]$ with $[\text{Li}(\text{THF})_2\text{SiHMe}_2]$ yielded the metallacyclic dehydrohalogenation product **1** and Mes_2SiH_2 .¹⁴ **1** was also obtained from $[\text{ZrCl}(\text{SiHMe}_2)\text{Cp}^*_2]$ and $[\text{Li}(\text{THF})_2\text{SiHMe}_2]$.¹⁴ $[\text{ZrMe}(\text{SiHMe}_2)\text{Cp}^*_2]$ reacted rapidly with gaseous HCl in toluene at –78 °C to give methane and the chloro complex in 76% yield.¹⁴

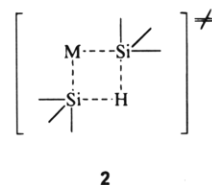


A more general route to hydrogensilyl complexes is the σ -bond metathesis of silyl or germyl complexes with primary or secondary silanes under fluorescent room light.^{9,11,15} In contrast, the stannyl derivative $[\text{HfCl}(\text{SnPh}_3)\text{CpCp}^*]$ failed to react with PhSiH_3 .¹¹ Unsymmetrically 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,



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



$[\text{MCl}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$ ($M = \text{Zr or Hf}$) reacts with Ph_3SnH to give $(\text{SiMe}_3)_3\text{SiH}$ 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 $[\text{HfCl}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$.⁹ No reaction was observed between $[\text{MCl}(\text{SiR}_3)\text{Cp}^*(\eta\text{-C}_5\text{R}'_5)]$ ($M = \text{Zr, Hf, R} = \text{Me, SiMe}_3, \text{R}' = \text{H, Me}$) and bulky silanes such as Me_3SiH , Et_3SiH , $\text{Bu}^t_2\text{SiH}_2$, or CyMeSiH_2 .¹⁵ Bulky

cyclopentadienyl ligands also prevent the formation of isolable silyl derivatives. For example, [MCl(SiPh₃)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(SiMe₃)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(SiMe₃)₃}CpCp*] with MeSiH(OMe)₂ gave the hydrogensilyl complex [HfCl(SiH₂R)-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-(SiH₂)₂C₆H₄}] was obtained from the reaction of [HfCl{Si(SiMe₃)₃}CpCp*] with 1,4-(SiH₃)₂C₆H₄ (2:1 reaction).¹⁵ The 1:1 reaction allowed the observation by NMR of [HfCl(SiH₂C₆H₄SiH₃)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)(η -C₅R''₅)₂] (M = Zr, Hf, R = Cl, alkyl, silyl, R' = Me, Ph, SiMe₃, R'' = H, Me) act as catalyst precursors for the dehydrogenative coupling reaction of silanes RSiH₃ 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 [ZrMe₂Cp₂] with phenyl-,¹⁷ diphenyl-, phenylmethyl-, or butylmethylsilane yielded the hydrido-bridged dimeric complexes [Cp₂RZr(μ -H)₂ZrR'Cp₂] (**3**)^{17,18} [(**3a**) R = PhSiH₂, R' = MePhSiH,¹⁷ (**3b**) R = MePhSiH, R' = Me₂PhSi; (**3c**) R = Ph₂SiH, R' = MePh₂Si; (**3d**) R = Me, R' = Ph₂SiH; (**3e**) R = Me, R' = MePh₂Si; (**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(SiHPh₂)(PMe₃)Cp₂], which was obtained as two geometric isomers from the reaction of [ZrH(SiPh₃)(PMe₃)Cp₂] with Ph₂SiH₂.¹⁹

[ZrBu₂Cp₂] decomposes readily to give [Zr(η^2 -1-butene)Cp₂], which reacts with 2 equiv of Ph₂SiH₂ to give **3** (R = R' = Ph₂SiH, 85% yield) and BuPh₂SiH.²⁰ The proposed intermediate in this reaction, [ZrH(SiHPh₂)Cp₂], resulting from oxidative addition of Ph₂SiH₂ to zirconocene(II), was trapped as the phosphine adducts [ZrH(SiHPh₂)(L)Cp₂] (L = PMe₃, PMePh₂) 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' = Ph₂SiH) did not react with PMe₃ to give a monomeric hydrogensilyl complex.²⁰ Oxidative addition of Ph₃SiH to the zirconocene(II) or hafnocene(II) complexes or of diphenylsilane to the zirconocene(II) complexes [M(η^2 -alkene)(PMe₃)Cp₂] (M = Zr, alkene = 1-butene; M = Hf,

alkene = isobutylene), which were generated in situ in THF, also afforded [MH(SiPh₃)(PMe₃)Cp₂] and [ZrH(SiHPh₂)(PMe₃)Cp₂] in 40–60% yield. The hafnocene derivative is unstable in benzene solution. Of two plausible pathways for the addition of Ph₃SiH—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(CH₂CHMe₂)(SiPh₃)Cp₂]” was observed by ¹H NMR.¹⁹ [ZrH(SiHPh₂)(PMe₃)Cp₂] was also shown by ¹H NMR to be formed in the σ -bond metathesis of [ZrH(SiPh₃)(PMe₃)Cp₂] with Ph₂SiH₂.¹⁹

The black zirconocene, [(ZrCp₂)₄], synthesized by reduction of zirconocene dihydride with red phosphorus, was reported to oxidatively add trimethylchlorosilane in refluxing toluene to give [ZrCl(SiMe₃)Cp₂] as a pale yellow solid in 79% yield. The reaction with trimethyltin chloride afforded the pale-orange zirconocene(III) complex [{Zr(μ -SnMe₃)Cp₂]₂] as well as [ZrCl₂Cp₂] and Me₆Sn₂. The products were characterized by elemental analysis, ¹H NMR and MS. The parent ion peaks showed the expected isotope pattern.²¹ Decomposition of [ZrBu₂(η -C₅H₄R)₂] (R = H, Me), generated in situ, in the presence of 2 equiv of [Sn{CH(SiMe₃)₂]₂] yielded the red-purple zirconocene(II) complex [Zr(Sn{CH(SiMe₃)₂})₂(η -C₅H₄R)₂], which was characterized by a crystal structure determination.²²

The η^2 -silanimine complex [Zr(η^2 -NBu^tSiMe₂)(PMe₃)Cp₂] has been prepared by the reaction of [ZrI(NBu^t-SiMe₂H)Cp₂] with LiCH₂SiMe₃ in the presence of PMe₃ (elimination of LiI, Me₄Si).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 [HfCl₂{Ge(SiMe₃)₃}Cp*] the Hf-Ge bond length is 2.740(1) Å⁷ and the only crystal structures reported for a metallocene compound with a metal-tin bond are those of [Zr(Sn{CH(SiMe₃)₂})₂Cp₂] [Zr-Sn 2.8715(11) Å]²² and [TiCl(SnPh₃)Cp₂] [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(SiH₂Ph)CpCp*] and [HfCl{Si(SiMe₃)₃}CpCp*].¹⁵ While the Hf-Si bond length of 2.729(3) Å in the former is comparable to that found in [HfCl₂{Si(SiMe₃)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 [Cp₂(SiH₂-Ph)Zr(μ -H)₂Zr(SiHMePh)Cp₂]^{17,18} and [Cp₂(SiHMePh)Zr(μ -H)₂Zr(SiMe₂Ph)Cp₂]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(μ -H)(SiHPh₂)Cp₂]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(SiPh₃)(PMe₃)Cp₂] [Zr-Si 2.721(2) Å, hydride

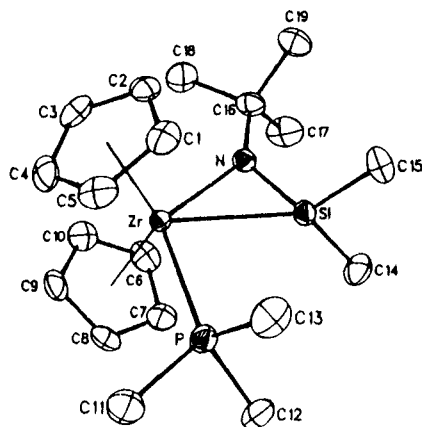
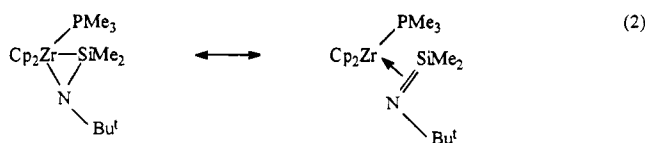


Figure 1. Molecular structure of $[\text{Zr}(\eta^2\text{-NBu}^i\text{SiMe}_2)(\text{PMe}_3)\text{Cp}_2]$. (Reprinted from ref 23. Copyright 1991 American Chemical Society.)

located by difference maps¹⁹ and $[\text{ZrH}(\text{SiHPh}_2)(\text{PMe}_3)\text{Cp}_2]$ [$\text{Zr}-\text{Si}$ 2.707(5) Å]²⁰ exhibit shorter Zr—Si bonds than the previously characterized $[\text{ZrCl}(\text{SiPh}_3)\text{Cp}_2]$ [$\text{Zr}-\text{Si}$ 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 $[\text{Zr}(\eta^2\text{-S}_2\text{CNET}_2)(\text{SiMe}_3)\text{Cp}_2]$.¹²

The short Zr—Si bond [2.654(1) Å] and the long Si—N bond [1.687(3) Å] in $[\text{Zr}(\eta^2\text{-NBu}^i\text{SiMe}_2)(\text{PMe}_3)\text{Cp}_2]$ (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



C. Spectroscopic Properties

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

1. ¹H NMR

In the ¹H NMR $[\text{MCl}(\text{EPh}_3)\text{Cp}(\eta\text{-C}_5\text{R}_5)]$ ($\text{M} = \text{Zr}, \text{Hf}, \text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{R} = \text{H}, \text{Me}$) exhibit sharp resonances for the phenyl protons, while $[\text{ZrCl}(\text{EPh}_3)\text{Cp}^*_2]$ ($\text{E} = \text{Si}, \text{Ge}$) show broad signals due to restricted rotation about the E—C bond.¹¹ Sharp resonances were observed for the stannyl derivative ($\text{E} = \text{Sn}$).¹¹ This observation is consistent with the expected steric demand of the EPh_3 group ($\text{SiPh}_3 > \text{GePh}_3 > \text{SnPh}_3$). A ΔG^\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 $[\text{Zr}(\text{SiHMe}_2)(\text{X})\text{Cp}^*_2]$ ($\text{X} = \text{Cl}, \text{Me}$) 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) ($\text{X} = \text{Me}, \Delta G^\ddagger = 43.5 \pm 0.9$ kJ mol⁻¹; $\text{X} = \text{Cl}, \Delta G^\ddagger = 53.6 \pm 0.9$ kJ mol⁻¹) and Zr—Si bonds ($\text{X} = \text{Me}, \Delta G^\ddagger = 49.4 \pm 0.9$ kJ mol⁻¹; $\text{X} = \text{Cl}, \Delta G^\ddagger = 56.1 \pm 2.0$ kJ mol⁻¹) were determined.¹⁴ For $[\text{ZrMe}(\text{SiHMe}_2)\text{Cp}_2]$ unrestricted rotation was observed down to -85 °C.¹⁴

2. ²⁹Si NMR

²⁹Si NMR data have been reported for $[\text{M}\{\text{Si}(\text{SiMe}_3)_3\}(\text{X})\text{CpCp}^*]$ ($\text{M} = \text{Zr}, \text{X} = \text{Me}, -105.72;$ ⁸

$\text{M} = \text{Zr}, \text{X} = \text{Cl}, -87.30;$ ⁸ $\text{M} = \text{Hf}, \text{X} = \text{Cl}, -77.87$ ppm¹⁵), $[\text{ZrCl}(\text{SiH}_2\text{Ph})\text{CpCp}^*]$ (-14.33 ppm),^{9,15} $[\text{HfCl}(\text{SiH}_2\text{R})\text{CpCp}^*]$ ($\text{R} = \text{Ph}, p\text{-Tol}, 4\text{-MeOC}_6\text{H}_4, 4\text{-FC}_6\text{H}_4, \text{Mes}, \text{Bz}, \text{Cy}, 4\text{-SiH}_3\text{C}_6\text{H}_4, 1.49\text{--}14.83$ ppm;¹⁵ $\text{R} = \text{Me}, -7.36$; $\text{R} = \text{H}, -46.52$ ppm¹⁵), $[\text{HfBr}\{\text{SiH}_2(p\text{-Tol})\}\text{CpCp}^*]$ (7.74 ppm),¹⁵ $[\text{HfCl}(\text{SiH}_2\text{Cy})\text{Cp}_2]$ (11.07 ppm),¹⁵ $[\text{HfCl}(\text{SiHPh}_2)\text{Cp}(\eta\text{-C}_5\text{R}_5)]$ ($\text{R} = \text{H}, \text{Me}, \text{ca. } 32$ ppm),¹⁵ $[\text{HfCl}(\text{SiHPhR})\text{CpCp}^*]$ [$\text{R} = \text{Me}, 21.75, 25.10$ (diastereomers); $\text{R} = \text{SiH}_2\text{Ph}, -9.05, -9.86$ ppm (diastereomers)],¹⁵ $[\text{MCl}(\text{SiPh}_3)\text{Cp}^*(\eta\text{-C}_5\text{R}_5)]$ ($\text{M} = \text{Zr}, \text{R} = \text{H}, 42.42$; $\text{M} = \text{Hf}, \text{R} = \text{H}, 39.96$ ppm; $\text{M} = \text{Zr}, \text{R} = \text{Me}, 47.34$; $\text{M} = \text{Hf}, \text{R} = \text{Me}, 42.86$ ppm).¹¹ Clearly, the substituents bound directly to silicon play a dominant role in determining the ²⁹Si chemical shift. For example, replacement of hydrogen atoms with phenyl ligands resulted in pronounced down-field shifts, while silyl substituents [i.e. $\text{Si}(\text{SiMe}_3)_3$ or $\text{SiHPh}(\text{SiH}_2\text{Ph})$] lead to pronounced up-field shifts.¹⁵ Significant steric interaction between the Cp* and the Mes ligands in $[\text{ZrMe}(\text{SiHMe}_2)\text{Cp}^*_2]$ led to an up-field shift (-21.94 ppm)¹⁴ compared with other hydrogensilyl complexes, such as $[\text{ZrMe}(\text{SiHMe}_2)\text{Cp}_2]$ (-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 $[\text{ZrH}(\text{SiPh}_2\text{R})(\text{PMe}_3)\text{Cp}_2]$ show ²⁹Si NMR resonances at 39.48 ($\text{R} = \text{Ph}$) and 50.46 ppm ($\text{R} = \text{H}$), 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 $\nu(\text{M}-\text{E})$ modes ($\text{M} = \text{Zr}, \text{Hf}, \text{E} = \text{Si}, \text{Ge}, \text{Sn}$) have not been made. The $\nu(\text{Si}-\text{H})$ 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. $[\text{HfCl}(\text{SiH}_2\text{Ph})\text{CpCp}^*]$,¹⁵ $\nu(\text{Si}-\text{H})$ 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 $[\text{ZrCl}(\text{SiMe}_3)\text{Cp}_2]$ and the zirconocene(III) complex $[\{\text{Zr}(\mu\text{-SnMe}_3)\text{Cp}_2\}_2]$. 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 $[\text{Zr}\{\text{Si}(\text{SiMe}_3)_3\}(\text{X})\text{CpCp}^*]$ exhibit low-intensity absorptions at 461 ($\text{X} = \text{Cl}$)^{9,15} or 435 nm ($\text{X} = \text{Me}$).¹⁵ The hafnocene analogues show transitions at higher energy: 405 ($\text{X} = \text{Cl}$)^{9,15} or 398 nm ($\text{X} = \text{Me}$),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 $[\text{HfCl}(\text{SiH}_2\text{R})\text{CpCp}^*]$ ($\text{R} = \text{Ph},$

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(SiMe₃)Cp₂] reacted with water to give the known [(ZrClCp₂)₂O]; with oxygen the siloxide [ZrCl(OSiMe₃)Cp₂] was formed.¹² The latter is possibly the product isolated from the reaction of [ZrCl₂Cp₂] with [Hg(SiMe₃)₂].¹³

As was observed earlier,² protic species (HCl or HBr) cleave the metal–group 14 element bond. Thus, [ZrCl(EPh₃)Cp₂]^{*} (E = Si, Ge) reacted with HCl to give zirconocene dichloride and Ph₃EH; the stannyl analogue (E = Sn) afforded zirconocene dichloride, but no Ph₃SnH was observed due to cleavage of the Sn–C(Ph) bonds.¹¹ Treatment of [ZrH(SiHPh₂)(PMe₃)Cp₂] with 3 N HCl gave Ph₂SiH₂,²⁰ while {[Zr(μ-H)(SiHPh₂)Cp₂]₂} did not react under analogous conditions.²⁰ Silver triflate oxidatively cleaved the Zr–Si bond in [ZrMe(SiHMe₂)Cp₂]^{*} with quantitative formation of pale-green [ZrMe(OSO₂CF₃)Cp₂]^{*} and silanes.¹⁴

1. Thermolysis

The compounds are generally stable in the solid state, but slow decomposition in solution was observed for [MCl(EPh₃)Cp^{*}(η-C₅R₅)] (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 Ph₃EH.¹¹ The decomposition is accelerated by light. The following trends in stability were found: MCpCp^{*} > MCp₂^{*}; Hf > Zr; Sn > Ge > Si.¹¹

Thermolysis of [MCl(SiMe₃)Cp₂] (M = Zr, Hf) in C₆D₆ (monitored by ¹H NMR) gave Me₃SiH and unidentified products after 2 (M = Zr) and 24 h (M = Hf).¹² Similarly, thermal or photochemical decomposition of [ZrCl{Si(SiMe₃)₃CpCp^{*}}] gave (SiMe₃)₃SiH after 2 h. The zirconium product was shown to be {[Zr(μ-Cl)Cp^{*}]₂(η⁵:η⁵-C₁₀H₈)}.¹⁵ The methyl derivatives [MMe(SiPh₃)Cp₂]^{*} (M = Zr, Hf),¹¹ [ZrMe{Si(SiMe₃)₃CpCp^{*}}],⁸ and [ZrMe(SiHMe₂)Cp₂]¹⁴ are thermally unstable in solution at room temperature, while [ZrMe(SiHMe₂)Cp₂]¹⁴ decomposed on heating in C₆D₆ for 24 h with formation of Me₂SiH₂. The hydrogensilyl complexes [MCl(SiH₂Ph)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

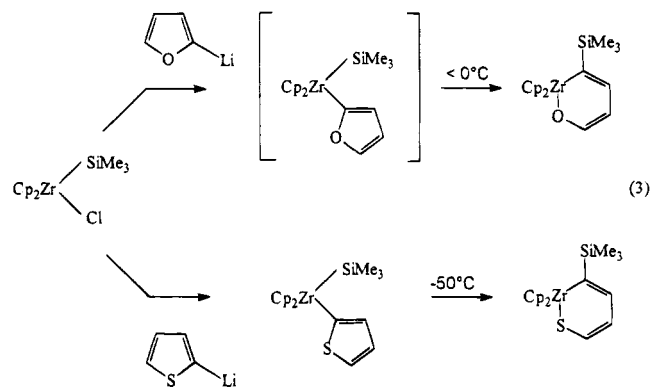
Hydrogenolysis of [Zr(SiMe₃)(X)Cp₂] [X = Cl, Si(SiMe₃)₃]⁶ and [MCl(SiPh₃)Cp^{*}(η-C₅R₅)] (M = Zr, Hf, R = H, Me)¹¹ rapidly yielded zirconocene hydride chloride and the corresponding silanes. Reaction of [ZrMe(SiHMe₂)Cp₂]^{*} with hydrogen showed that the Zr–Si bond is cleaved faster than the Zr–Me bond. After 10 min (NMR experiment) zirconocene methyl hydride and Me₂SiH₂ had formed quantitatively.¹⁴ The reaction of [MMe(SiPh₃)Cp₂]^{*} with hydrogen gave zirconocene dihydride (M = Zr), while the less labile hafnocene silyl derivative (M = Hf) gave [HfH-

(Me)Cp₂]^{*}.¹¹ The germyl complexes [ZrCl(GePh₃)Cp^{*}(η-C₅R₅)] (R = H, Me) react more slowly with hydrogen than the corresponding silyl complexes, yielding metallocene hydride chloride and triphenylgermane. The stannyl complexes [MCl(SnPh₃)Cp^{*}(η-C₅R₅)] (M = Hf, R = H; M = Zr, R = Me) failed to react.¹¹ Hydrogenolysis of [Zr(η²-NBu^tSiMe₂)(PMe₃)Cp₂] yields [ZrH{NBu^t(SiHMe₂)}Cp₂].²³ General reactivity trends were established for hydrogenolysis: MCp₂^{*} > MCpCp^{*}; M{Si(SiMe₃)₃} > M(SiPh₃); MMe(SiR₃) > MCl(SiR₃); M–Si > M–Ge >> M–Sn; Zr > Hf.

3. Salt Elimination

The halide in metallocene silyl complexes [MCl(SiR₃)Cp₂] can be displaced by a salt elimination route via reaction with M'R' (M' = Li or Na; M = Zr, Hf, R = Me, R' = S₂CNEt₂, BH₄, OBU^t; M = Zr, R = SiMe₃, R' = BH₄).^{6,12,26} The η²-coordination of the dithiocarbamate ligand and the presence of a M(μ-H)₂BH₂ unit were shown by IR spectroscopy^{6,12} and crystal structure determination (R' = S₂CNEt₂, M = Zr, R = Me).¹²

[ZrCl(SiMe₃)Cp₂] reacted with 2-furyl- or 2-thienyllithium at –78 °C in Et₂O, as shown in eq 3. The substitution products underwent dyotropic rearrangement to give an oxa- or thiazirconacyclohexadiene complex.²⁶

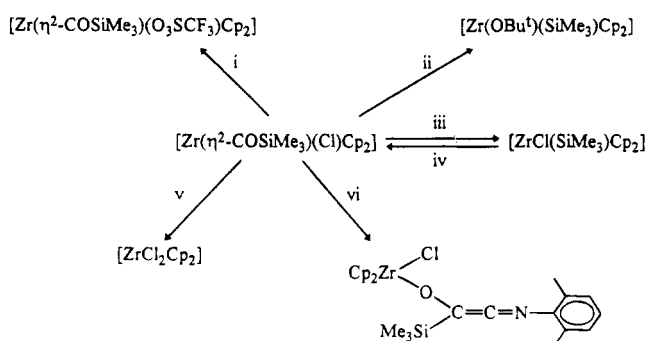


Reaction of [MCl(SiR₃)(η-C₅R'₅)(η-C₅R''₅)] with MeMgBr in diethyl ether at –78 °C allowed the synthesis of the corresponding methyl silyl complexes in 62–82% yield (M = Zr, R = SiMe₃, R' = R'' = H;⁶ M = Zr, Hf, R = Ph, R' = R'' = Me;¹¹ M = Zr, R = SiMe₃, R' = H, R'' = Me⁸).

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(SiMe₃)Cp₂] is readily carbonylated,^{6,31} the Si(SiMe₃)₃ analogue is not.⁶ The pink reaction product, [Zr(η²-COSiMe₃)(Cl)Cp₂], obtained in 90% yield, is a versatile starting material for further reactions (Scheme 1). The Ti analogue [TiCl(SiMe₃)Cp₂] re-

Scheme 1^a

^a (i) $\text{Me}_3\text{SiO}_3\text{SCF}_3$, 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 ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$), ref 6.

acted with CO by an apparent ligand-induced reductive elimination to furnish $[\text{Ti}(\text{CO})_2\text{Cp}_2]$ and $\text{Me}_3\text{-SiCl}$.⁶

In the reaction of $[\text{Zr}(\text{SiMe}_3)\{\text{Si}(\text{SiMe}_3)_3\}\text{Cp}_2]$ or $[\text{ZrMe}\{\text{Si}(\text{SiMe}_3)_3\}\text{Cp}_2]$ with CO, insertion into the Zr–SiMe₃ or Zr–Me bond occurred exclusively,⁶ with formation of the corresponding η^2 -silaacyl or η^2 -acyl complex. With benzoic acid, $[\text{Zr}(\eta^2\text{-COSiMe}_3)\{\text{Si}(\text{SiMe}_3)_3\}\text{Cp}_2]$ underwent substitution of the η^2 -silaacyl ligand by an η^2 -carboxylato ligand.⁶ The presence of the bulkier Cp* ligand in $[\text{ZrCl}\{\text{Si}(\text{SiMe}_3)_3\}\text{-CpCp}^*]$ 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 $[\text{Zr}\{\eta^2\text{-COSi}(\text{SiMe}_3)_3\}(\text{Cl})\text{CpCp}^*]$ in 71% yield.^{8,32} The same trend in reactivity is observed in the reaction of $[\text{ZrCl}(\text{SiPh}_3)\text{Cp}^*(\eta\text{-C}_5\text{R}_5)]$ ($\text{R} = \text{H}, \text{Me}$) with CO. While the complex with $\text{R} = \text{H}$ failed to give a pure product, the more crowded compound ($\text{R} = \text{Me}$) cleanly inserts CO to give dark purple $[\text{Zr}(\eta^2\text{-COSiPh}_3)(\text{Cl})\text{Cp}^*_2]$.¹¹ On reaction with gaseous HCl these silaacyl complexes formed zirconocene dichloride and the first stable formylsilanes, $(\text{Me}_3\text{Si})\text{SiCHO}$ ³² and Ph_3SiCHO .¹¹ Like the chloro derivative, $[\text{ZrMe}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$ reacted with CO to give the pink intermediate $[\text{Zr}\{\eta^2\text{-COSi}(\text{SiMe}_3)_3\}(\text{Me})\text{CpCp}^*]$, which rearranged in pentane solution during 1 h to the beige enolate hydride complex $[\text{Zr}\{\text{OC}(\text{=CH}_2)\text{Si}(\text{SiMe}_3)_3\}(\text{H})\text{CpCp}^*]$.⁸

The influence of steric effects was also evident in the reaction of $[\text{ZrMe}(\text{SiHMe}_2)(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}, \text{Me}$) 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 $[\text{Zr}\{\text{OC}(\text{=CH}_2)\text{SiHMe}_2\}(\text{H})\text{Cp}^*_2]$.¹⁴ Due to the lower reactivity of Zr–Ge and Zr–Sn bonds compared to Zr–Si bonds, $[\text{ZrCl}(\text{EPh}_3)\text{Cp}^*(\eta\text{-C}_5\text{R}_5)]$ ($\text{E} = \text{Ge}, \text{R} = \text{H}; \text{E} = \text{Ge}, \text{Sn}, \text{R} = \text{Me}$) failed to react with CO.¹¹

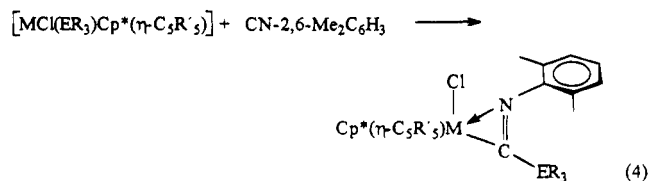
b. Olefin Insertion. The enhanced reactivity of zirconocene silyl complexes with sterically demanding ligands is also demonstrated by the photochemically induced reaction of $[\text{ZrCl}(\text{SiR}_3)\text{Cp}_2]$ ($\text{R} = \text{Me}, \text{SiMe}_3$) or $[\text{ZrCl}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$ with ethylene. Whereas the former did not react,^{6,31} the latter gave the yellow insertion product $[\text{Zr}\{\text{CH}_2\text{CH}_2\text{Si}(\text{SiMe}_3)_3\}(\text{Cl})\text{CpCp}^*]$ in 50% yield.³³ The quantum yield for this reaction ($\lambda = 380\text{--}470\text{ nm}$) 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 $[\text{ZrCl}(\text{EPh}_3)\text{Cp}^*(\eta\text{-C}_5\text{R}_5)]$ ($\text{E} = \text{Si}, \text{Ge}, \text{R} = \text{H}; \text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{R} = \text{Me}$)¹¹ or $[\text{ZrMe}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$;³⁴ the latter also failed to react with styrene.³⁴ Reaction of $[\text{ZrH}(\text{SiHPh}_2)(\text{L})\text{Cp}_2]$ ($\text{L} = \text{PMe}_3, \text{PMePh}_2$) with 1-octene gave the hydrosilylation product $\text{Oct}^n\text{Ph}_2\text{-SiH}$.²⁰ $[\text{Zr}(\mu\text{-H})(\text{SiHPh}_2)\text{Cp}_2]_2$ did not react with 1-octene under analogous conditions.²⁰

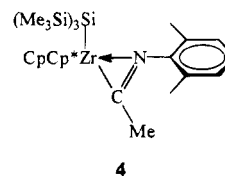
$[\text{Zr}(\eta^2\text{-NBu}^t\text{SiMe}_2)(\text{PMe}_3)\text{Cp}_2]$ reacts with ethylene or formaldehyde with insertion into the Zr–Si bond to yield the five-membered metallacycles $[\text{Zr}(\text{CH}_2\text{CH}_2\text{-SiMe}_2\text{NBu}^t)\text{Cp}_2]$ or $[\text{Zr}(\text{OCH}_2\text{SiMe}_2\text{NBu}^t)\text{Cp}_2]$.²³

c. Alkynes. To date insertion of alkynes into M–E bonds has not been observed. Attempted reactions include: $[\text{ZrCl}(\text{SiR}_3)\text{Cp}_2]$ ($\text{R} = \text{Me}, \text{SiMe}_3$) with phenylacetylene,⁶ $[\text{ZrCl}(\text{EPh}_3)\text{Cp}^*(\eta\text{-C}_5\text{R}_5)]$ ($\text{E} = \text{Si}, \text{Ge}, \text{R} = \text{H}; \text{E} = \text{Si}, \text{Ge}, \text{Sn}, \text{R} = \text{Me}$)¹¹ and $[\text{ZrCl}\{\text{Si}(\text{SiMe}_3)_3\}\text{-CpCp}^*]$ ⁸ with phenylacetylene or acetylene, and $[\text{ZrMe}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$ with acetylene.³⁴ $[\text{ZrH}(\text{SiPh}_3)(\text{PMe}_3)\text{Cp}_2]$ reacts with dimethylacetylene to give the metallacycle $[\text{Zr}(\text{CMe}=\text{CMe}-\text{CMe}=\text{CMe})\text{Cp}_2]$ 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 ($\text{M} = \text{Hf}, \text{E} = \text{Si}, \text{R} = \text{Ph}, \text{R}' = \text{H}$;¹¹ $\text{M} = \text{Zr}, \text{Hf}, \text{E} = \text{Si}, \text{R} = \text{Ph}, \text{R}' = \text{Me}$, formation of products observed in solution by ¹H NMR;¹¹ $\text{M} = \text{Zr}, \text{E} = \text{Ge}, \text{R} = \text{Ph}, \text{R}' = \text{H}$;¹¹ $\text{M} = \text{Zr}, \text{E} = \text{Si}, \text{R} = \text{Me}$ or $\text{SiMe}_3, \text{R}' = \text{H}$;⁶ $\text{M} = \text{Zr}, \text{E} = \text{Si}, \text{R} = \text{SiMe}_3, \text{R}' = \text{H}$ ⁸). The stannyl complexes $[\text{MCl}(\text{SnPh}_3)\text{Cp}^*(\eta\text{-C}_5\text{R}'_5)]$ ($\text{M} = \text{Hf}, \text{R}' = \text{H}; \text{M} = \text{Zr}, \text{R}' = \text{Me}$) did not react.¹¹ $[\text{Zr}\{\eta^2\text{-C}(\text{N-}2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{Si}(\text{SiMe}_3)_3\}(\text{Cl})\text{CpCp}^*]$ was structurally characterized.⁸

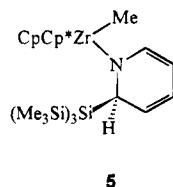


The methyl complex $[\text{ZrMe}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$ undergoes exclusively insertion of the isocyanide into the Zr–Me bond, forming **4**.⁸ $[\text{ZrH}(\text{SiPh}_3)(\text{PMe}_3)\text{Cp}_2]$ underwent insertion of Bu^tNC into the Zr–H bond to give $[\text{Zr}\{\eta^2\text{-C}(\text{H})\text{NBu}^t\}(\text{SiPh}_3)\text{Cp}_2]$.¹⁹



e. Nitriles, Pyridines. Insertion of nitriles (RCN , $\text{R} = \text{Me}, \text{CH}=\text{CH}_2, \text{Ph}$) into the Zr–Si bond of $[\text{ZrMe}\{\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$ gave the orange to yellow azomethine derivatives $[\text{ZrMe}\{\text{N}=\text{C}(\text{R})\text{Si}(\text{SiMe}_3)_3\}\text{CpCp}^*]$ 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 diaste-

reomer 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 ¹H NMR.³⁴ The related complexes [Zr{Si(SiMe₃)₃}(X)Cp(η-C₅R₅)] (X = Me, R = H; X = Cl, R = Me) were much less reactive toward nitriles or pyridine.³⁴



No reaction was observed between [ZrCl(SiR₃)Cp₂] (R = Me, SiMe₃) and benzonitrile (R = Me) or 4-methoxybenzonitrile (R = SiMe₃).⁶ [ZrCl{Si(SiMe₃)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(SiPh₃)(PMe₃)Cp₂] undergoes insertion of Bu^tCN into the Zr-H bond yielding [Zr(η¹-N=CHBu^t)(SiPh₃)Cp₂] in 95% yield.¹⁹

f. Isocyanates. [ZrCl{Si(SiMe₃)₃}Cp₂]⁶ and [ZrCl(EPh₃)Cp*(η-C₅R₅)] (E = Si, Ge, R = H; E = Si, Ge, Sn, R = Me)¹¹ did not react with phenyl isocyanate.

[Zr{Si(SiMe₃)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(SiPh₃)(PMe₃)Cp₂] underwent insertion of acetone into the Zr-H bond to give [Zr(OCHMe₂)(SiPh₃)Cp₂].¹⁹ No reaction of [{Zr(μ-H)(SiHPh₂)Cp₂}]₂ with acetone was observed.²⁰

No reaction occurred between [ZrCl(SiMe₃)Cp₂]^{6,31} or [ZrMe{Si(SiMe₃)₃}CpCp*]³⁴ and CO₂ or CS₂, nor between [ZrCl(EPh₃)Cp*(η-C₅R₅)] (E = Si, Ge, R = H; E = Si, Ge, Sn, R = Me) and CS₂.¹¹ [ZrCl{Si(SiMe₃)₃}CpCp*] reacted with CO₂ to give a mixture of unidentified products.⁸

No reaction of [Zr{Si(SiMe₃)₃}(X)CpCp*] with PMe₃ (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-SiHR₂) to produce terminal silylene (M=SiR₂) or bridging silylene (M-SiR₂-M) complexes has not been observed up to now. However, as mentioned above, reaction of [Zr(NBu^tSiMe₂H)Cp₂] with LiCH₂-SiMe₃ in the presence of PMe₃ leads to deprotonation of the silyl group, elimination of LiI, and formation of the η²-silanimine complex [Zr(η²-NBu^tSiMe₂)(PMe₃)Cp₂].²³ The phosphine ligand is displaced by CO to give the corresponding carbonyl complex [Zr(η²-NBu^t-SiMe₂)(CO)Cp₂].²³

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

A. Metallocene(IV) Amides

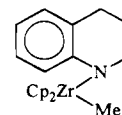
1. Synthesis and Spectroscopic Properties

A general synthetic approach to metallocene bis-amido 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')₂Cp₂] (M = Zr, NRR' = pyrrolyl,³⁷ M = Zr, NRR' = 2,5-dimethylpyrrolyl,³⁸ M = Zr, R = R' = SiMe₃,³⁹ M = Zr, Hf, R = H, R' = Me,⁴⁰ M = Zr, R = H, R' = 2,6-Me₂C₆H₃, 4-Bu^tC₆H₄, *o*-Tol,⁴¹ M = Zr, R = H, R' = Ph⁴²). [Zr{N(SiMe₃)₂}₂Cp₂] exhibits one ¹H NMR signal for the equivalent Cp ligands, and two for the inequivalent SiMe₃ groups. A variable-temperature study gave a rotation barrier of ΔG[‡] (357 K) = 75.3 kJ mol⁻¹.³⁹

Reaction of zirconocene hydride chloride with LiN-(SiMe₃)₂ gives the metallacycle [M{CH₂SiMe₂N-(SiMe₃)₂}Cp₂] (**6**) (M = Zr), formed via a facile γ-hydrogen elimination. Interestingly, [TiCl₂Cp₂] reacts with the lithium amide with formation of (**6**) (M = Ti) exclusively, independent of the stoichiometry employed.³⁹

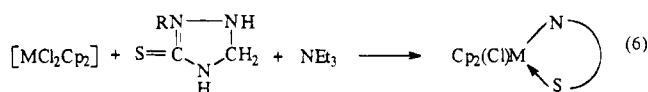
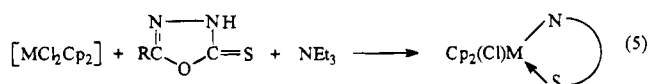
The metallocene dichlorides of Ti, Zr, and Hf react with equivalent amounts of the dilithium salts of 2-aminobenzenethiol or *o*-phenylenediamine to give the colored complexes [M(1-NH-2-X-C₆H₄)Cp₂] (X = S, NH) in 33–79% yield.⁴³ Variable-temperature ¹H NMR studies suggest a folding of the five-membered MNC₂S 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 (ΔG[‡] = 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)Cp₂] (R = Me, R' = 2,6-Me₂C₆H₃, 4-Bu^tC₆H₄, Bu^t,^{41,44} R = CH₂CH₂Bu^t, R' = *o*-Tol, SiMe₂Bu^t)⁴¹ are accessible by the salt elimination route from [ZrCl(R)Cp₂] and LiNHR'. The methyl zirconocene amides (R = Me) react with a further equivalent of amine to give bisamido zirconocene complexes [Zr(NHR')₂Cp₂] (R' = 2,6-Me₂C₆H₃, 4-Bu^t-C₆H₄, Bu^t).⁴¹ Alternatively, [ZrMe₂Cp₂] 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')₂Cp₂] (R = 2,6-Me₂C₆H₃, 4-Bu^t-C₆H₄, Bu^t, SiMe₂Bu^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

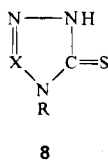


Mixed zirconocene alkoxide amides $[\text{Zr}(\text{NMe}_2)(\text{OR}')\text{Cp}_2]$ are obtained by reaction of $[\text{Zr}(\text{NMe}_2)_2\text{Cp}_2]$ with $\text{R}'\text{OH}$ ($\text{R}' = 2,6\text{-Bu}^t_2\text{C}_6\text{H}_3$, $2,6\text{-Bu}^t_2\text{-4-MeC}_6\text{H}_2$, $2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2$) in benzene.⁴⁶ However, the zirconocene alkoxide chloride $[\text{ZrCl}(\text{OR}')\text{Cp}_2]$ did not react with LiNMe_2 ($\text{R}' = 2,6\text{-Bu}^t_2\text{-4-MeC}_6\text{H}_2$).⁴⁶

Zr-N or Hf-N σ -bonds are accessible by the reaction of $[\text{MCl}_2\text{Cp}_2]$ ($\text{M} = \text{Zr}, \text{Hf}$) with amines in the presence of base. Thus, the heterocyclic thiones, i.e. oxadiazole thione and thiohydantoin derivatives, shown in eqs 5 ($\text{M} = \text{Zr}, \text{Hf}$, $\text{R} = \text{Ph}$, 3- or 4- $\text{NO}_2\text{C}_6\text{H}_4$, 2- ClC_6H_4) and 6 ($\text{M} = \text{Zr}, \text{Hf}$, $\text{R} = \text{Ph}$, *p*-Tol, Bz, 2- or 4- MeOC_6H_4 , nap) were prepared in 52–60 ($\text{M} = \text{Zr}$)⁴⁷ and 40–70% yield ($\text{M} = \text{Hf}$).⁴⁸ If an excess of reagent is used, trisubstituted monocyclopentadienyl complexes of Zr or Hf are obtained (cf. dithiocarbamate complexes, section VI.E.1).^{47,48} Mono- and disubstituted zirconocene complexes of 3-substituted 2-mercaptoquinazol-4-ones were also prepared.⁴⁹

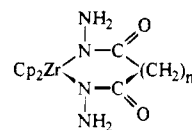


With $[\text{HfCl}_2\text{Cp}_2]$, derivatives of 3-substituted 4-amino-*S*-triazole-5-thione (**8**) ($\text{R} = \text{NH}_2$, $\text{X} = \text{CMe}$, CEt , CPr ;⁴⁸ $\text{R} = \text{NH}_2$, $\text{X} = \text{CCF}_3$)⁵⁰, 1-substituted tetrazoline-5-thione (**8**) ($\text{R} = \text{Ph}$, 4- MeOC_6H_4 , 4- ClC_6H_4 , *p*-Tol, $\text{X} = \text{N}$)⁴⁸ and the triazolone thione derivatives (**8**) ($\text{R} = \text{benzylidene}$, furylidene, salicylidene, $\text{X} = \text{CCF}_3$)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 ($\text{M} = \text{Zr}$)⁴⁷ and 403–431 nm ($\text{M} = \text{Hf}$),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 $\nu(\text{Zr-N})$ and $\nu(\text{Hf-N})$ mode, respectively. The ^1H NMR resonance of the Cp protons was observed at 6.5–6.8 ppm.^{47,48}

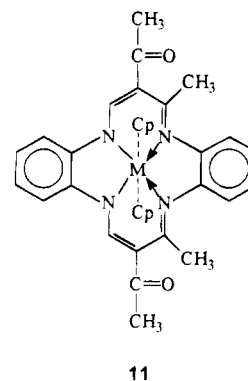
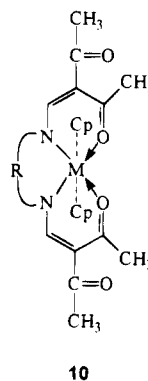


The synthetic approach of eqs 5 and 6 was used for the synthesis of **9** ($n = 0, 2, 4$) from $[\text{ZrCl}_2\text{Cp}_2]$, base (NEt_3), and aliphatic acid dihydrazides.⁵² Again, excess of reagent in the presence of BuNH_2 gave monocyclopentadienyl complexes. The products are yellow to brown, monomeric nonelectrolytes, and were characterized spectroscopically.⁵² The reaction of **9** with β -diketones has been studied.⁵² Derivatives

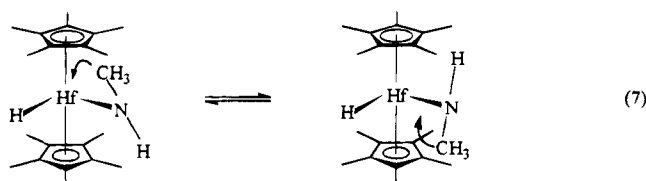
of 6-aminopenicillanic acid were obtained in the same way and characterized spectroscopically.⁵³



The reaction of $[\text{MCl}_2\text{Cp}_2]$ ($\text{M} = \text{Zr}, \text{Ti}$) with Jäger-type ligands in refluxing THF for 10–38 h yields the corresponding amido complexes **10** ($\text{M} = \text{Ti}, \text{Zr}$, $\text{R} = -\text{CH}_2\text{CH}_2-$, *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 $\nu(\text{M-N})$ band appears at 410–430 cm^{-1} and $\nu(\text{M-O})$ at 475–490 cm^{-1} .⁵⁴ Reaction of **10** ($\text{R} = \text{o}$ -phenylene) with *o*-phenylenediamine gives the macrocyclic complex **11**.⁵⁴



Reaction of hafnocene or zirconocene dihydride with excess NH_3 ⁵⁵ or of hafnocene dihydride with excess MeNH_2 ⁵⁶ gave the colorless complexes $[\text{MH}(\text{NH}_2)\text{Cp}^*_2]$ ($\text{M} = \text{Zr}, \text{Hf}$) (84–97% yield)⁵⁵ and $[\text{HfH}(\text{NHMe})\text{Cp}^*_2]$ (52% yield).⁵⁶ The Zr complex is also obtained from the oxidative addition of ammonia to $[\{\text{Zr}(\text{N}_2)\text{Cp}^*_2\}_2(\text{N}_2)]$ (40–50% yield).⁵⁵ In the ^1H NMR spectrum the $\text{C}_5(\text{CH}_3)_5$ protons appear as a singlet ($\delta = 2.03$ ppm), the *NHMe* 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 $[\text{HfH}(\text{NH}_2)\text{Cp}^*_2]$ (δ Hf–H 9.3 ppm).⁵⁵ It was concluded on the basis of the up-field chemical shifts of the hydride resonance in $[\text{HfH}(\text{NHR})\text{Cp}^*_2]$ ($\text{R} = \text{Me}$,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_π – p_π interaction, leading to a Hf–N bond order > 1 .⁵⁶ A crystal structure of the amido complex $\text{R} = \text{Me}$ confirmed this assumption (see section III.A.2). However, in this case inequivalent Cp^* ligands should be observed in the ^1H 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 ^1H NMR experiments gave an upper limit of the activation barrier for this oscillation of $\Delta G^\ddagger \cong 41.9$ kJ mol^{-1} .⁵⁶

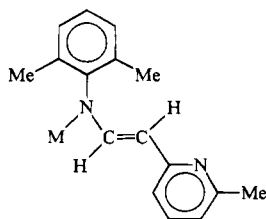


For [HfH(NMe₂)Cp*₂] the down-field shift of the hydride resonance ($\delta = 11.2$ ppm) suggests little Hf–N π -back-bonding. Clearly, steric interaction between the NMe₂ ligand and the Cp* ligands prevents the former from adopting the necessary orientation for π -back-bonding.^{55,56} Thus, in the complexes [HfH(NRR')Cp*₂] Hf \leftarrow N π -back-bonding increases in the order NMe₂ < NHMe \approx NH₂, 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 H₂) or thermolysis of the corresponding triazenido complexes [HfH(NHNR)Cp*₂] at 80 °C (elimination of N₂).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, RN₃ (R = Ph, *p*-Tol).⁵⁷ The same product is obtained from the hafnocene monoamido complex and primary amine at 80 °C.⁵⁷

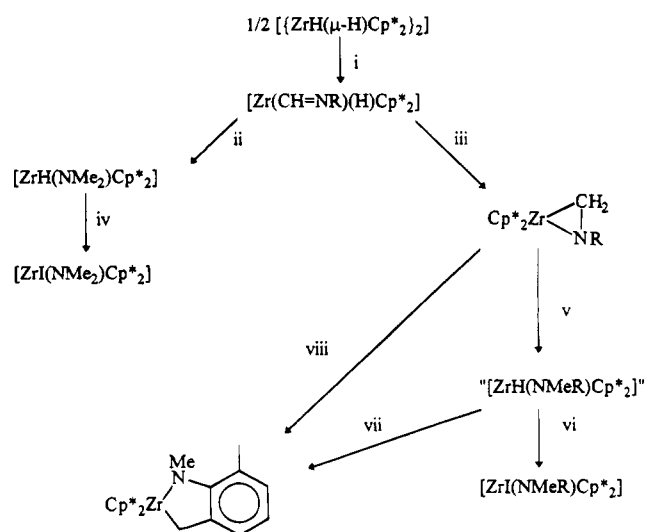
Zirconocene dihydride complexes react with isonitriles to give formimidoyl complexes. Subsequent reaction with hydrogen or thermolysis yields methylamido zirconocene complexes (Scheme 2).⁵⁸ Alternatively, zirconocene hydride chloride or dimethylzirconocene react with benzylisonitrile to give imidoyl complexes [Zr(CR=NBz)(X)Cp₂] (X = Cl, R = H; X = R = Me). Subsequent reaction with a zirconocene hydride derivative yields zirconocene monoamido complexes.⁵⁹

The dialkyl complexes [MR₂Cp₂] (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)Cp₂] (M–NRR' = **12**).^{60,61} Insertion of a second isocyanide molecule yields [M(NRR')₂Cp₂]. Both products are formed by a facile 1,2-hydrogen shift in intermediate η^2 -iminoacyl complexes.^{60,61}



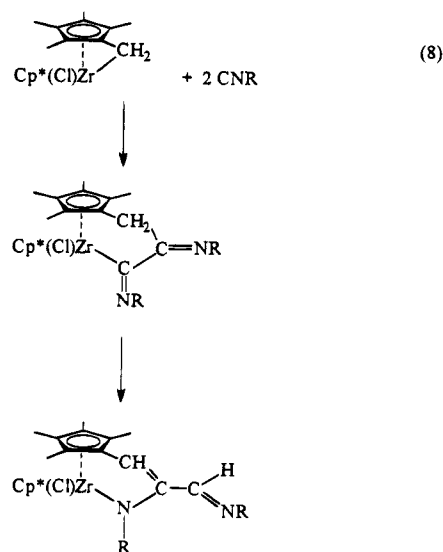
12

In a comparable reaction (eq 8; R = 2,6-Me₂C₆H₃) insertion of isocyanide 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

Scheme 2^a

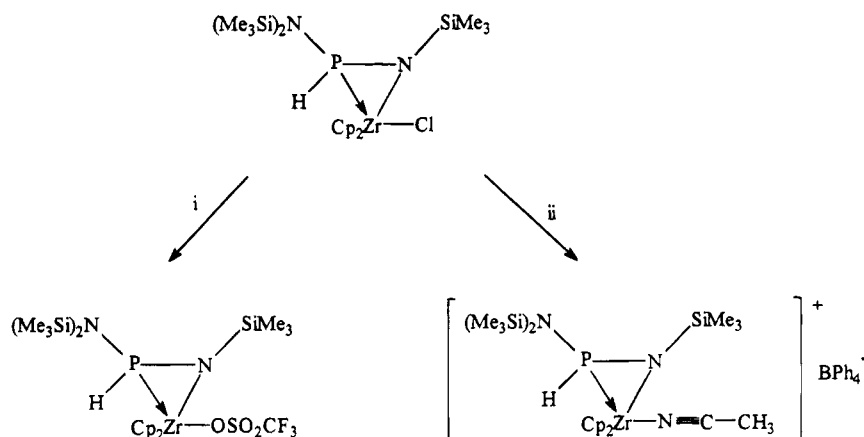
^a (i) RNC (R = Me, 2,6-Me₂C₆H₃); (ii) H₂ (R = Me); (iii) 25 °C (R = 2,6-Me₂C₆H₃); (iv) +MeI, –MeH; (v) H₂; (vi) +MeI, –MeH; (vii) 25 °C, –H₂; (viii) 65 °C.

group to a C atom of the second inserted isonitrile with concurrent formation of a Zr–N σ bond.⁶²

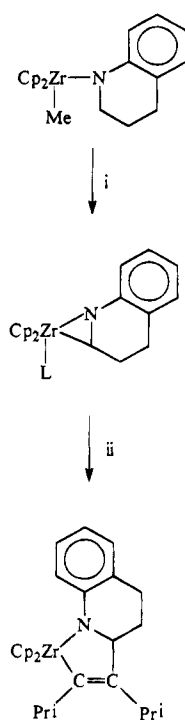


Schiff bases RR'C=NR'' react with zirconocene hydride chloride with hydrozirconation and formation of [ZrCl{N(R'')CHRR'}Cp₂] (R, R', R'' = alkyl or aryl).⁶³ The reaction of these amido complexes, which were not isolated or characterized, with acetyl chloride or methyl oxalyl chloride gives enamides, imides or amides as products.⁶³

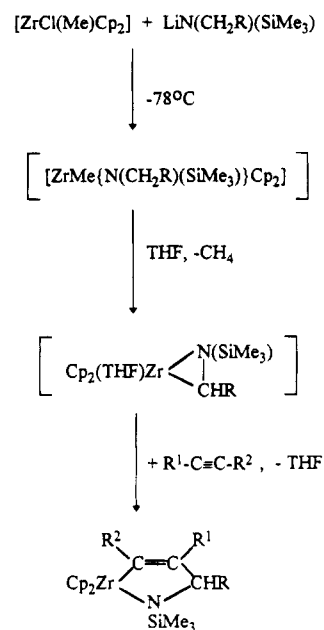
Hydrozirconation of phosphaimines RP=NR' (R = N(SiMe₃)₂, R' = SiMe₃,^{64,65} R = N(SiMe₃)Bu^t, R' = Bu^t; R = tetramethylpiperidino, R' = SiMe₃,⁶⁴), the phosphalkene (SiMe₃)₂NP=C(H)SiMe₃,^{64,66} or the bis(imino)phosphorane (SiMe₃)₂NP(=NSiMe₃)₂,^{64,66} with zirconocene hydride chloride gives the three- 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 (SiMe₃)₂NP=N(SiMe₃), which gives [ZrH{N(SiMe₃)P(H)N(SiMe₃)₂}Cp₂], while [ZrMe₂Cp₂] gave the metalla-

Scheme 4^a

^a (i) + RSO₃CF₃ (R = SiMe₃, Me), -RCl; (ii) + NaBPh₄/CH₃CN, -NaCl.

Scheme 5^a

^a (i) 60 °C, +L (L = THF, PMe₃), -CH₄; (ii) PrⁱC≡CPrⁱ.

Scheme 6^a

^a R = Ph, R¹ = H, R² = Ph, H, Pr, CH₂OSiBu₃, SiMe₃, CH₂CH₂CH₂CN; R = R¹ = Ph, R² = Ph; R = Ph, R¹ = R² = Me; R = H, R¹ = R² = Me; R = H, R¹ = n-C₈H₁₇, R² = H; R = n-C₅H₁₁, R¹ = Ph, H, R² = Ph; R = 2-thienyl, 5-methyl-2-pyrrolyl, R¹ = H, R² = Pr; R = 2-furyl, R¹ = H, R² = Ph;⁷² and R = Ph, R¹ = H, R² = Ph; R = H, R¹ = R² = Ph; R = n-C₅H₁₁, R¹ = R² = Et.⁷³

2. Structural Data

Structural data are available for [Zr(η¹-NC₄H₂-Me₂)₂Cp₂],³⁸ [HfH(NHMe)Cp*₂],⁵⁶ (Figure 2), [Hf{N(2,6-Me₂C₆H₃)[(6-methylpyridyl)vinyl]}₂Cp₂],^{60,61}

[Zr(NHPh)(OSO₂CF₃)Cp₂],⁴² [Zr{N(SiMe₃)P(H)N(SiMe₃)₂}Cl]Cp₂,⁶⁵ [Zr(η²-NBuⁱSiMe₂)(PMe₃)Cp₂],²³

(see section II.2, Figure 1), [Zr(NPhCPh=CPhNPh)Cp₂],⁷⁰ and [Zr{η²-N(SiMe₃)CHPh}(THF)Cp₂].⁷³

The structure of the bis(2,5-dimethylpyrrolyl)zirconocene complex³⁸ is very similar to that of the previously described pyrrolyl derivative [Zr(η¹-NC₄H₂-Cp₂),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_π-p_π interaction. The overall structure of the vinylamido complex [Hf{N(2,6-Me₂C₆H₃)[(6-methyl-

pyridyl)vinyl]}₂Cp₂] 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)(OSO₂CF₃)Cp₂] (2.072(3) Å) and the amido ligand orientation also suggest π-donation from the amido group to Zr.⁴²

The central ZrN₂C₂ five-membered ring of the enediamido complex [Zr(NPhCPh=CPhNPh)Cp₂]

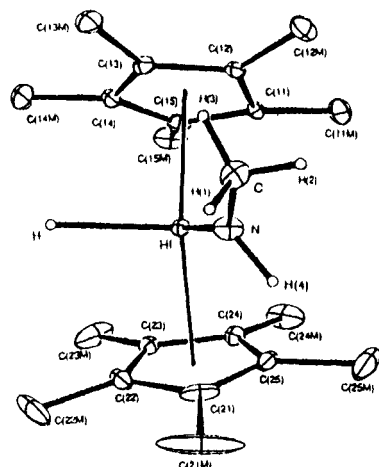


Figure 2. Molecular structure of $[\text{HfH}(\text{NHMe})\text{Cp}^*_2]$. (Reprinted from ref 56. Copyright 1988 American Chemical Society.)

$[\text{Zr}-\text{N} 2.100(4), 2.123(5) \text{ \AA}]$ is folded along the $\text{N}\cdots\text{N}$ axis [dihedral angle $39.2(3)^\circ$], thus confirming the assumptions made from variable-temperature NMR data.⁷⁰

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

In the crystal structure of the zirconazaazaphosphirane $[\text{Zr}\{\text{N}(\text{SiMe}_3)\text{P}(\text{H})\text{N}(\text{SiMe}_3)_2\}(\text{Cl})\text{Cp}_2]$ 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

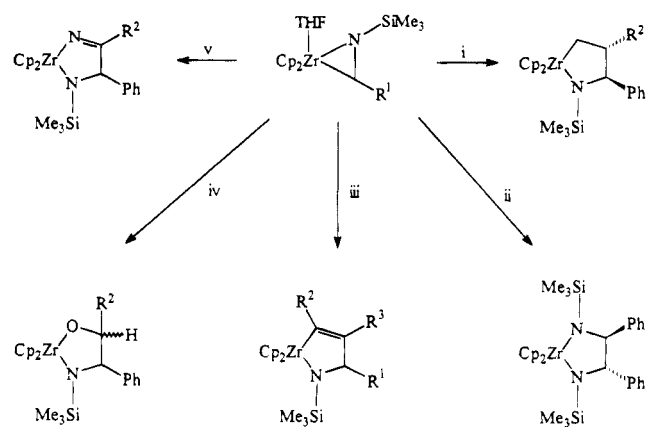
Amides of group 4 metallocenes with a direct M–NR₂ linkage exhibit a wide range of chemical behavior.⁷⁵ Loss of electron density at nitrogen through internal $p_\pi-d_\pi$ bonding weakens their donor capacity. Facile bond cleavage of the M–N bond with protic reagents (e.g., phenylacetylene, HXBu^t with X = O or S)^{35,76} and group redistribution or scrambling with metal or metalloid halides are observed. $[\text{HfH}(\text{NH}_2)\text{Cp}^*_2]$ reacts with water to afford $[\text{HfH}(\text{OH})(\text{NH}_2)\text{Cp}^*_2]$ (cf. section V.E) and ammonia; formation of $[\text{Hf}(\text{OH})(\text{NH}_2)\text{Cp}^*_2]$ was not observed.⁵⁵

Group exchange reactions have been observed in the reaction of $[\text{Zr}(\text{NMe}_2)_2\text{Cp}_2]$ with MCl_4 (M = Si, Ge, Sn, Ti, Zr, Hf) to give $[\text{ZrCl}_2\text{Cp}_2]$ and $[\text{MCl}_2(\text{NMe}_2)_2]$.⁷⁷

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

The reaction between $[\text{Zr}(\text{NMe}_2)(\text{R})\text{Cp}_2]$ (R = Cl, NMe₂) and $[\text{ReH}_7(\text{PPh}_3)_2]$ results in the formation of the heterometallic polyhydrides $[\text{Cp}_2(\text{R})\text{Zr}(\mu\text{-H})_n-$

Scheme 7^a



^a (i) $\text{CH}_2=\text{CHR}^2$ (R¹ = Ph, R² = H, Buⁿ, Me); (ii) $\text{PhHC}=\text{N}(\text{SiMe}_3)$ (R¹ = Ph); (iii) $\text{R}^2\text{C}\equiv\text{CR}^3$ (R¹ = R² = Ph, R³ = H; R¹ = H, R² = R³ = Ph; R¹ = C₆H₁₁, R² = R³ = Et; R¹ = Ph, R² = CH₂(CH₂)₂C≡N, R³ = H); (iv) $\text{R}^2\text{HC}=\text{O}$ (R¹ = Ph, R² = Bu^t; R¹ = R² = Ph); (v) R^2CN (R¹ = Ph, R² = Prⁿ, CH₂CH₂CH₂CH=CH₂, CH₂(CH₂)₂-C(OCH₂CH₂O)Me).

$\{\text{ReH}_{6-n}(\text{PPh}_3)_2\}$ ($n > 1$) (see section VII.A, Scheme 33) with elimination of dimethylamine.⁷⁹

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

$[\text{Zr}(\text{NMe}_2)(\text{OR})\text{Cp}_2]$ (R = 2,6-Bu^t₂C₆H₃) reacts with PhNCO in hexane with insertion and formation of $[\text{Zr}\{\text{NPhC}(\text{=O})\text{NMe}_2\}(\text{OR})\text{Cp}_2]$.⁴⁶

The zirconocene bisamido complexes $[\text{Zr}(\text{NHR})_2\text{Cp}_2]$ (R = 2,6-Me₂C₆H₃, 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 $[\text{Zr}\{\eta^2\text{-N}(\text{SiMe}_3)\text{CHR}^1\}(\text{THF})\text{Cp}_2]$ undergoes a number of chemo-, regio-, and diastereoselective coupling reactions with unsaturated organic compounds, forming zirconazaazacyclopentane derivatives (Scheme 7).⁷³

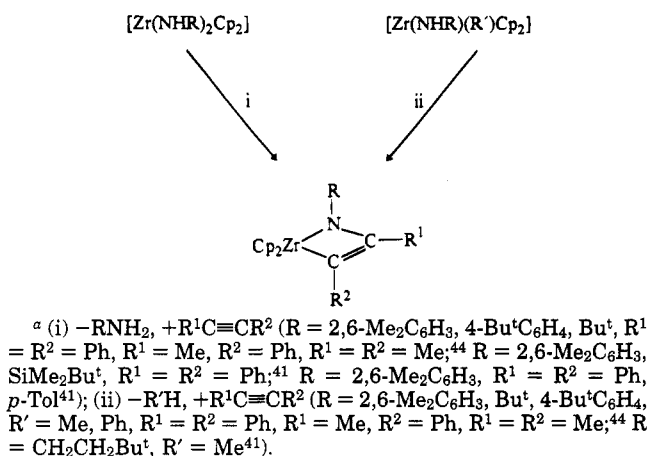
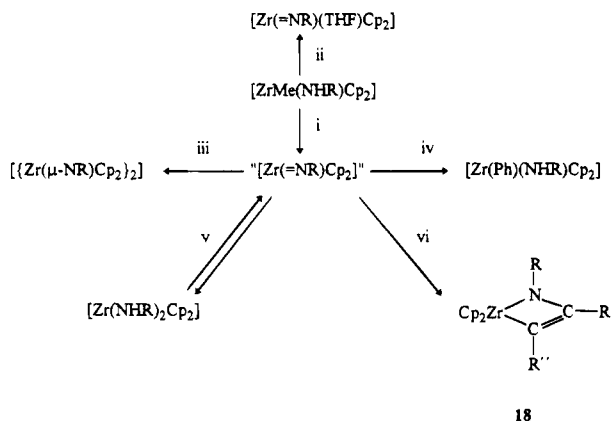
η^2 -Ketimine complexes of zirconocene can be generated by a C–H activation process from α,α -disubstituted amines and react with a variety of unsaturated substrates to afford α,α,α -trisubstituted amines upon hydrolysis.⁸⁰

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 $[\text{CpTi}(\mu\text{-NMe}_2)_3\text{M}(\text{CO})_3]$ (M = Cr, Mo, W).⁸¹

C. Zirconocene Imido Complexes $[\text{Zr}(\text{=NR})\text{Cp}_2]$; 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

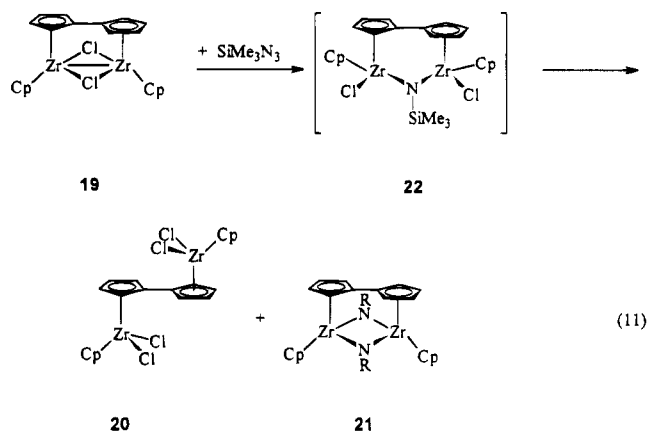
Scheme 8^aScheme 9^a

in formation of azametallacyclobutenes.^{41,44} No reaction was observed between [Zr(NHSiMe₂Bu^t)₂Cp₂] and diphenylacetylene. The formation of the metal-lacycles shown in Scheme 8 was shown to be reversible. Formation of a transient zirconocene imido complex was suggested.

The generation of [Zr(=NR)Cp₂] (R = 4-Bu^tC₆H₄, Bu^t, 2,6-Me₂C₆H₃)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^tC₆H₄), 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)Cp₂] and of dimeric [{Zr(μ-NR)Cp₂}]₂ (R = 4-Bu^tC₆H₄) 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)Cp₂] (R = 2,6-Me₂C₆H₃, Bu^t) dissociate rapidly and are therefore a convenient source of the reactive intermediate [Zr(=NR)Cp₂]. Thus, diphenylacetylene reacts rapidly with the THF adduct (R = 2,6-Me₂C₆H₃) 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)Cp₂] (R = 4-Bu^tC₆H₄) is discussed above (cf. section III.C). The orange complex **21** (R = SiMe₃) 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**.



Oxidation of [Cp₂Zr(PMe₃)(η¹:η⁵-C₅H₄)]₂ by SiMe₃N₃ gave the deep-blue dinuclear imido-bridged complex [Cp₂Zr(η¹:η⁵-C₅H₄)]₂(μ-NSiMe₃) in 88% yield.⁸³ The imido group of the latter is located in the region between the two η¹:η⁵-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=CR₂) derivatives] is the hydrozirconation of nitriles R'CN with [ZrH(X)(η-C₅R₅)₂] to give [Zr(N=CHR')(X)(η-C₅R₅)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(NPr₂)₂⁸⁸]. 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 [ZrMe₂-Cp*₂] and tolunitrile.⁸⁵

The salt elimination route can successfully be employed for the synthesis of bis(alkylideneamido) complexes [Zr(N=CR₂)₂Cp₂] from zirconocene dichloride and LiN=CR₂ (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 prerduced metal complex [ZrLCp₂] (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-

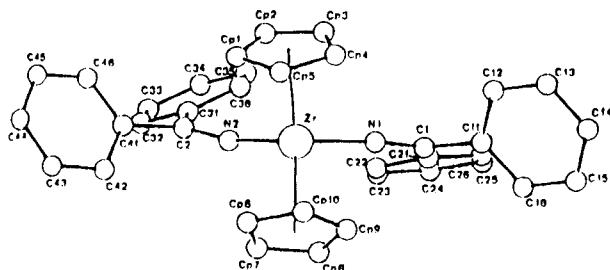


Figure 3. Molecular structure of $[\text{Zr}(\text{N}=\text{CPh}_2)_2\text{Cp}_2]$. (Reprinted from ref 89. Copyright 1988 American Chemical Society.)

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

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

2. Structural Data

The molecular structures of $[\text{Zr}(\text{N}=\text{CPh}_2)_2\text{Cp}_2]$ ⁸⁹ and $(E)\text{-}[\text{ZrCl}(\text{N}=\text{CHPh})\text{Cp}_2]$ ⁸⁷ have been determined. The short $\text{Zr}-\text{N}$ bonds (2.013–2.063 Å) indicate some multiple-bond character. The $\text{C}=\text{N}$ bond distances range from 1.259(1) to 1.266(4) Å.^{87,89} The molecular symmetry of $[\text{Zr}(\text{N}=\text{CPh}_2)_2\text{Cp}_2]$ (Figure 3) differs from the apparent symmetry in solution (cf. section III.E.3).⁸⁹ The $\text{Zr}-\text{N}-\text{C}$ linkages are nearly linear [173.7(2), 164.1(2)°]. The $\text{N}-\text{Zr}-\text{N}$ angle [106.5(1)°] and the $\text{Zr}-\text{N}$ bond lengths [2.058(2), 2.063(2) Å]⁸⁹ are larger than those of $(E)\text{-}[\text{ZrCl}(\text{N}=\text{CHPh})\text{Cp}_2]$. The core atoms of the alkylideneamido ligands are almost coplanar.

In $(E)\text{-}[\text{ZrCl}(\text{N}=\text{CHPh})\text{Cp}_2]$ a nearly linear $\text{Zr}-\text{N}-\text{C}$ arrangement [170.5(5)°] was found. The $\text{Zr}-\text{N}$ bond is very short [2.013(5) Å]. The atoms Cl , Zr , N , C are coplanar with E orientation of the substituents of the $\text{Zr}-\text{N}=\text{C}$ 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 $\nu(\text{C}=\text{N})$ mode between 1630 and 1700 cm^{-1} .^{85,86,88,89}

The solid-state structure of $[\text{Zr}(\text{N}=\text{CPh}_2)_2\text{Cp}_2]$ (cf. section III.E.2, Figure 3) shows a clear distinction of the (E) - and (Z) -oriented phenyl substituents at the $\text{Ph}_2\text{C}=\text{NZr}$ 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 $[\text{TiCl}(\text{N}=\text{CR}_2)\text{Cp}_2]$ ($\text{R} = p\text{-Tol}$, Bu^t) had revealed the nonequivalence of the two C -substituents in the ketimides, implying a high rotational barrier about the $\text{C}=\text{N}$ bond.⁹⁰

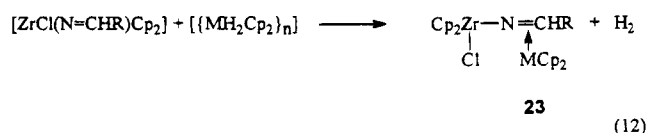
In $[\text{ZrCl}(\text{N}=\text{CHPh})\text{Cp}_2]$ only the (E) -isomer is present in the solid state.⁸⁷ The (E) -isomer was synthesized stereoselectively,⁸⁶ and it was shown that

the isomerization $(E) \leftrightarrow (Z)$ could not be effected thermally or photochemically.^{86,89}

Due to the molecular structure of $[\text{ZrCl}(\text{N}=\text{CHPh})\text{Cp}_2]$ 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 $[\text{ZrCl}(\text{N}=\text{CHMe})\text{Cp}_2]$.⁸⁷

4. Chemical Properties

$[\text{ZrCl}(\text{N}=\text{CHPh})\text{Cp}_2]$ reacts with tolyllithium with elimination of LiCl and formation of $[\text{Zr}(p\text{-Tol})(\text{N}=\text{CHPh})\text{Cp}_2]$;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; $\text{M} = \text{Zr}$, Hf , $\text{R} = \text{Ph}$; $\text{M} = \text{Zr}$, $\text{R} = \text{Me}$).⁸⁶ In **23** four signals for the four inequivalent cyclopentadienyl rings are observed.⁸⁶ The hydrido complex $[\text{ZrH}\{\text{N}=\text{CH}(p\text{-Tol})\}\text{Cp}^*_2]$ reacts with methyl iodide with elimination of methane and formation of the corresponding iodo complex.⁸⁵

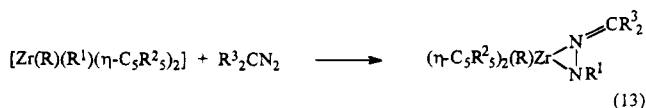


$[\text{ZrCl}\{\text{N}=\text{CHP}(\text{NPr}^i_2)_2\}\text{Cp}_2]$ is a useful starting material for the synthesis of a variety of C -phosphanyl-, N -phosphanyl-, or N -boranylimines. Thus, reaction with $\text{RR}'\text{MCl}$ ($\text{M} = \text{P}$, $\text{R} = \text{R}' = \text{Ph}$; $\text{M} = \text{P}$, $\text{R} = \text{NPr}^i_2$, $\text{R}' = \text{Cl}$; $\text{M} = \text{P}$, $\text{R} = \text{R}' = \text{NPr}^i_2$; $\text{M} = \text{B}$, $\text{R} = \text{R}' = \text{NPr}^i_2$; $\text{M} = \text{B}$, $\text{R} = \text{N}(\text{SiMe}_3)\text{N}(\text{SiMe}_3)_2$, $\text{R}' = \text{Cl}$; $\text{MRR}' = \text{SnMe}_3$)⁸⁸ leads to formation of $[\text{RR}'\text{M}\{\text{N}=\text{CHP}(\text{NPr}^i_2)_2\}]$ with elimination of $[\text{ZrCl}_2\text{Cp}_2]$.

F. Metallocene(IV) Hydrazido and Hydrazonato Complexes

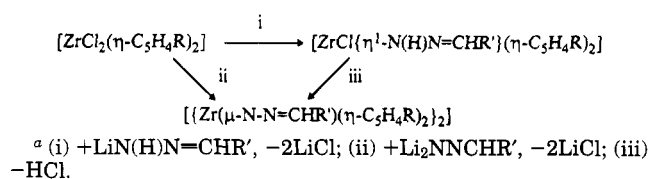
1. Synthesis

Salt elimination reactions have been employed for the synthesis of metallocene hydrazido complexes $[\text{Zr}(\text{NR}^1\text{NPhR}^2)(\text{R})\text{Cp}_2]$ from $[\text{ZrCl}(\text{R})\text{Cp}_2]$ and $\text{MNR}^1\text{NPhR}^2$ ($\text{R} = \text{Me}$, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$, $\text{M} = \text{K}$;^{91,92} $\text{R} = \text{CH}_2\text{CH}_2\text{Bu}^t$, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$, $\text{M} = \text{Li}$)⁹³ in 72–83% yield. Insertion of diazoalkanes into $\text{Zr}-\text{C}$ or $\text{Zr}-\text{H}$ bonds yields hydrazonato(1-) complexes (eq 13; $\text{R} = \text{R}^1 = \text{Me}$, Bz , $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$; $\text{R} = \text{R}^1 = \text{Bz}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{CO}_2\text{Et}$;⁹⁴ $\text{R} = \text{Cl}$, $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$;⁹⁵ $\text{R} = \text{OH}$, $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{R}^3 = p\text{-Tol}$;⁹⁶ $\text{R} = \text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$)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}

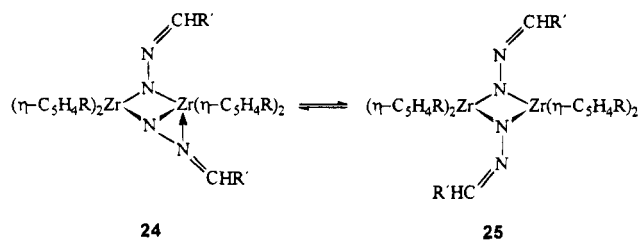


Zirconocene phosphido complexes react with diazoalkanes with insertion into the $\text{Zr}-\text{P}$ bond and formation of phosphido hydrazonido(1-) ligands (cf. section IV.A.4).^{97–99}

The hydrazone derivatives shown in Scheme 10 ($\text{R} = \text{H}$, Me , $\text{R}' = \text{Ph}$;¹⁰⁰ $\text{R} = \text{H}$, $\text{R}' = 4\text{-MeOC}_6\text{H}_4$,^{100,101} Ph , $4\text{-ClC}_6\text{H}_4$, $4\text{-(NC)}_6\text{H}_4$ ¹⁰¹) are readily available by

Scheme 10^a

ligand metathesis. The two-step synthesis gave higher yields.^{100,101} The crystal structure of [$\{Zr(\mu\text{-NN}=\text{CHPh})(\eta\text{-C}_5\text{H}_4\text{Me})_2\}_2$] revealed an unusual unsymmetrical bridging ligand system (**24**) (cf. section III.F.4), while the ¹³C NMR data suggest a fluxional behavior in solution (eq 14).¹⁰⁰



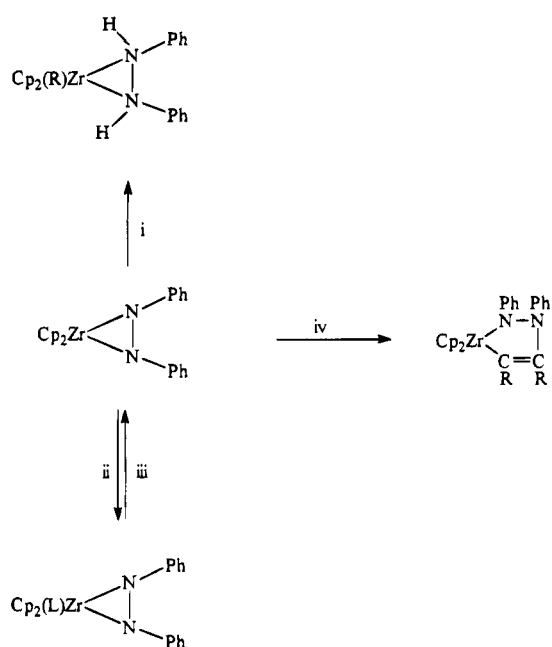
Bimetallic hydrazido(3-) complexes [$Zr\{N(H)N=WMe_3Cp^*\}_n(R)_{2-n}Cp_2$] ($n = 1, 2, R = \text{Me, Bz}$) are formed in the reaction of dimethyl or dibenzyl zirconocene with the tungsten hydrazido(2-) complex [$W(=NNH_2)Me_3Cp^*$].¹⁰² The monosubstituted zirconocene complexes do not readily eliminate methane or toluene to generate hydrazido(4-) complexes. Thus, heating or irradiation in the presence of THF or PMe₃ 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 ¹⁵N NMR spectrum is 403–410 ppm for N_α and 246–260 ppm for N_β.¹⁰²

2. Spectroscopic Properties

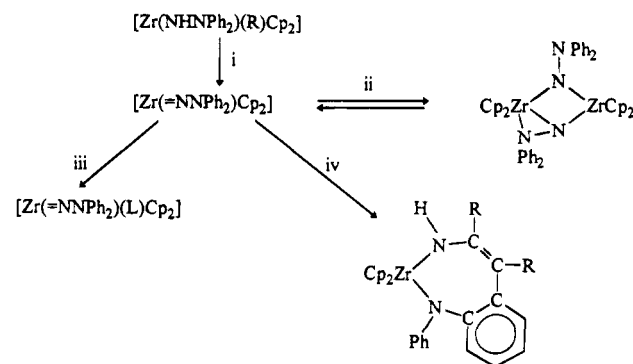
The η^2 -bonding of the hydrazido(1-) ligand in these complexes is appeared from ¹H and ¹³C NMR spectroscopy; coordination of the β -nitrogen of the hydrazido ligand freezes the inversion at the N atom, thus making the cyclopentadienyl ligands chemically inequivalent.⁹¹

3. Chemical Properties

Heating [$ZrMe\{\eta^2\text{-NPhN(H)Ph}\}Cp_2$] 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-diphenylhydrazine in ether/THF at room temperature.^{91,92} The THF ligand can be replaced by a variety of σ -donor ligands to form [$Zr(N_2Ph_2)(L)Cp_2$] ($L = \text{py, PMe}_3, \text{PhCN, Bu}^t\text{NC}$).^{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 PhCOCH₃, R = C≡CPh or PhC(=CH₂)O; (ii) L (L = THF, py, PMe₃, Bu^tNC, PhCN); (iii) -THF; (iv) RC≡CR (R = Me, Et).

Scheme 12^a

^a (i) 110 °C, 12 h, -RH (R = CH₂CH₂Bu^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 ($R'HC=CR''R'''$), N₂, 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-

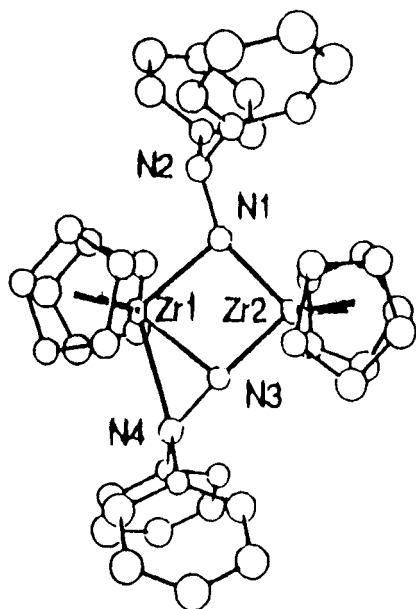
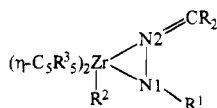


Figure 4. Molecular structure of $[\{Zr(=NNPh_2)Cp_2\}_2]$. (Reprinted from ref 93. Copyright 1991 American Chemical Society.)

bond distances. Both N atoms of the hydrazido(2-) ligand are pyramidal [torsion angle $C_{ipso}-N-N-C_{ipso}$ $91.3(4)^\circ$]. The Zr-N(hydrazido) bond lengths are 2.161(3) and 2.105(4) Å [$N-Zr-N$ $39.25(12)^\circ$, 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 $36.38(15)^\circ$].⁹¹

The molecular structures of the hydrazonato(1-) complexes (**26**; R = Ph, $R^1 = R^2 = Me$, $R^3 = H$,^{94,95} R = CO₂Et, $R^1 = R^2 = Bz$, $R^3 = H$; 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,R² 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 $[Zr(=NNPh_2)(4-NMe_2\text{-pyridine})Cp_2]$ 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 $168.7(6)^\circ$].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 $[\{M(\mu-PR_2)Cp_2\}_2]$ 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 $[\{M(\mu-PR_2)Cp_2\}_2]$ (M = Ti, Zr, Hf, R = Me;¹⁰⁵ M = Ti, R = Ph;¹⁰⁵ M = Ti, Zr, R = Et;¹⁰⁷ M = Ti, Zr, R = Et, Bu¹⁰³) and P_2R_4 are formed.

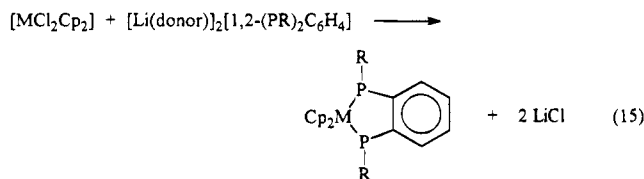
Metallocene monophosphido complexes with dialkyl- or diarylphosphido ligands are scarce. The bisphosphido complexes $[M(PPh_2)_2Cp_2]$ produce equilibrium mixtures with metallocene dihalides $[MX_2Cp_2]$ to give $[M(PPh_2)(X)Cp_2]$ (M = Zr, Hf, X = Cl, I).¹⁰⁵ The same mixture is obtained on mixing metallocene 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 $[ZrCl(PPh_2)_2Cp_2]$, which was obtained in 5% yield at 0 °C from the reaction of $[Zr(PPh_2)_2Cp_2]$ with PPh_2-Cl .¹⁰⁵

Using bulky silylphosphido ligands, $Li(THF)_2P-(SiMe_3)_2$, enables the synthesis of metallocene mono- and bisphosphido complexes $[M\{P(SiMe_3)_2\}_n(X)_{2-n}(\eta-C_5H_4R)_2]$ in 43–92% yield (M = Zr, X = Cl, R = H, SiMe₃, $n = 1$;^{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 = SiMe₃, $n = 2$;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 [ZrCl₂{η-1,3-(SiMe₃)₂C₅H₃}₂] and the lithium phosphide.⁹⁷ [ZrCl{P(SiMe₃)(2,4,6-Bu^t₃-C₆H₂)}Cp₂] was obtained in 85% yield from zirconocene dichloride and the corresponding lithium phosphide in THF at 0 °C.¹¹¹

Extrusion of H₂ 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 Cy₂PH 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-(SiMe₃)₂C₅H₃ 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 = H¹¹⁵) cleanly in 64–87% yield.



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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(μ-PHR')(η-C₅H₄R)₂]₂, (ii) (R/S,S'/R)-[M(PR'-PR'-PR')(η-C₅R₅)₂], (iii) [M(PHR')(X)(η-C₅R₅)₂], (iv) [M(PHR')₂(η-C₅R₅)₂], (v) [M(PR-PR)L₂], (vi) [ZrCl(η-C₅H₄R)₂]₂(μ-PMes) (R = H, Me).

Metallocene(III) complexes of type i were first prepared with dialkylphosphido ligands.^{105,107} *cis*-[Zr(μ-PHR')(η-C₅H₄Me)₂]₂ (R' = Bu^t, adamantyl) are obtained from LiPHR' and the appropriate zirconocene dichloride.¹¹⁶ The structurally characterized *trans*-[Zr(μ-PHCy)Cp₂]₂ was obtained from the reaction of zirconocene dichloride with CyPH₂ 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 [MX₂Cp₂] 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, K₂(PR')_n, R' = Ph, Et, Me, Bu^t, n = 3–5¹¹⁹) 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' = Cy¹²² or

Ph¹²³) 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-Bu^t₃C₆H₂, 40% yield,¹²⁴ Mes, low yield⁹⁸) and iv (M = Zr, R = H, R' = 2,4,6-Bu^t₃C₆H₂,¹²⁴ Mes;⁹⁸ M = Zr, Hf, R = Me, R' = Bu^t, 30–71% yield¹²¹) are obtained when either the metal or the P atom bears a sterically demanding ligand.

[ZrCl₂{η-1,3-(SiMe₃)₂C₅H₃}₂] reacts with 2 equiv of LiPHBu^t to give the terminal phosphido complex iv [Zr(PHBU^t)₂{η-1,3-(SiMe₃)₂C₅H₃}₂] (11% yield) and the diphosphene complex v (M = Zr, R = Bu^t, L = η-1,3-(SiMe₃)₂C₅H₃) in 48% yield, while the hafnocene analogue gives only complex iv (M = Hf, R' = Bu^t, C₅R₅ = η-1,3-(SiMe₃)₂C₅H₃) in 55% yield.¹²¹

[ZrCl₂Cp*₂] reacts with 2 equiv of LiPHMes to give [Zr(PHMes)₂Cp*₂] in 90% yield. In solution, this complex slowly eliminates H₂PMes with formation of transient [Zr(=PMes)Cp*₂], which either rearranges to [Zr(PMes-PMes)Cp*₂] or [Zr(1-PH-2-CH₂-4,6-Me₂C₆H₂)Cp*₂], or can be trapped with MeCN as [Zr(N=CMe-PMes-CMe=N)Cp*₂].^{124b}

Diphosphene complexes (v) are obtained from the reaction of [MCl₂L₂] with 2 equiv of LiPHR (M = Zr, Hf, L = η-1,3-(SiMe₃)₂C₅H₃, R = Ph;¹²¹ M = Zr, L = η-C₅Me₄Et, R = Mes¹²⁵) in 26–70% yield.

The phosphinidene-bridged complex [ZrCl(η-C₅H₄R)₂]₂(μ-PMes) (R = H, Me) (vi) is obtained as dark green crystals on reaction of the corresponding zirconocene dichloride with LiPHMes, together with [ZrCl(PHMes)(η-C₅H₄R)₂] or [Zr(PHMes)₂(η-C₅H₄R)₂], depending on the stoichiometry employed.¹²⁶ The same product is obtained from the reaction of zirconocene dichloride with magnesium and MesPH₂ (*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(μ-PMe₂)Cp₂]₂ (M = Zr, Hf) are obtained in 38–45% yield from metallocene dichloride, magnesium, and Me₂PPMe₂.¹²⁷ In the case of M = Zr, the byproduct [(MCp₂)₂(μ-Cl)(μ-PMe₂)] was obtained in 10% yield.¹²⁷

The complexity of the ¹H NMR spectrum of the final product [ZrH(PH₂)Cp*₂]₂ which was obtained from [Zr(N₂)Cp*₂]₂(N₂) and PH₃ at low temperature is best explained by a dimeric structure. However,

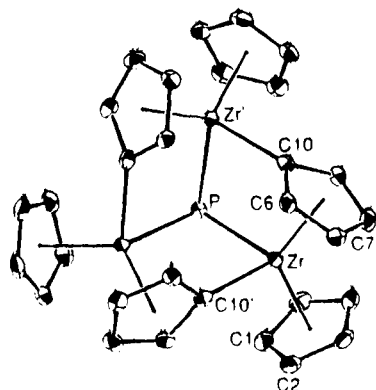
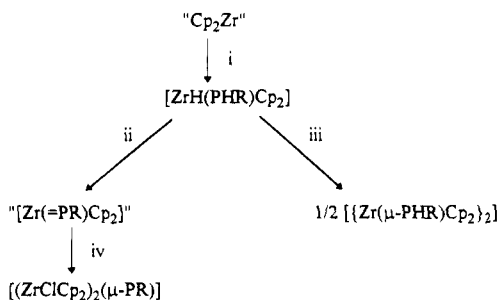


Figure 5. Molecular structure of a trimeric phosphido-capped complex. (Reprinted from ref 129. Copyright 1992 American Chemical Society.)

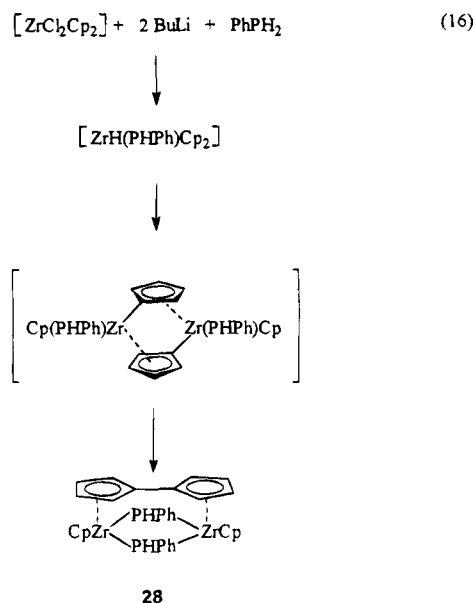
Scheme 13^a



^a (i) RPH₂; (ii) -H₂, intramolecular; (iii) -H₂, intermolecular; (iv) [ZrCl₂Cp₂].

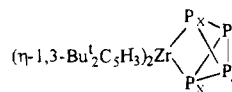
an unambiguous assignment to bridging or terminal ligands (H/PH₂) was not possible.¹²⁸

C-H activation and subsequent C-C bond formation in the intermediate [ZrH(PHPh)Cp₂] yields the Zr(III) complex **28** as the final product (eq 16).¹²⁹ In the analogous reaction with (2,4,6-Bu^t₃C₆H₂)PH₂ and Mg the isolated product (10% yield) is a trimeric phosphido-capped Zr(IV) species (Figure 5).¹²⁹ However, if MesPH₂ is employed instead of the bulkier (2,4,6-Bu^t₃C₆H₂)PH₂, the mono(phosphinidene)-bridged dinuclear complex [(ZrClCp₂)₂(μ-PMes)] was obtained.¹¹⁷



Zirconocene dichloride reacts with Mg and CyPH₂ with formation of *trans*-[Zr(μ-PHCy)Cp₂]₂.¹¹⁷ When the bulky [ZrCl₂Cp*₂] was used as the starting material, monitoring by ³¹P NMR revealed the initial formation of [ZrH(PHCy)Cp*₂], which is unstable and loses H₂, yielding a compound which could not be isolated (³¹P 220.2 ppm, no coupling to protons).¹¹⁷ The route by which H₂ is lost appears to be controlled by steric factors (Scheme 13).¹¹⁷

[M(CO)₂(η-1,3-Bu^t₂C₅H₃)₂] (M = Zr, Hf) reacts with white phosphorus in refluxing xylene to give **29**, which contains the P₄²⁻ anion.¹³⁰ The analogous Cp*-substituted complexes are only stable in solution and decompose in the solid state with formation of P₄.¹³⁰



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2. Spectroscopic Properties

Molecular weight measurements on [M(PR₂)₂Cp₂] (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(PPh₂)₂Cp₂] was assigned as ν(M-P).¹⁰⁵ Two absorptions were observed for [Hf(PCy₂)₂Cp₂] (299, 270 cm⁻¹).¹⁰⁵ In [Zr{1,2-(PH)₂C₆H₄}Cp₂] the ν(Zr-P) mode was observed at 338 cm⁻¹.¹¹⁵ The monophosphido chloro complexes [ZrCl(PR₂)Cp₂] exhibit the ν(Zr-Cl) mode in the range of 330–350 cm⁻¹ (R = Ph,¹⁰⁵ SiMe₃⁹⁷). The complexes with primary phosphido groups (PHR) show the ν(P-H) mode between 2240 and 2340 cm⁻¹.^{98,112,115}

b. ³¹P 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 ³¹P NMR resonances that are usually significantly shifted to low field compared to the former.

Complexes in which the P(SiMe₃)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(SiMe₃)₂ ligand acts as a three-electron donor are observed between -55 and -100 ppm [[M{P(SiMe₃)₂}₂Cp₂], [M{P(SiMe₃)₂}₂{η-C₅H₄(SiMe₃)₂}, M = Zr, Hf] and -108 and -154 ppm ([ZrCl{P(SiMe₃)₂}{η-C₅H₄(SiMe₃)₂}, [M{P(SiMe₃)₂}(X)Cp₂], M = Zr, Hf, X = Me; M = Hf, X = Cl].^{97,109} For [ZrI{P(SiMe₃)₂}Cp₂], the signal is shifted down field to -22.9 ppm.⁹⁷ The molecular structure determination of [Hf{P(SiMe₃)₂}₂Cp₂] (cf. section IV.A.3) revealed the presence of both types of phosphido ligand (σ- and π-donor) in the solid state¹⁰⁹ while that of [Zr{P(SiMe₃)₂}₂(η-C₅H₄Me)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(SiMe₃)₂}₂Cp₂] and [Zr{P(SiMe₃)₂}₂(η-C₅H₄-

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(SiMe₃)₂}(X)Cp₂] (X = Me, ca. -120 ppm,^{97,109} X = Cl, -108.9 ppm⁹⁷) and [ZrCl{P(SiMe₃)₂}(η-C₅H₄Me)₂] (-132.5 ppm)¹³¹ show resonances at higher field than the bisphosphido complexes.¹⁰⁹ The ³¹P resonance of [ZrCl{P(SiMe₃)(2,4,6-Bu^t₃C₆H₂)}Cp₂] (156 ppm) is shifted to low field compared to P(SiMe₃)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(PR₂)₂Cp₂] (M = Zr, Hf, R = Et, Cy, Ph) show a singlet in the ³¹P NMR spectra between 100 and 160 ppm.¹⁰⁵ As the crystal structure determination of [Hf(PEt₂)₂Cp₂] 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 PCy₂ ligand. Thus, [Hf(PCy₂)₂Cp₂] shows two broad resonances (270.2, -15.3 ppm) at -126 °C, which coalescence at -100 °C (Δ*G*[‡] = 25.1 ± 0.8 kJ mol⁻¹). The Cp ligands appear as singlets in the ¹H NMR (5.7–5.9 ppm) with ²*J*(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(PPh₂)Cp*₂] show singlets in the ³¹P{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 PPh₂ (14.7) > PPh (13.9) > PHCy (12.9 ppm), indicating increasing π-interaction from PPh₂ to PHCy.¹¹² Apparently, for steric reasons the PPh₂ 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)Cp₂] (R = Mes, -5.6 ppm, *J*(PH) 230 Hz,⁹⁸ 2,4,6-Bu^t₃C₆H₂, 90.4 ppm, *J*(PH) 271 Hz¹²⁴) show a singlet in the ³¹P{¹H} NMR spectra. A singlet is observed (1.87–2.02 ppm) for the Cp* ligands in the ¹H NMR spectrum.¹¹² The PHR resonance occurs as a doublet between 3.23 and 4.58 ppm (for R = Ph, Cy,¹¹² Mes⁹⁸) or at 6.18 ppm (for R = 2,4,6-Bu^t₃C₆H₂).¹²⁴

The bisphosphido complexes [Hf(PHBU^t)₂Cp₂], [M(PHBU^t)₂Cp*₂], and [M(PHBU^t)₂{η-1,3-(SiMe₃)₂C₅H₃}₂] (M = Zr, Hf) show a singlet in the ³¹P{¹H} NMR spectrum between 101 and 131 ppm.¹²¹ The PHR resonance occurs between 3.6 and 4.4 ppm in the ¹H NMR (¹*J*(PH) 239–247 Hz, ³*J*(PH) 11.1–11.8 Hz).¹²¹ The complexes [Zr(PHR)₂(η-C₅R'₅)₂] show a singlet (R' = H: 13.9, R = Mes,⁹⁸ 51.6 ppm, R = 2,4,6-Bu^t₃C₆H₂,¹²⁴ R' = Me: 39.0 ppm, R = Mes^{124b}) in the ³¹P{¹H} NMR, which splits into a multiplet on coupling to protons.

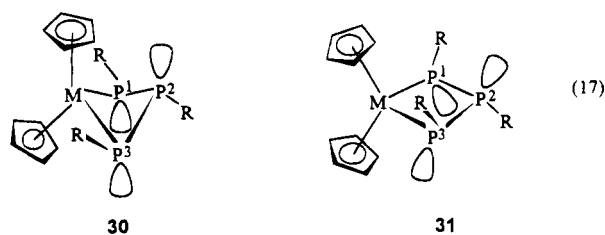
The diphosphene complexes [M(PR–PR){η-1,3-(SiMe₃)₂C₅H₃}₂] (M = Zr, Hf, R = Ph; M = Zr, R = Bu^t, δ = 193–271 ppm),¹²¹ [Zr(PMes–PMes)(η-C₅Me₄-Et)₂] (δ = 138.7 ppm),¹²⁵ and [Zr(PMes–PMes)Cp*₂]

(δ = 134.9 ppm)^{124b} show a singlet in the ³¹P NMR spectrum.

Extreme down-field shifts are observed in [{ZrCl(η-C₅H₄R)₂}(μ-PMes)] (ca. 325 ppm for R = H^{117,126} or R = Me¹²⁶) and for the μ₃-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}

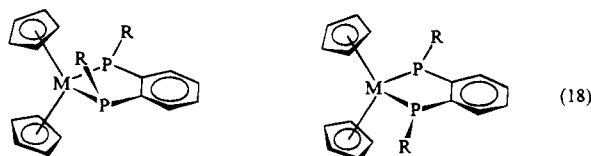
The complexes [M(PR–PR)Cp₂] (M = Ti, Zr, Hf; R = Ph, Et, Me, Bu^t;¹¹⁹ M = Zr, Hf, R = Ph;¹²¹ M = Zr, R = Cy¹²²) exhibit A₂X patterns in the ³¹P NMR spectra, with the A₂ part at 182–254 (M = Ti), 92–138 (M = Zr), and 67–106 ppm (M = Hf) and the X part at -143 to -187 (M = Ti), -156 to -190 (M = Zr), and -160 to -195 ppm (M = Hf). In the

analogous complexes [M(PPh–PPh)Cp*₂], the ³¹P resonances of the A₂ part are shifted to high field [M = Zr, (A₂ part) 60.87 (X part) -134.89 ppm; M = Hf, (A₂ 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 P¹ or *S* or *R* configuration at P³ 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**) MP₃ 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



The *o*-phenylenebisphosphido metallocene derivatives (eq 18, M = Ti, Zr, Hf, R = Ph;¹¹⁴ M = Zr, R = H¹¹⁵) exhibit two resonances in the ³¹P 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-(PPh)₂C₆H₄}{η-1,3-(SiMe₃)₂C₅H₃}₂] at 30 °C (105 ppm) splits into two signals (-3.9 and +211.5 ppm) at -70 °C (Δ*G*[‡] = 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(PR₂)PP(PR₂)P}Cp₂] (R = SiMe₃) six multiplets are observed for the six inequivalent P nuclei;



chemical shifts and coupling constants are given in Figure 6.¹³²

The complexes **29** and the Cp* analogue (M = Zr) show A₂X₂ spectra with $\delta = 93\text{--}166$ ppm (P_X) and $\delta = -206$ to -219 ppm (P_A) [$J(\text{PP}) = 193\text{--}201$ Hz].¹³⁰

The mass spectra of [M(PR-PR-PR)Cp₂] (M = Ti, Zr, Hf, R = Ph, Et, Me, Bu^t) exhibit the parent ion peak as well as the P₃R₃⁺ fragment and fragmentation products thereof.¹¹⁹ Parent ion peaks were also observed for [ZrCl{P(SiMe₃)₂(2,4,6-Bu^t₃C₆H₂)Cp₂},¹¹¹ [M{P(SiMe₃)₂(X)Cp₂}] (M = Zr, Hf, X = P(SiMe₃)₂, Me; M = Hf, X = Cl),¹⁰⁹ [Zr{P(SiMe₃)₂}₂(η -C₅H₄-Me)₂],¹¹⁰ and [M{1,2-(PPh)₂C₆H₄}Cp₂] (M = Ti, Zr, Hf).¹¹⁴ In the latter, the fragment (C₆H₄)₂P⁺ gives the most intense peak.

Elimination of SiMe₃Cl or SiMe₄ 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(PPh₂)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(PET₂)₂Cp₂],¹⁰⁶ [Hf{P(SiMe₃)₂}₂Cp₂],¹⁰⁹ and [Zr{1,2-(PPh)₂C₆H₄}{ η -1,3-(SiMe₃)₂C₅H₃}₂}]¹¹³ show two distinctly different bonding modes of the phosphido ligands. While the geometry about one P atom is pyramidal (sp³), the other is trigonal planar (sp²), suggesting donor interaction (**32**). Accordingly, unequal M-P bond lengths are observed ($\Delta = 0.20\text{--}0.09$ Å). However, the difference in Zr-P bond lengths and P environments in [Zr{P(SiMe₃)₂}₂(η -C₅H₄Me)₂]¹¹⁰ and [Zr{PH(2,4,6-Bu^t₃C₆H₂)₂}Cp₂]¹²⁴ is minor, suggesting the presence of delocalized π -electrons (**33**). According to Lauher and Hoffmann¹³³ π -interaction is strongest in these complexes if the trigonal-planar PR₂ ligand is orthogonal to the MP₂ plane. This is true for [Hf(PET₂)₂Cp₂],¹⁰⁶ but the other complexes (Table 1) have a less favorable orientation for complete overlap of the ligand lone pair with the empty a₁ orbital of the M^{IV}Cp₂ 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.

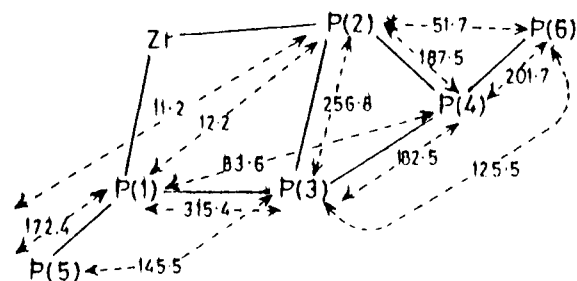
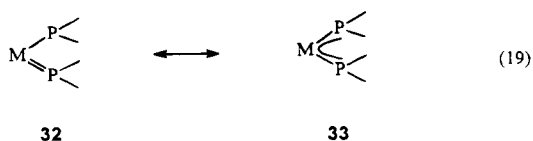


Figure 6. NMR coupling constants (hatched lines) (Hz) for [Zr{P(PR₂)PP(PR₂)P}Cp₂] (R = SiMe₃). Chemical shifts are P(1) 88.7, P(2) 62.9, P(3) -236.4, P(4) -110.6, P(5) -163.5, and P(6) -139 ppm. (Reprinted from ref 132. Copyright 1987 Chemical Society of London.)

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

compound	M-P (Å)	sum of angles at P (deg)	refs
[ZrCl{P(SiMe ₃) ₂ (2,4,6-Bu ^t ₃ C ₆ H ₂)Cp ₂ }]	2.541(4)	359.5(5)	111
[Zr{1,2-(PPh) ₂ C ₆ H ₄ }{ η -1,3-(SiMe ₃) ₂ C ₅ H ₃ } ₂ }]	2.560(4) 2.647(6)	350 327	113
[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) ₂ Cp ₂]	2.488(1) 2.682(1)	360 336	106
[Hf{P(SiMe ₃) ₂ } ₂ Cp ₂]	2.553(1) 2.654(1)	360 335	109
[Zr{P(SiMe ₃) ₂ } ₂ (η -C ₅ H ₄ Me) ₂]	2.600(2) 2.634(2)	351.2(1) 358.3(1)	110
[HfH(PHPh)Cp* ₂] ^b	2.549(8)		112
[Zr{PH(2,4,6-Bu ^t ₃ C ₆ H ₂) ₂ }Cp ₂]	2.681(5) 2.682(5)	356(1) ^a 321(2)	124

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

Molecular structures of [M(PR-PR-PR)Cp₂] (M = Zr, R = Ph;¹²³ M = Hf, R = Ph;¹²⁰ M = Zr, R = Cy¹²²) show that the central MP₃ 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) Å¹²²]. 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 [(ZrClCp₂)₂(μ -PMes)] has Zr-P bond lengths [2.597(6), 2.637(6) Å]¹¹⁷ comparable to those of terminal phosphido complexes. The Zr₂PC central core is planar with a Zr-P-Zr angle of 134.7(2)°.

[Zr{P(PR₂)PP(PR₂)P}Cp₂] (R = SiMe₃) (Figure 7) has a planar ZrP₃ 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

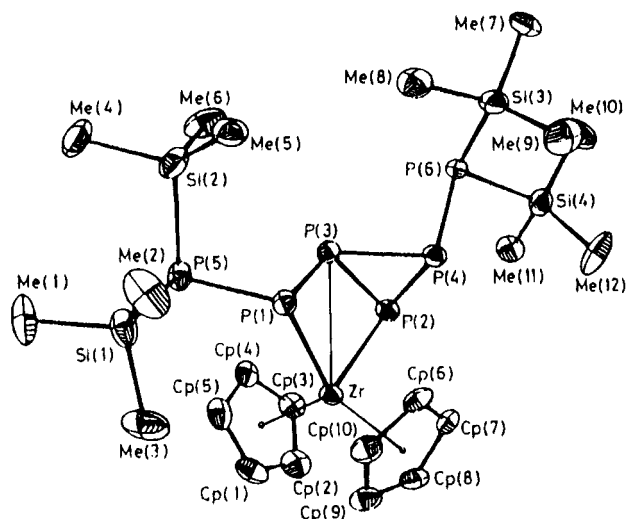
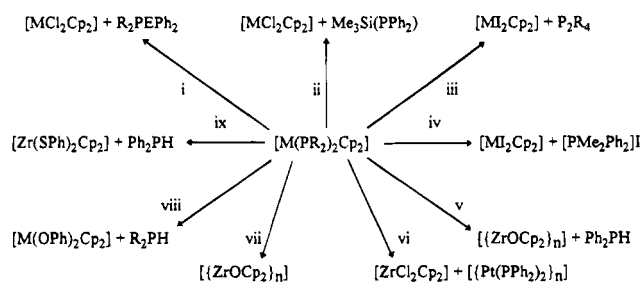


Figure 7. Molecular structure of $[\text{Zr}\{\text{P}(\text{PR}_2)\text{PP}(\text{PR}_2)\text{P}\}\text{Cp}_2]$ ($\text{R} = \text{SiMe}_3$). (Reprinted from ref 132. Copyright 1987 Chemical Society of London.)

Scheme 14^a



^a (i) 2Ph₂ECl ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Ph}; \text{M} = \text{Hf}, \text{R} = \text{Cy}, \text{E} = \text{P}$ or As); (ii) Me₃SiCl ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Ph}$); (iii) I₂ ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Ph}; \text{M} = \text{Hf}, \text{R} = \text{Cy}$); (iv) 4MeI ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Ph}$); (v) H₂O ($\text{M} = \text{Zr}, \text{R} = \text{Ph}$); (vi) [PtCl₂(PhCN)₂]; (vii) excess dry O₂ ($\text{M} = \text{Zr}, \text{R} = \text{Ph}$); (viii) 2PhOH ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Ph}; \text{M} = \text{Hf}, \text{R} = \text{Cy}$); (ix) 2PhSH ($\text{M} = \text{Zr}, \text{R} = \text{Ph}$). For i–v and vii–ix ref 105; for vi ref 138.

Disorder of the 1,3-Bu^t₂C₅H₃ ligands in **29** ($\text{M} = \text{Zr}, \text{Hf}$) prevented determination of the crystal structure to complete crystallographic satisfaction.¹³⁰ However, the presence of a P₄-butterfly fragment with a $\text{M}(\eta\text{-}1,3\text{-Bu}^t_2\text{C}_5\text{H}_3)_2$ bridge was shown unambiguously.¹³⁰

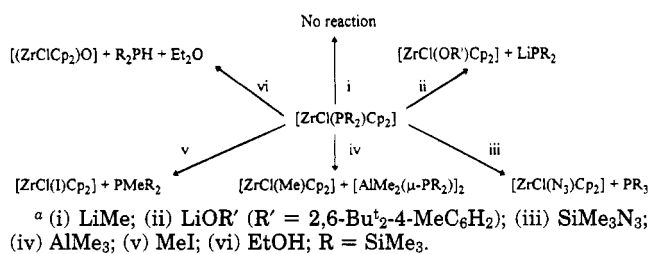
4. Chemical Properties

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

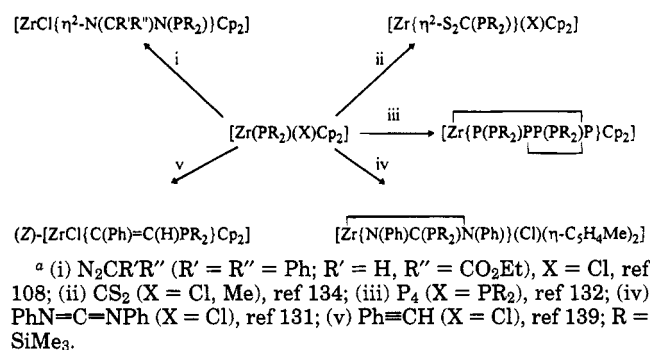
The complexes $[\text{M}(\text{PR}_2)_2\text{Cp}_2]$ ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Ph}; \text{M} = \text{Hf}, \text{R} = \text{Cy}$) react with a variety of protic and halogen-containing species with cleavage of the M–P bond (Scheme 14).¹⁰⁵ When Me₂SiCl₂ instead of Me₃SiCl is reacted with $[\text{Zr}(\text{PPh}_2)_2\text{Cp}_2]$, an equilibrium mixture of starting materials and $[\text{ZrCl}(\text{PPh}_2)\text{Cp}_2]$, zirconocene dichloride, Me₂SiCl(PPh₂), and Me₂Si(PPh₂)₂ is produced.¹⁰⁵ Aliphatic alcohols (MeOH, EtOH, Bu^tOH) and Et₂NH displace the PR₂ groups from $[\text{Zr}(\text{PPh}_2)_2\text{Cp}_2]$ as Ph₂PH, but the Zr products were poorly defined.¹⁰⁵

Scheme 15^a



^a (i) LiMe; (ii) LiOR' ($\text{R}' = 2,6\text{-Bu}^t_2\text{-}4\text{-MeC}_6\text{H}_2$); (iii) SiMe₃N₃; (iv) AlMe₃; (v) MeI; (vi) EtOH; $\text{R} = \text{SiMe}_3$.

Scheme 16^a



^a (i) N₂CR'R'' ($\text{R}' = \text{R}'' = \text{Ph}; \text{R}' = \text{H}, \text{R}'' = \text{CO}_2\text{Et}$), $\text{X} = \text{Cl}$, ref 108; (ii) CS₂ ($\text{X} = \text{Cl}, \text{Me}$), ref 134; (iii) P₄ ($\text{X} = \text{PR}_2$), ref 132; (iv) PhN=C=NPh ($\text{X} = \text{Cl}$), ref 131; (v) Ph≡CH ($\text{X} = \text{Cl}$), ref 139; $\text{R} = \text{SiMe}_3$.

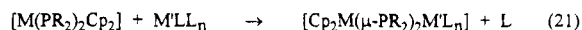
$[\text{ZrCl}\{\text{P}(\text{SiMe}_3)_2\}\text{Cp}_2]$ reacts with polar or protic reagents with displacement of the P(SiMe₃)₂ ligand (Scheme 15). Similarly, $[\text{ZrMe}\{\text{P}(\text{SiMe}_3)_2\}\text{Cp}_2]$ reacts with (2,4,6-Bu^t₃C₆H₂)PCL₂ to give $[\text{ZrCl}(\text{Me})\text{Cp}_2]$ and the diphosphenes P₂(2,4,6-Bu^t₃C₆H₂)₂ and (2,4,6-Bu^t₃C₆H₂)P=PSiMe₃, the latter being unstable.¹⁰⁹ The reaction of $[\text{Zr}\{\text{P}(\text{SiMe}_3)_2\}_2\text{Cp}_2]$ with MeI led to elimination of MeP(SiMe₃)₂ and formation of $[\text{ZrI}\{\text{P}(\text{SiMe}_3)_2\}\text{Cp}_2]$.⁹⁷

Reactions of $[\text{HfH}(\text{PPh}_2)\text{Cp}^*_2]$ with H₂, CO, and C₂H₄ proceed with reductive elimination of Ph₂PH and formation of the corresponding hafnocene derivatives $[\text{HfL}_2\text{Cp}^*_2]$ ($\text{L} = \text{H}, \text{CO}, \text{L}_2 = \text{butadiene}$).¹¹² Reaction of CO with $[\text{M}(\text{PHBu}^t)_2\text{Cp}^*_2]$ ($\text{M} = \text{Zr}, \text{Hf}$) led to reductive elimination of diphosphane (PHBu^t)₂ and formation of $[\text{M}(\text{CO})_2\text{Cp}^*_2]$.¹²¹ However, if a heterocumulene, white phosphorus, or phenylacetylene is reacted with $[\text{Zr}\{\text{P}(\text{SiMe}_3)_2\}(\text{X})\text{Cp}_2]$ [$\text{X} = \text{Cl}, \text{P}(\text{SiMe}_3)_2$] insertion occurs with formation of novel P-functionalized ligands (Scheme 16, for CS₂ insertion cf. section VI.E.1; for diazoalkane insertion cf. section III.F.1).⁹⁷ $[\text{ZrCl}(\text{PHMe})\text{Cp}_2]$ inserts diphenyl diazomethane into the Zr–P bond with formation of $[\text{ZrCl}\{\eta^2\text{-N}(\text{CPh}_2)\text{N}(\text{PHMe})\}\text{Cp}_2]$.⁹⁸ No reaction was observed between $[\text{Zr}\{\text{P}(\text{SiMe}_3)_2\}_2\{\eta\text{-C}_5\text{H}_4(\text{SiMe}_3)\}_2]$ and Ph₂CN₂.¹⁰⁸ $[\text{ZrCl}\{\text{P}(\text{SiMe}_3)_2\}\text{Cp}_2]$ did not react with CO, while CO₂ led to decomposition.⁹⁷ However, $[\text{HfH}(\text{PPh}_2)\text{Cp}^*_2]$ undergoes successive insertion of CO₂ into the Hf–P and Hf–H bonds, with formation of $[\text{HfH}(\eta^2\text{-O}_2\text{CPPH}_2)\text{Cp}^*_2]$ and $[\text{Hf}\{\text{OC}(\text{O})\text{H}\}\{\text{OC}(\text{O})\text{-PPh}_2\}\text{Cp}^*_2]$, respectively.¹¹²

Reaction of $[\text{Zr}\{\text{P}(\text{SiMe}_3)_2\}_2\text{Cp}_2]$ and $[\text{ZrMe}\{\text{P}(\text{SiMe}_3)_2\}\text{Cp}_2]$ with sulfur gives $[\{\text{Zr}(\mu\text{-S})\text{Cp}_2\}_2]$ and unidentified P products.¹³⁴ In contrast, $[\text{M}(\text{PR}_2)_2\text{Cp}_2]$ ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Cy}, \text{Ph}$) reacts cleanly with sulfur to give $[\text{M}(\text{SPR}_2)_2\text{Cp}_2]$ in 65–80% yield (³¹P δ = 25.7–64.3 ppm) (cf. section VI.A.1).¹³⁵ The same products are obtained on reaction with SPR₂H.¹³⁵

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

Table 2

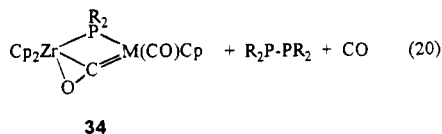
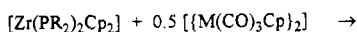


M	R	M'LL _n	M'L _n	yield (%)	refs
Zr,Hf	Et,Ph	Rh(C ₂ H ₄) ₂ (η-indenyl)	Rh(η-indenyl)	86–90	150
Zr	Ph	cis-Mo(NHC ₅ H ₁₀) ₂ (CO) ₄	Mo(CO) ₄	80	144,147
Zr	Ph	M'(PPh ₃) ₄ (M' = Ni, Pd, Pt) or Pt(PPh ₃) ₂ (CO) ₂	M'(PPh ₃)	50–80	138,148
Zr	Ph	Ni(CO) ₂ (PPh ₃) ₂	Ni(CO) ₂	85–90	138,148
Zr,Hf	Ph	M'(H)(CO)(PPh 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 C₅H₄Me ligands. ^b Product is contaminated with PPh₃ and [Cp₂M(μ-PET)₂Pd(μ-PET)₂MCp₂].

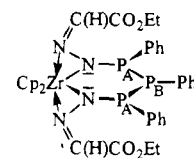
Reduction of [M(PR₂)₂Cp₂] (M = Zr, Hf, R = Et, Cy, Ph) with sodium naphthalenide (THF, 25 °C) produced the thermally stable Zr(III) and Hf(III) complexes [Cp₂M(μ-PR₂)₂Na(THF)_n] as shown by ESR spectroscopy.¹⁰⁶

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(PR₂)₂Cp₂] (R = Ph, Cy) with [{M(CO)₃Cp₂}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(μ-PET₂)Cp₂]₂ with [Mo(CO)₃Cp₂] in 70% yield.¹³⁷ Alternatively, **34** and Ph₂PH are formed in the reaction of [MoH(CO)₃Cp] with [Zr(PPh₂)₂Cp₂] in 80% yield.¹³⁶ A crystal structure determination was carried out on **34** (R = Et, M = Mo;¹³⁷ R = Ph, M = Mo¹³⁶). The metal–metal distance [3.243(1),¹³⁷ 3.250(1) Å¹³⁶] is comparable to that found in heterobimetallic phosphido-bridged complexes (cf. section IV.B.3), suggesting that direct Zr–Mo bonding is weak.



The 1,2,3-trisubstituted triphosphane-1,3-diyl metallocene complexes [M(PR–PR)Cp₂] (M = Ti, Zr, Hf, R = Ph, Et, Me, Bu^t) react with CCl₄ and CHCl₃ with cleavage of the M–P bonds. Reaction with CS₂ was also observed, but the products were not characterized.¹¹⁹ The reaction of [Zr(PPh–PPh–PPh)Cp₂] with ethyl diazoacetate leads to insertion into both Zr–P bonds and formation of **35**. The stereochemistry of the P₃Ph₃ fragment of the starting material is retained in the product.⁹⁹

The diphosphene complexes [M(PR–PR){η-1,3-(SiMe₃)₂C₅H₃}₂] (M = Zr, Hf, R = Ph; M = Zr, R =



35

Bu^t) are readily hydrolyzed to [M(OH)₂{η-1,3-(SiMe₃)₂C₅H₃}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 SiMe₃Cl from [ZrCl{P(SiMe₃)(2,4,6-Bu^t₃C₆H₂)Cp₂}].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(SiMe₃)₂] resulted in product mixtures.¹¹² However, when [Hf(PHPh)Cp*₂] was treated with NaN(SiMe₃)₂ at –78 °C, HN(SiMe₃)₂ and NaI were liberated and a red product of empirical formula [Hf(PPh)Cp*₂]_k was obtained (³¹P 376 ppm).¹¹² Also, [Zr(=PMes)Cp*₂] is the proposed intermediate in the decomposition of [Zr(PHMe)₂Cp*₂], which yields [Zr(PMes–PMes)Cp*₂] or [Zr(1-PH-2-CH₂-4,6-Me₂C₆H₂)Cp*₂] as the final products.^{124b}

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

1. Synthesis

Although preparation of [Cp₂Zr(μ-PRR')₂Mo(CO)₄] (R = R' = Me; R = H, R' = Ph; R = Ph, R' = SiMe₃) 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(PR₂-Li)₂] to give [Cp₂Zr(μ-PR₂)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% yield¹⁴³].

In the reaction between [Hf(PET₂)₂Cp₂] and Fe₂(CO)₉ in hexane at room temperature the initially formed

complex [Cp₂Hf(PEt₂)(μ-PEt₂)Fe(CO)₄] was isolated in 44% yield. Thermolysis of this product (toluene, 110 °C; solid state 139–140 °C) yields [Cp₂Hf(μ-PEt₂)₂Fe(CO)₃].¹⁴⁴

Reaction of [Zr(PPh₂)₂Cp₂] with Re₂(CO)₁₀ gave [Cp₂Zr(μ-PPh₂)₂Re(H)(CO)₃] in 17% yield. Monitoring of the reaction over 12 h by ³¹P NMR showed the formation of numerous P species, including P₂Ph₄ and Ph₂PH.¹⁴⁵ The mechanism of formation and the source of the proton are unknown.

The reaction of metallocene bisphosphido complexes [M(PR₂)₂Cp₂] with [Pd(η-2-Me-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 [Cp₂M(μ-PR₂)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 [Cp₂M(μ-PPh₂)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 [Cp₂M(μ-PEt₂)₂M'L_n] have been reacted with [M(PEt₂)₂Cp₂] (M = Zr, Hf) to give phosphido-bridged heterotrimetallic complexes [{Cp₂M(μ-PEt₂)₂}₂M'] (M = Zr, Hf, M' = Ni, L_n = 1,5-cod; M = Zr, Hf, M' = Pd, L_n = PPh₃; M = Zr, Hf, M' = Pt, L_n = PPh₃).¹⁴⁶ The products are obtained as orange or dark red crystals in 31–74% yield. The red-purple complex [Cp₂Hf(μ-PPhCH₂CH₂CH₂PPh)]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(PEt₂)₂Cp₂] with Pd(PPh₃)₄ or Pt(PPh₃)₄ followed by addition of [Hf(PEt₂)₂Cp₂].¹⁴⁶ The products were characterized in situ by ³¹P NMR; the spectra also showed the presence of PPh₃ 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 [Cp₂Zr(μ-PPh₂)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 [Cp₂M(μ-PR₂)₂Rh(η-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 (ΔG[‡] = 58.2–62.8 kJ mol^{–1}).¹⁵⁰

b. ³¹P 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 ³¹P 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 [Cp₂M(μ-PPh₂)₂M'(PPh₃)] (M = Zr, Hf; M' = Pd, Pt).¹⁴⁶ In [Cp₂M(μ-PR₂)₂Rh(η-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 [Cp₂M(μ-PPh₂)₂M'(H)(CO)(PPh₃)] (M = Zr, Hf, M' = Rh, Ir) and [Cp₂Zr(μ-PCy₂)₂Rh(H)(CO)(PPh₃)] exhibit two absorption bands in the range 274–284 and 364–376 nm, respectively.¹⁴⁹ The orange-yellow complex [Cp₂Zr(μ-PPh₂)₂Mo(CO)₄] shows three absorptions at 306, 347, and 416 nm.¹⁴⁷

e. Mass Spectra. The complexes [Cp₂Zr(μ-PR₂)₂M(CO)_n] (R = Ph, M = W, n = 4; R = Cy, Ph, M = Fe, n = 3)¹⁴² and [Cp₂Zr(μ-PPh₂)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 [Cp₂Zr(μ-PEt₂)₂Ni(μ-PEt₂)₂HfCp₂] the Zr and Hf atoms are disordered with respect to their crystallographic positions (50:50 occupancy).¹⁴⁶ The MP₂Ni rings are nearly planar, with Ni showing a distorted tetrahedral coordination.¹⁴⁶

The influence of the bridging PR₂ group on the observed metal–metal distance is exemplified by comparing the structure of [Cp₂Hf(μ-PEt₂)₂Mo(CO)₄]¹⁴⁴ with [Cp₂Zr(μ-PPh₂)₂M'(CO)₄] (M' = W¹⁴² or Mo¹⁴⁷). As the covalent radii of Zr and Mo are very similar to those of Hf and W the shorter M–M' distance in the PPh₂-bridged complexes must result primarily from the bulkier PPh₂ 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 MP₂M' 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 $[(\eta\text{-C}_5\text{H}_4\text{R})_2\text{M}(\mu\text{-PR}')_2\text{M}'\text{L}_n]$

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)	<i>a</i>	78.70(2)	150
Zr	H	Ph	W(CO) ₄	2.619(3)	3.289(1)	1.6	79.2(1)	142
				2.631(3)				
Zr ^b	H	Ph	Mo(CO) ₄	2.618(3)	3.290(1)	2.8	79.2(1)	152
				2.631(3)			79.1(1)	
Zr ^b	H	Ph	Mo(CO) ₄	2.631(1)	3.299(1)	<i>a</i>	79.1(1)	147
				2.630(1)			79.2(1)	
Zr ^c	H	Ph	Rh(H)(CO)(PPh ₃)	2.671(2)	2.980(1)	9.94	72.4(1)	149
				2.698(2)			73.0(1)	
Hf ^c	H	Ph	Rh(H)(CO)(PPh ₃)	2.640(2)	2.964(1)	9.73	73.2(1)	149
				2.672(2)			72.4(1)	
Hf	H	Et	Mo(CO) ₄	2.592(1)	3.400(1)	7.7	83.01(3)	144
				2.596(1)				
Zr	Me	SiMe ₃	Cr(CO) ₄	2.654(4)	3.414(1)	14.7	82.65(7)	151
				2.657(4)			82.80(7)	
Zr	H	SiMe ₃	Mo(CO) ₄	2.6585(7)	3.461(1)	14.2	81.56(2)	151
				2.6711(9)			81.71(2)	
Hf	H	Ph	Pd(PPh ₃)	2.627(2)	2.896(1)	24.49	71.43(5)	146
				2.615(2)			71.63(4)	
Hf	H	Ph	Pd(dmpe) ^d	2.618(3)	2.983(1)	27.25	74.30(7)	146
				2.607(3)			74.36(7)	
Zr	H	Ph	Re(H)(CO) ₃	2.629(3)	3.274(1)	<i>a</i>	72.4(1)	145
				2.615(3)			73.0(1)	

^a Not reported. ^b The crystal structure was determined independently by two groups (refs 147 and 152); the only difference is that one crystal structure¹⁵² has solvent of crystallization. ^c Zr and Hf complex are isostructural; the hydride was not located. ^d dmpe = (Me₂PCH₂)₂.

Extended Hückel molecular orbital calculations performed on the model complexes [Cp₂Zr(μ -PPh₂)₂M'L_n] [M'L_n = Pt(PH₃), Pt(dmpe) (dmpe = (Me₂-PCH₂)₂), Rh(η -indenyl), Ni(μ -PH₂)₂ZrCp₂, Mo(CO)₄] indicate the presence of M' \Rightarrow Zr donor-acceptor metal-metal bonds that become weaker along the series Pt > Rh > Ni > Mo.¹⁴⁶

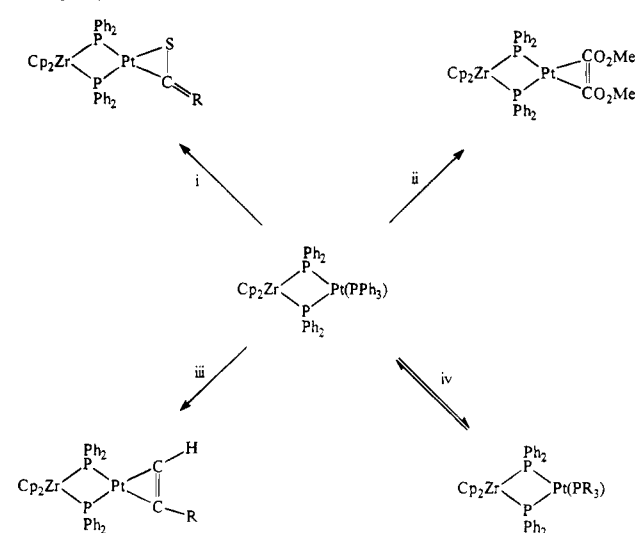
4. Chemical Reactivity

The complexes [Cp₂M(μ -PPh₂)₂M'(H)(CO)(PPh₃)] (M = Zr, Hf, M' = Ir, Rh) and [Cp₂M(μ -PCy₂)₂Rh(H)(CO)(PPh₃)] (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'(PPh₃) fragments (M' = Ni, Pd, Pt) are air sensitive.¹⁴⁸

Ligand substitution reactions at the late transition metal center of [Cp₂Hf(μ -PETe₂)₂Ni(cod)],¹⁴⁶ [Cp₂M(μ -PPh₂)₂M'(PPh₃)] (M = Hf, M' = Pd; M = Zr, M' = Pt),¹⁴⁶ and [Cp₂Zr(μ -PPh₂)₂Rh(H)(CO)(PPh₃)]¹⁴⁹ have been intensively studied.

The electrophilic substitution reactions shown in Scheme 17 are typical for Pt(0). However, oxidative addition of MeI and Me₃O⁺BF₄⁻ 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 [Cp₂M(μ -PETe₂)₂Rh(η -indenyl)] (M = Zr, Hf) with MeI proceeds with formation of [Cp₂M(μ -PETe₂)₂Rh(Me)(η -indenyl)]⁺I⁻, while no reaction is observed with H₂ (1 atm), CO (1 atm), or acetyl chloride.¹⁵⁰

No reaction was observed between [Cp₂M(μ -PPh₂)₂M'(PPh₃)] (M = Hf, M' = Pd; M = Zr, M' = Pt) and CO, H₂, ethylene (1 atm), excess Bu^tCN, benzaldehyde, paraformaldehyde, or MeI.¹⁴⁶ More reactive oxidative agents such as acetyl bromide react with disruption of the PPh₂ bridge.¹⁴⁶

Scheme 17^a

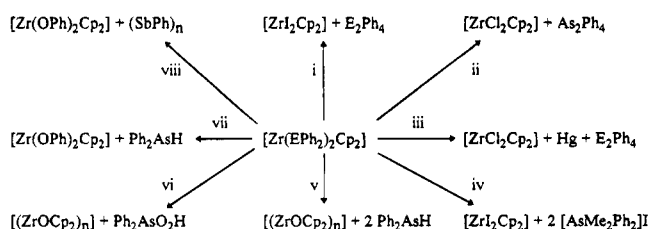
^a (i) SCNPh or CS₂, ref 148 [R = S, NPh (for NPh product was not isolated)]; (ii) MeO₂CC≡CCO₂Me, ref 148; (iii) HC≡CPh or HC≡CO₂Me, with MeI, refs 138, 148 (R = CO₂Me, Ph), -[PPh₃Me]I; (iv) PEt₃ or PCy₃, ref 148 (R = Et, Cy; an equilibrium mixture is obtained, products were not isolated).

[Cp₂Zr(μ -PPh₂)₂W(CO)₄] did not react with diphenylacetylene, PPh₂Me, or CS₂ thermally or photochemically.¹⁴² The reaction with LiR (R = Me, Bu, Ph, BEt₃H) led to unidentifiable products.¹⁴²

[Cp₂Zr(μ -PPh₂)₂Rh(H)(CO)(PPh₃)] 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) I₂ (E = As, Sb); (ii) Ph₂AsCl, (E = As); (iii) HgCl₂ (E = As, Sb); (iv) excess MeI (E = As); (v) H₂O (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(η-C₅H₄R)₂] (E = As, Sb, R = H, R' = Ph,¹⁵³ E = As, R = H, Me, R' = SiMe₃¹⁵⁴) is known. The synthesis is based on salt-elimination reactions between zirconocene dichloride and the appropriate lithium reagent. Only one monoarsenido complex [Zr{As(SiMe₃)₂}(Cl)(η-C₅H₄-Me)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(EPh₂)₂Cp₂] 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(AsPh₂)₂Cp₂] failed to detect Zr-containing fragments; only ions derived from polyarsenic species were observed.¹⁵³

3. Structural Data

The crystal structures of [Zr{As(SiMe₃)₂}(Cl)(η-C₅H₄Me)₂] and [Zr{As(SiMe₃)₂}₂Cp₂] 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(EPh₂)₂Cp₂] (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/EPh₂ 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(η-C₅H₄R')₂] (M = Ti, Zr, Hf, R' = H, Me, R = Ph, 4-Bu^tC₆H₄, 2,4-Cl₂C₆H₃, 2,4,6-Cl₃C₆H₂, 2,5-Me₂C₆H₃, *m*-Tol, base = NaNH₂ or NaH,¹⁵⁶ M = Hf, R' = SiMe₃, R = Me, Et, base = NEt₃,¹⁵⁷ M = Zr, R' = H, R = 3,5-Me₂C₆H₃, 2,4-Me₂C₆H₃, base = NEt₃,¹⁵⁸ M = Ti, Zr, Hf, R' = alkyl, R = Ph, Tol, halophenyl, base = NaNH₂, NEt₃,¹⁵⁹ M = Ti, Zr, Hf, R' = Me, R = aryl, base = NaNH₂,¹⁶⁰ M = Ti, Zr, Hf, R' = H, R = aryl, base = NaNH₂, NEt₃,¹⁶¹ 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 = NEt₃,¹⁶³ M = Ti, Zr, R' = H, R = α- or β-nap, base = NEt₃¹⁶⁴) and, second, the reaction of a metallocene dichloride with alkali metal alkoxides or aryloxides (M'OR) to give [MCl(OR)(η-C₅H₄R')₂] (M = Zr, R' = H, M' = Li, R = 2,6-PrⁱC₆H₃, 2,6-Bu^tC₆H₃, 2,6-Bu^t-4-MeC₆H₂, 2,4,6-Bu^tC₆H₂,⁴⁶ M = Hf, R' = SiMe₃, M' = Na, R = Me¹⁵⁷).

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 [ZrCl₂(η-C₅H₄Me)₂] and NaOR (R = α- or β-nap).^{163,164} Treatment of [(ZrClCp₂)₂O] with ROH (R = Ph, 4-ClC₆H₄, 4-BrC₆H₄) in the presence of NEt₃ gives [{Zr(OR)Cp₂}₂O].¹⁵⁶ The reaction of [MCl₂(η-C₅H₄)₂X] [M = Ti, Zr, Hf, X = (Me₂Si)_n with *n* = 2 or 3, Me₂SiOSiMe₂] with phenols was studied.¹⁶⁵

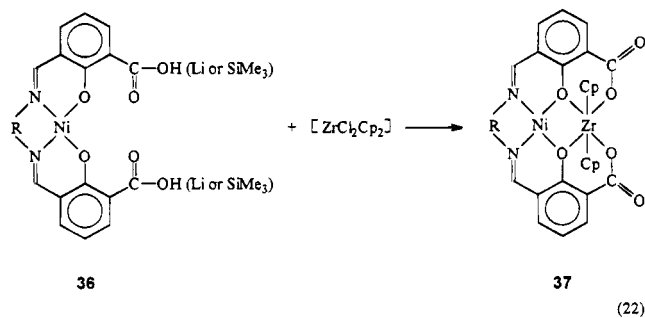
The reaction of zirconocene dichloride with bulky lithium aryloxides [Li(OEt₂)(OR)]₂ [R = 2,6-PrⁱC₆H₃, 2,6-Bu^tC₆H₃, 2,6-Bu^t-4-MeC₆H₂, 2,4,6-Bu^tC₆H₂] is slow in refluxing THF (2–4 days), but addition of TMEDA leads to significant acceleration.⁴⁶ No further substitution was observed when an excess of lithium reagent⁴⁶ or the sodium alkoxide¹⁵⁷ was used. No reaction of the lithium reagents was observed with [ZrCl₂{η-1,3-(SiMe₃)₂C₅H₃}₂], [ZrCl₂{η-C₅H₄-(SiMe₃)₂}], or [ZrCl₂(η-C₅H₄Bu^t)₂],⁴⁶ and zirconocene dichloride did not react with [Li(OEt₂)(OR)]_n (R = 3,5-Bu^tC₆H₃, 2,4-Bu^tC₆H₃).⁴⁶

Zirconocene bisaryloxides with bulky aryloxo ligands [Zr(OR)₂Cp₂] (R = 2,6-PrⁱC₆H₃, 3,5-Bu^tC₆H₃) are obtained from [Zr(NMe₂)₂Cp₂] 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^tC₆H₃, 2,6-Bu^t-4-MeC₆H₂) gave only the monosubstituted products [Zr(OR)(NMe₂)Cp₂] regardless of the stoichiometry employed.⁴⁶ However, reaction of [Zr(OR)(NMe₂)Cp₂] (R = 2,6-Bu^tC₆H₃) with methanol gave [Zr(OMe)(OR)Cp₂] in 11% yield.⁴⁶

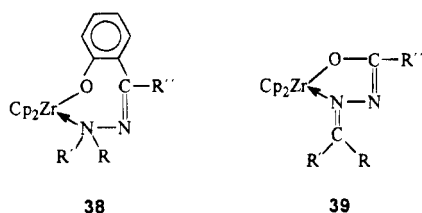
Schiff base derivatives of zirconocene have been obtained from zirconocene dichloride and the bidentate Schiff bases SBH (SBH = 2-HO-C₆H₄CH=NR; with R = Ph, *o*-, *m*-, or *p*-Tol;¹⁶⁶ R = Bz, nap, C₆H₄R¹, with R¹ = 2- or 3-MeO, 2-EtO, 2- or 3-Cl, 3-NO₂,¹⁶⁷ R = 4-R²C₆H₄, with R² = Cl, Br, I, NO₂, OMe, OEt¹⁶⁸), the terdentate Schiff bases SB'H₂ [SB'H₂ = *N*-(3-oxo-

1-methylbutylidene)-*o*-aminophenol and *N*-(3-oxo-1-phenylbutylidene)-*o*-aminophenol],¹⁶⁶ and the quadridentate Schiff base SB''H₂ (SB''H₂ = *N,N'*-disalicylidene-*o*-phenylenediamine)¹⁶⁶ in the presence of NEt₃. The resulting products show *O,N*-, *O,O',N*-, or *O,O',N,N'*-coordination of the Schiff base derivatives.

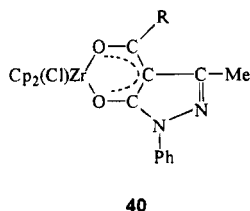
The Ni(II) complex of a quadridentate Schiff base **36** [R = (CH₂)₂, (CH₂)₃, *o*-C₆H₄] has been employed as a ligand for Cp₂Zr in **37** (eq 22).¹⁶⁹



Hydrazone **38** (R = Bz, R' = R'' = H; R = Ac, R' = Ph, R'' = H;¹⁷⁰ R = H, Ph, 2,4-(NO₂)₂C₆H₃, R' = H, R'' = H, Me¹⁷¹) and azine derivatives **39** (R = Me, R' = Me, Ph, R'' = 2- or 3-py; R = H, Me, R' = *o*-OC₆H₄, R'' = 2- or 3-py; R = Me, R' = Me, Ph, R'' = 2- or 3-py)¹⁷² of Zr have been prepared by treating [ZrCl₂Cp₂] with the appropriate hydrazone or azine at elevated or room temperature in the presence of butylamine or NEt₃. Complexes of type **39** with the tetracoordinated ligands {OCR''=N=N=C(Me)-}₂ (R'' = 4-MeOC₆H₄)¹⁷³ and (*o*-OC₆H₄-CR''=N-N)₂ (R'' = H, Me)¹⁷¹ were prepared analogously. The products were characterized by IR, NMR, and UV-vis spectroscopy.¹⁷¹⁻¹⁷³



[ZrCl₂Cp₂] reacts with pyrazolone derivatives in the presence of NEt₃ with formation of the monosubstituted complexes **40** (R = Me, Et, Ph, 4-ClC₆H₄).¹⁷⁴



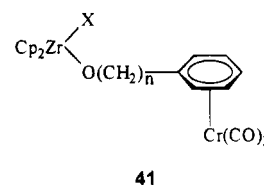
The solubility of polyoximes of zirconocene or hafnocene was evaluated. Monomeric model complexes such as [M(ON=R)₂Cp₂] (M = Zr, Hf, R = Cy) were prepared and their solubility studied.¹⁷⁵

The reaction of [ZrMe₂Cp₂] with alcohols proceeds rapidly with elimination of methane and formation of the corresponding alkoxide or aryloxy.^{176,177} Thus, R₃SiOH (R = Et, Ph) gives [Zr(OSiR₃)₂Cp₂] in

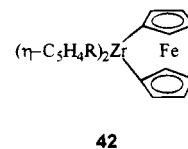
60% (R = Ph) or quantitative (R = Me) yield,¹⁷⁷ and Bu^tMe₂SiOH yields [ZrMe(OSiBu^tMe₂)Cp₂].¹⁷⁸ Similarly, (*E*)-HOCRR'CH=CHR'' gives (*E*)-[ZrMe-(OCRR'CH=CHR'')Cp₂] (R = R' = Me, R'' = H; RR' = (CH₂)₄, R'' = H; R = H, R' = R'' = Me) in 74–95% yield.¹⁷⁹ The diols 2,2-dimethylpropane-1,3-diol and 1,3-benzenedimethanol afford the macrocyclic zirconocene dialkoxides [Cp₂Zr(μ-OCH₂-X-CH₂O)₂-ZrCp₂] (X = CMe₂, C₆H₄) in 65 and 29% yield, respectively.¹⁸⁰

Elimination of toluene was employed in the synthesis of [ZrBz(OR)Cp₂] from dibenzyl zirconocene and ROH (R = 2-Me-6-Bu^tC₆H₃, 2,4-Me₂-6-(α-methylcyclohexyl)C₆H₂)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 = OCH₂C₆H₅Cr(CO)₃] and [(HOCH₂C₆H₅)Cr(CO)₃] in 32–46% yield,¹⁸³ or from [ZrCl₂Cp₂] or [Zr(NMe₂)₂Cp₂] and [NEt₄][OC₆H₅Cr(CO)₃] (*n* = 0, X = OC₆H₅Cr(CO)₃) in 60% yield.¹⁸⁴



Complex **42** (R = Bu^t) reacts with R'OH (R' = Me, Bz, 3,5-(MeO)₂Bz) with successive formation of [Zr(OR')(Fc)(η-C₅H₄Bu^t)₂] and [Zr(OR')₂(η-C₅H₄Bu^t)₂].¹⁸⁵



Oligomeric zirconocene hydride chlorides react with methanol at -75 °C with formation of [ZrCl(OMe)(η-C₅H₄R)₂] (R = H, Me) and elimination of H₂.¹⁸⁶

Other synthetic routes include:

(i) Autoxidation of dialkyl zirconocenes gives [Zr(OR)₂Cp₂] (R = Me,¹⁷⁹ R = Me, Bz, substituted Bz¹⁸⁷) 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(O₂R)(R)Cp₂] are the proposed intermediates. In the autoxidation of [ZrR(X)Cp*₂] (R = Me, Bz, X = R, Cl) and [ZrBz₂CpCp*] formation of alkoxo complexes is not observed.¹⁸² Rates of initiation and oxidation have been compared with those of the corresponding Cp₂Zr complexes.¹⁸² However, the reaction of Bu^tCOOH with [HfH(R)Cp*₂] gives stable *tert*-butyl peroxy complexes [Hf(OOBu^t)(R)Cp*₂] (R = Cl, H, Me, Et, Pr, CH=CHBu^t, Ph, 3,5-Me₂C₆H₃,¹⁸⁸

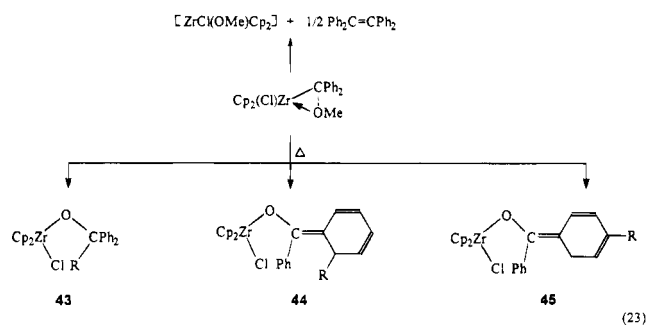
or CH₂CH₂CMe₃¹⁸⁹); [Hf(CH₂CHMeCH₂)Cp*₂] and [Hf(CH₂CH₂CH₂CH₂)Cp*₂] yield [Hf(OOBu^t)RCp*₂] (R = CH₂CHMe₂, Bu).¹⁸⁸ The thermal stability of these complexes is sufficient for their isolation, except for [HfH(OOBu^t)Cp*₂], which decomposes above -35 °C. In the IR spectra the ν(OO) mode is observed at

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, CH₂CHMe₂,¹⁸⁸ and CH₂CH₂Bu^t 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 [ZrCl₂Cp₂] furnishes both [ZrCl{OCH(CH₂-Cl)CH₃}Cp₂] (90%) and [ZrCl(OCH₂CHClCH₃)Cp₂] (10%).¹⁹⁰

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

(a) Thermolysis of [ZrCl{CHMe(OEt)}Cp₂] at 145 °C gives [ZrCl(OEt)Cp₂] and ethylene.¹⁹¹ Similarly, [Zr{CH₂(OMe)}₂(η-C₅H₄R)₂] (R = H, Me) lose ethylene upon heating at 70 °C with formation of [Zr(OMe)₂(η-C₅H₄R)₂].¹⁸⁶ Rearrangement of [ZrCl{CPh₂(OMe)}Cp₂] 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

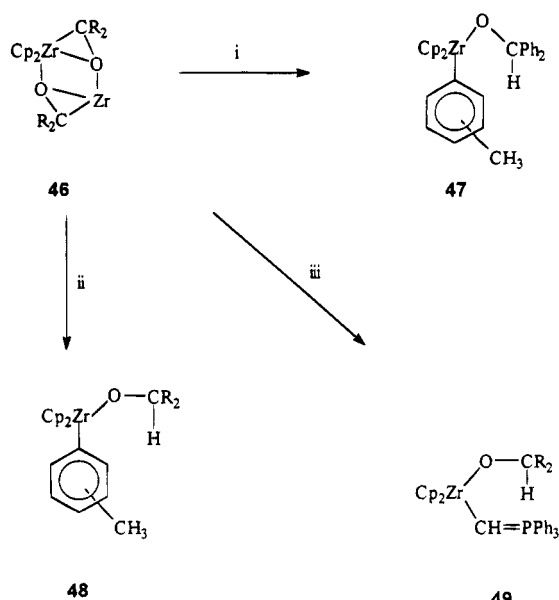


Comparable is the reaction of the ketone complex [Zr(η²-CPh₂O)Cp₂]₂ with alkyl halides, which yields the products **43**–**45** (R = Me, Et, tetrahydrofurfuryl, allyl, 2-propyl, 2-octyl, Bu^t).^{193,194} [ZrCl{CH₂(OCH₂-Ph)}Cp₂] underwent a Wittig rearrangement at 110 °C to give [ZrCl(OCH₂CH₂Ph)Cp₂] as the major product.¹⁹⁵ A radical mechanism is discussed for all these reactions.

(b) Reaction of the zirconocene alkyl ether [ZrCl{CH₂(OMe)}Cp₂] with zirconocene hydride chloride at 40 °C gives [ZrCl(OMe)Cp₂] and methyl zirconocene chloride.¹⁹⁶ Similarly, [ZrCl{CPh₂(OMe)}Cp₂] gives [ZrCl(OMe)Cp₂] and [ZrCl(CHPh₂)Cp₂], but also [ZrCl₂Cp₂] and [Zr(CHPh₂)(OMe)Cp₂].¹⁹⁷ Therefore, two different pathways have been suggested for this reaction.

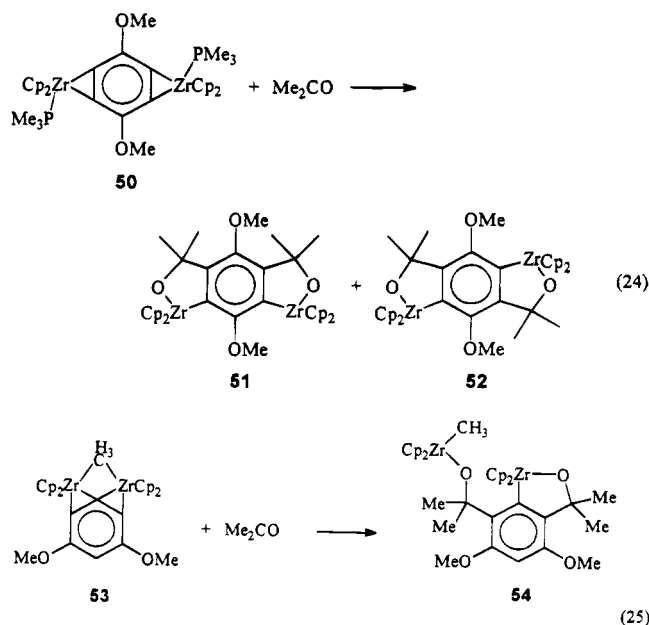
(c) Ring-opening reactions of η²-diaryl ketone metallocenes are observed in the following reactions, which occur via activation of a C–H bond. Thermolysis of the ketone complex **46** (R = Ph) at 100 °C in toluene gives a mixture of isomers **47** (Scheme 19).^{194,198} If the thermolysis of **46** (R = *p*-Tol) is carried out in benzene, **48** is obtained.¹⁹⁹ With the phosphorus ylide CH₂=PPh₃, **49** is obtained at 70 °C in hexane.¹⁹⁹

(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 ¹H

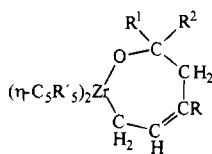
Scheme 19^a

^a (i) Toluene, 100 °C; (ii) benzene, Δ; (iii) CH₂=PPh₃.

NMR (eqs 24 and 25). The same reaction was observed for the alkyne complex [Zr(η²-SiMe₃C≡CPh)-(PMe₃)Cp₂], which reacts with acetophenone with replacement of the phosphine and CC coupling of the π-ligands at the zirconocene template to give the oxametallacyclopentene [Zr{OCMePhCPh=C(SiMe₃)}Cp₂].²⁰²



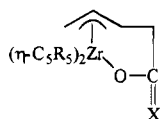
The diene complexes [Zr(diene)Cp*₂] (diene = *s*-*cis*-isoprene, *s*-*trans*-butadiene) react with 2,4-dimethyl-3-pentanone regio- and stereoselectively to give **55** (R = H, Me, R' = Me, R¹ = R² = Prⁱ).²⁰³ The crystal structure analysis revealed the *Z* configuration with respect to the C–C double bond.²⁰³ An isomeric mixture of (*s*-*trans*- and *s*-*cis*-η⁴-butadiene)zirconocene reacts with carbonyl compounds R¹R²C=O to give **55** (R = R' = H for all complexes, R¹ = R² = Ph, Me; R¹ = Me, R² = Ph; R¹ = Me, R² = Bu^t; R¹ = H, R² = CH₂CHMe₂; CR¹R² = cyclododecane).²⁰⁴



55

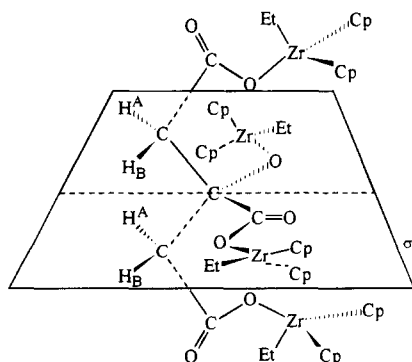
The 1:1 reactions of $[\text{Zr}(\text{butadiene})(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}, \text{Me}$) with CO_2 , Bu^tNCO , PhNCO , or $\text{PhMeC}=\text{C}=\text{O}$ yield $\text{Zr}-\text{O}$ bound complexes having (σ , $\text{syn-}\eta^3$ -allyl) metal structures **56** ($\text{X} = \text{NBu}^t$, NPh , CMePh , O), while $[\text{Zr}(\text{isoprene})(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}, \text{Me}$) gave seven-membered rings with (*Z*)-oxametallacyclic structures

$[\text{Zr}\{\text{OC}(=\text{X})\text{CH}_2\text{CH}=\text{CHCH}_2\}(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{X} = \text{NBu}^t$, NPh , CMePh , O).²⁰⁵ $[\text{Zr}(\text{isoprene})(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H}, \text{Me}$) reacts with $\text{Ph}_2\text{C}=\text{C}=\text{O}$ to give a six-membered oxametallacycle $[\text{Zr}\{\text{OC}(=\text{CPh}_2)\text{CHMeCMe}=\text{CH}\}(\eta\text{-C}_5\text{R}_5)_2]$.²⁰⁵



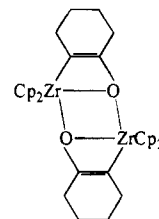
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(v) With equimolar amounts of ROH , $[\text{Zr}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2\text{Cp}_2]$ undergoes protonation of the ethylene ligand to give $[\text{ZrEt}(\text{OR})\text{Cp}_2]$ ($\text{R} = \text{Me}, \text{Et}, \text{Ph}$);^{206,207} excess ROH leads to formation of $[\text{Zr}(\text{OR})_2\text{Cp}_2]$.²⁰⁶ Trifunctional alcohols $\text{X}(\text{OH})_3$ afford bridged trinuclear complexes $[\{\text{Cp}_2(\text{Et})\text{ZrO}\}_3(\mu_3\text{-X})]$ [$\text{X} = \text{CH}_2\text{-CHCH}_2$, $\text{CH}_2\text{CMe}(\text{CH}_2)\text{CH}_2$, $2,4,6\text{-C}_6\text{H}_3$],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 $[\{\text{ZrEtCp}_2\}_2(\mu\text{-1,2-O}_2\text{C}_6\text{H}_4)]$ and $[\text{Zr}(\text{1,2-O}_2\text{C}_6\text{H}_4)\text{Cp}_2]$.²⁰⁹ The latter was described in 1969 but not fully characterized.²¹⁰



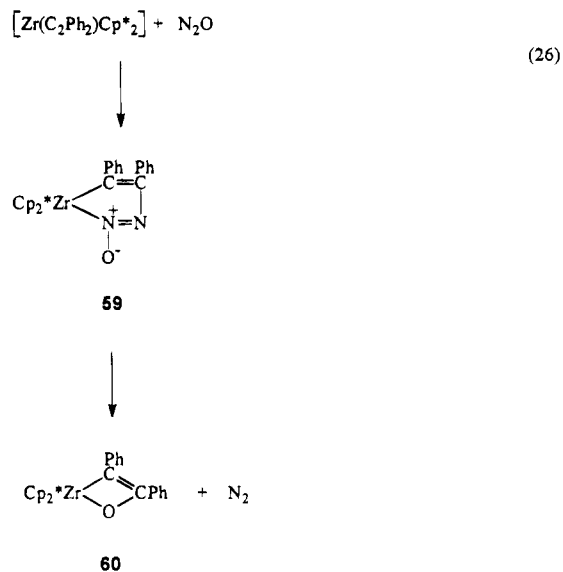
57

(vi) Oxygen atom transfer from N_2O to $[\text{HfH}(\text{Ph})\text{Cp}^*_2]$ gives $[\text{Hf}(\text{OH})(\text{Ph})\text{Cp}^*_2]$ and $[\text{HfH}(\text{OPh})\text{Cp}^*_2]$.²¹¹ An intermediate benzyne complex was implicated in the scrambling process, and it was shown that $[\text{Zr}(\eta^2\text{-cyclohexyne})(\text{PMe}_3)_2\text{Cp}_2]$ reacts with N_2O to give the dimeric oxametallacyclobutene derivative **58** with elimination of N_2 and PMe_3 .²¹² Similarly, $[\text{Zr}$



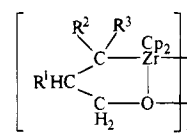
58

$(\text{C}_2\text{Ph}_2)\text{Cp}^*_2]$ reacts with N_2O to yield the adduct **59**, which loses N_2 at ambient temperature to give **60** (eq 26).⁶⁹



(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 $[\text{Cp}_2(\text{Cl})\text{Zr}(\text{CH}_2\text{CH}_2\text{-CY}_2\text{O})\text{Zr}(\text{Cl})\text{Cp}_2]$ ($\text{Y} = \text{Me}$) or $[\{\text{Zr}(\text{OCY}_2\text{CH}_2\text{CH}_2)\text{-Cp}_2\}_2]$ ($\text{Y} = \text{H}$) are obtained.²¹³

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



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(viii) When [Hf(CO)₂Cp*₂] is reacted with H₂ (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 [MX₂(η-C₅R₅)₂] (R = H, Me) and [MX₃Cp*] (M = Zr, Hf, X = hydrocarbyl, hydride, alkoxide, amide, halide).⁷⁴

Bis(alkylcyclopentadienyl)di(aryloxo)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-C₅H₄Me)₂] (*n* = 1, 2, R = α-, or β-*nap*).¹⁶³

The complexes [Zr(OR)₂Cp₂] (R = 2,6-Bu^t₂C₆H₃, 2,6-Bu^t₂-4-MeC₆H₂, 2,4,6-Bu^t₃C₆H₂)⁴⁶ and [Zr(OR)(X)Cp₂] (R = 2,6-Bu^t₂C₆H₃, X = NMe₂,^{46,220} 2,6-Bu^t₂-4-MeC₆H₂, X = NMe₂; R = 2,6-Bu^t₂C₆H₃, X = OMe⁴⁶) show a 1:1 doublet for the *o*-Bu^t groups in the ¹H NMR, which is attributed to restricted rotation about the carbon–oxygen bond.⁴⁶ In the NMR spectra of [M(OR)₂Cp₂] (M = Ti, Zr, Hf, R = Ph, 4-Bu^tC₆H₄, 2,4-Cl₂C₆H₃, 2,4,6-Cl₃C₆H₂, 2,5-Me₂C₆H₃, *m*-Tol), the deshielding of the Cp protons by the center metal decreases in the order Ti > Zr > Hf.¹⁵⁶ A ¹³C NMR study on [M(O-4-RC₆H₄)₂Cp₂] (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-C₅H₄(SiMe₃)₂}] (R = Me, Et) and [HfCl(OMe){η-C₅H₄(SiMe₃)₂}] exhibit molecular parent ion peaks in their field desorption mass spectra.¹⁵⁷

The ⁹¹Zr NMR spectrum of [ZrMe(OSiMe₂Bu^t)Cp₂] 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-Me₂-6-(α-methylcyclohexyl)C₆H₂}Cp₂] [Zr–O 1.981(6) Å, Zr–O–C 165.3(5)°],¹⁸¹ [ZrCl(O-2,6-Bu^t₂-4-MeC₆H₂)Cp₂] [Zr–O 1.98(2) Å, Zr–O–C 150(1)°],²²⁰ [Zr(NMe₂)(O-2,6-Bu^t₂C₆H₃)Cp₂] [Zr–O 2.056(1) Å, Zr–O–C 142.7(1)°],²²⁰ [Cp₂(Cl)Zr(μ-OCMe₂CH₂CH₂)Zr(Cl)Cp₂] [Zr–O 1.921(4) Å, Zr–O–C 165.9(4)°],²¹³ and the isostructural complexes [M(OR)₂(η-C₅H₄Me)₂] (R = 2,6-Cl₂C₆H₃, M = Hf²²² or Zr²²³). The ligands in these complexes occupy positions about the Zr atom typical of [ZrX(Y)Cp₂] type compounds. The large Zr–O–C angle of 165.3(5)° in [ZrBz{O-2,4-Me₂-6-(α-methylcyclohexyl)C₆H₂}Cp₂] 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)Cp₂]

(R = 2,6-Bu^t₂-4-MeC₆H₂, X = Cl; R = 2,6-Bu^t₂C₆H₃, X = NMe₂).²²⁰ The short Zr–O bond distances indicate a partial double bond, ascribable to π-donation from the oxygen atom to the empty 1a₁ orbital of Zr.

Crystal structures of the macrocyclic complexes [Cp₂Zr(μ-OCH₂XCH₂O)₂ZrCp₂] [(X = CMe₂) Zr–O 1.945(6) Å, Zr–O–C 142.5(5)°; (X = 1,3-C₆H₄) 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{OC₆H₅Cr(CO)₃}₂Cp₂]¹⁸⁴ and [Zr{OCH₂C₆H₅Cr(CO)₃}₂Cp₂]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) Å¹⁸³] 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 frag-

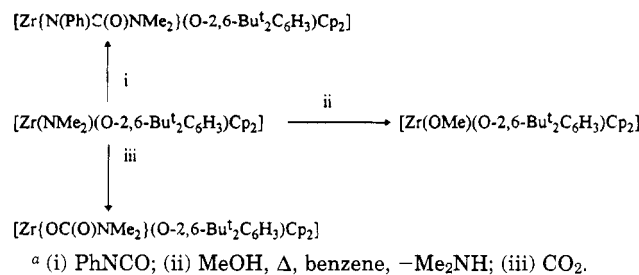
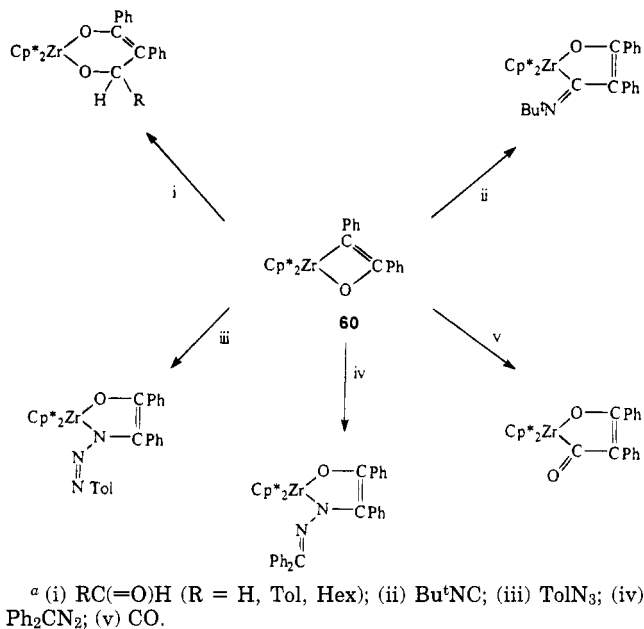
ment. In [Zr{CH₂(CH₂)₃O}Cp*₂] the Zr–O distance [2.008(13) Å] is comparable to that of acyclic alkoxo ligands, but the Zr–O–C bond angle is only 141.1–(12)°.²¹⁴ The oxametallacycloheptene complexes of zirconocene **55** [R = H, Me, R' = Me, R¹ = R² = Prⁱ, Zr–O 1.961(7) (R = H), 1.964(8) (R = Me) Å,²⁰³ and R = R' = H, R¹ = R² = Ph, Zr–O 1.946(4) Å²⁰⁴] are mononuclear in solution and in the solid state, whereas a structurally characterized oxametallacyclopentane derivative has a dimeric structure²¹⁵ 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) Å²¹²] are slightly longer due to the bridging alkoxo ligands.

Crystallographic data for [HfEt(OOBu^t)Cp*₂] show an η¹-bonding mode for the peroxy 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 a₁ 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-C₅H₄R)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-C₅H₄R)₂] (M = Ti, Zr, Hf, R = H, Me, R' = Ph, 4-Bu^tC₆H₄, 2,4-Cl₂C₆H₃, 2,4,6-Cl₃C₆H₂, 2,5-Me₂C₆H₃, *m*-Tol) react with HCl or AcCl to give [MCl₂(η-C₅H₄R)₂].¹⁵⁶ Protonation of **55** (R = R' = H for all complexes, R¹ = R² = Ph, Me; R¹ = Me, R² = Ph; R¹ = Me, R² = Bu^t; R¹ = H, R² = CH₂CHMe₂; CR¹R² = cyclododecane) gives MeCH=CHCH₂CR¹R²OH and CH₂=CH(CH₂)₂CR¹R²OH.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^aScheme 21^a

cycles (Scheme 21).⁶⁹ [ZrBz{O-2,4-Me₂-6-(α-methylcyclohexyl)C₆H₂}Cp₂] reacts with Bu^tNC to give the η²-iminoacyl derivative [Zr(η²-NBu^tCBz){O-2,4-Me₂-6-(α-methylcyclohexyl)C₆H₂}Cp₂].¹⁸¹

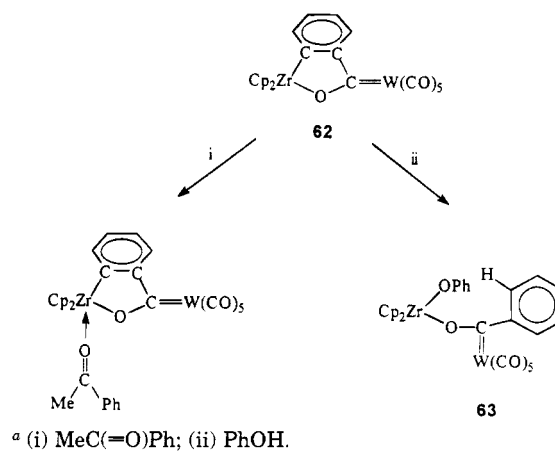
B. Metallocene Complexes with Transition Metal-Substituted Alkoxo Ligands

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(η²-OCMe)(Me)Cp₂] with reduction of the acyl ligand by hydrogen transfer and formation of [ZrMe(OCH₂Me)Cp₂], rhencene hydride and tungstocene dihydride give heterodinuclear complexes [Cp₂(Me)Zr-OCHMe-M(X)Cp₂] (M(X) = Re, W).²²⁵ The tungsten complex has a limited lifetime of several minutes.

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

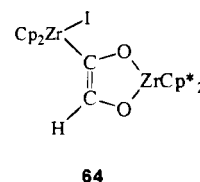
(Zirconoxy)carbene complexes [Cp₂(R)M=C(H)-O-Zr(H)Cp*₂] [M = Nb, R = H;²²⁶ M = Nb, R = H, Me, Bz, CH₂C₆H₄OMe, Ph, CH₂OZr(H)Cp*₂;²²⁷ M(R) = Cr, Mo,²²⁶ or W^{226,228}] are prepared by reacting [NbR(CO)Cp₂] (R = H, Me, Bz, CH₂C₆H₄OMe, Ph,

Scheme 22^a

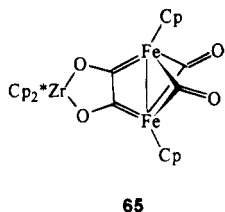
CH₂OZr(H)Cp*₂)²²⁷ or [M(CO)Cp₂] (M = Cr, Mo,²²⁶ or W^{226,228}) with [ZrH₂Cp*₂] at -78 °C in toluene. The molecular structure of the tungsten derivative [M(R) = W] shows strong W=C [2.008(7) Å] and Zr-O bonds [1.970(4) Å] and a moderately long C=O bond [1.350(8) Å].^{226,228} The mechanism of the reaction with niobocene derivatives has been discussed.²²⁷

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)Cp₂] with [(CO)₅W=C(OLi)(Ph)].²²⁹ **62** was shown to be polymeric in the solid state [Zr-O 2.082(7) Å].²²⁹ However, the C₅H₄Bu^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

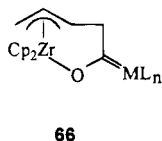
Treatment of [ZrL(CO)Cp₂] (L = CO, PMe₃) with [ZrH₂Cp*₂] affords the (zirconoxy)carbene complexes [Cp₂(L)Zr=CHO-Zr(H)Cp*₂]. The reaction of the PMe₃ adduct with MeI gives methane and the corresponding iodo complex [Cp₂(L)Zr=CHO-Zr(I)Cp*₂].²³⁰ The latter reacts with HCl to give [ZrCl₂Cp₂], PMe₃, and [ZrI(OMe)Cp*₂]; with CO the purple complex **64** is formed. **64** is also obtained from the reaction of [Cp₂(CO)Zr=CHO-Zr(H)Cp*₂] with MeI (elimination of CH₄).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



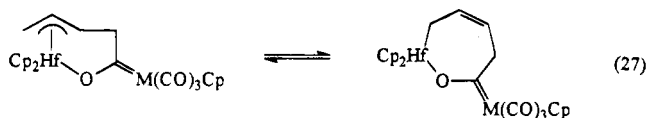
The structurally characterized complex **65** [Zr-O 2.11(1) Å] was obtained from the reaction of [{Zr(N₂)Cp*₂]₂(N₂)] with [{Fe(CO)₂Cp]₂], or from [ZrI₂Cp*₂] and Na[Fe(CO)₂Cp].^{231,232}



(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)₃PPh₃, Rh(CO)Cp, Co(CO)Cp, Co(CO)(η-C₅H₄Cl), Ni(CO)₃, Zr(CO)Cp₂, Hf(CO)Cp₂, 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



The complexes [M(Cl)_{2-n}{OCCO₃(CO)₉}_nCp₂] (M = Zr, Hf, n = 1, 2) have been prepared from metallocene dichloride and Li{OCCO₃(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 [Cp₂(Cl)Zr(OCHR'CHR')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 [Cp₂(Cl)Zr(OCHR'CHR')W(CO)₃Cp] gives [Cp₂(Cl)Zr-O-W(CO)₃Cp] via elimination of R'CH=CHR. The dinuclear complex rapidly decomposes at room temperature to give [(ZrClCp₂)₂O] and [W(CO)₃Cp]₂ as major products; however, it can be trapped with alkynes or PMe₃.²³⁴ The thermal sensitivity led to considerable loss of [Cp₂(Cl)Zr-O-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(R¹)(=CR²R³)}(X)Cp₂] (X = Me, R¹ = R² = R³ = H; X = Me, R¹ = H, R² = R³ = Me; X = OCH=CH₂, R¹ = R² = R³ = H; X = OCH=CH₂, R¹ = H, R² = R³ = Me;²³⁵ X = Cl, R¹ = SBu^t, R² = H, R³ = Me;²³⁶ X = Cl, R¹ = Et, R² = Me, R³ = H;²³⁷ X = Cl, C(=CR²R³)R¹ = 1-cyclopentenyl, 2-cyclohexenyl;²³⁷ X = Cl, R¹ = N(CHMe₂)₂, R² = R³ = H;²³⁸ X = Cl, R¹ = PPh₂, R² = R³ = H;²³⁹ X = Cl, R¹ = Fe(CO)(PPh₃)Cp, R² = R³ =

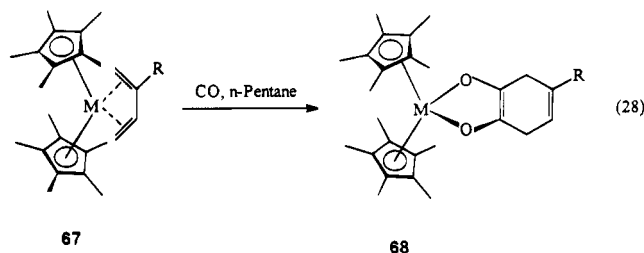
H²⁴⁰) are obtained from zirconocene chloride derivatives and the appropriate lithium reagent in 60–87% yield. Where R² ≠ R³ both isomers (*E*) and (*Z*) are obtained in varying ratios.

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=CH₂,²¹⁴ MR₂ = HfCH₂(CH₂)₂CH₂, RC=CR = CH₂CH₂C=CCH₂CH₂,²⁴² M = Zr, R = Me²⁴³). Molecular orbital calculations together with an isotope-crossover study showed the formation of the Me derivative to be an intramolecular process.²⁴⁴

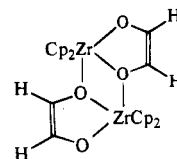
The (η⁴-*s-cis*-diene) metallocene complexes **67** (M = Hf, R = H, Me; M = Zr, R = Me) react with CO to give the metal enediolates **68** in 80–90% yield (eq 28).²⁴¹ However, reaction of the corresponding η⁴-*s-trans*-diene complexes with CO affords carbonyl complexes.²⁴¹ Alternatively, the enediolato 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(N₂)Cp*₂}₂(N₂)].²⁴⁵



c. CO Insertion. Carbonylation of [HfH(CH=C-Bu^tH)Cp*₂] gives [Hf{OCH=CHC(Bu^tH)Cp*₂}] (-10 °C) which reacts with further CO at 25 °C to give

[Hf{OCH=CHC(Bu^t)=CHO}Cp*₂].²⁴² A possible mechanism for this process is discussed. Carbonylation of zirconocene hydride chloride gives the η²-formaldehyde complex [(ZrClCp₂)₂(μ-CHO)], which reacts slowly with further CO to afford **69**.²⁴⁶ Carbonylation of



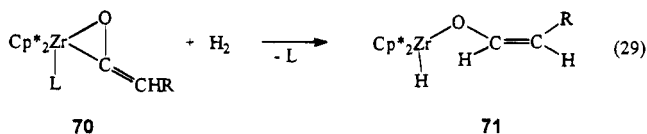
[ZrCl{CH(SiMe₃)R}Cp₂] (R = 9-anthryl) stereospecifically yields (*E*)-[ZrCl{OC(SiMe₃)=CHR}Cp₂] via 1,2-SiMe₃ migration.²⁴⁷ The insertion of CO into the Zr-C bond(s) in the 1-sila-3-zirconacyclobutane ring

of [Zr(CH₂SiMe₂CH₂)(η-C₅R₅)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 spe-

cies, [Zr{OC(=CH₂)SiMe₂CH₂}Cp₂]_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

dienolate, $[\text{Zr}\{\text{OC}(=\text{CH}_2)\text{SiMe}_2\text{C}(=\text{CH}_2)\text{O}\}\text{Cp}^*_2]$, and a bicyclic enediolate $[\text{Zr}\{\text{OC}(\text{CH}_2\text{SiMe}_2\text{CH}_2)=\text{CO}\}\text{Cp}^*_2]$.²⁴⁸

d. Hydrogenation. Hydrogenation of the ketene complexes **70** gives zirconocene enolates **71** (eq 29; R = H, L = py; R = Bu^t, L = CO, CH₂PMe₃).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 $[\text{ZrI}(\text{OCH}=\text{CBu}^t\text{H})\text{Cp}^*_2]$, which isomerizes to the *trans* isomer.²⁴⁹



$[\text{Hf}(\text{CO})_2\text{Cp}^*_2]$ reacts with $[\text{MH}_2\text{Cp}^*_2]$ (M = Zr or Hf) under H₂ to produce *cis*- $[\text{Cp}^*_2(\text{H})\text{Hf}(\mu\text{-OCH}=\text{CHO})\text{M}(\text{H})\text{Cp}^*_2]$.²¹⁶ Warming of $[\text{HfH}_2(\text{CO})\text{Cp}^*_2]$ above -10 °C under H₂ gives *cis*- or *trans*- $[(\text{HfHCp}^*_2)_2(\mu\text{-OCH}=\text{CHO})]$, $[(\text{HfHCp}^*_2)_2(\mu\text{-OCH}_2\text{CH}_2\text{O})]$, and $[\text{HfH}(\text{OMe})\text{Cp}^*_2]$,²¹⁶ while the *trans* enediolate dimer is the sole product in the thermal reaction of the Zr analogue $[\text{ZrH}_2(\text{CO})\text{Cp}^*_2]$.²⁵⁰ The oxametallacyclobutene complex **60** reacts with H₂ to give the enolate $[\text{ZrH}(\text{OCPH}=\text{CHPh})\text{Cp}^*_2]$.⁶⁹

e. Acidic Hydrogen. Substrates with acidic hydrogen R–H (HO–H, PhO–H, MeC(=O)CH₂–H, HCC–H, PhCC–H, Bu^tCC–H) react with the oxametallacyclobutene complex **60** to give $[\text{Zr}(\text{OCPH}=\text{CHPh})(\text{R})\text{Cp}^*_2]$.⁶⁹

f. Coordinated CO. The aldehyde complex $[\text{Zr}(\text{CO})(\eta^2\text{-OCHCH}_2\text{CHMe}_2)\text{Cp}^*_2]$ slowly loses its coordinated CO and rearranges to the enolate hydride complex $[\text{ZrH}(\text{OCH}=\text{CHCHMe}_2)\text{Cp}^*_2]$.²⁴² By contrast, the Hf derivative rearranges without loss of CO

to give the cyclic enolate tautomer $[\text{Hf}\{\text{OCH}=\text{C}(\text{CH}_2\text{-CHMe}_2)\text{O}\}\text{Cp}^*_2]$, most likely by a 1,2-hydrogen shift of the cyclic acyl derivative $[\text{Hf}(\eta^2\text{-COCH}(\text{CH}_2\text{-CHMe}_2)\text{O})\text{Cp}^*_2]$.²⁴² The acyl complex $[\text{Zr}(\eta^2\text{-COCH}_2\text{-CHMe}_2)(\text{H})\text{Cp}^*_2]$ reacts with ethylene or 2-butyne to

give the metallacycles $[\text{Zr}\{\text{OCH}(\text{CH}_2\text{CHMe}_2)\text{CH}_2\text{CH}_2\}\text{Cp}^*_2]$ or $[\text{Zr}\{\text{OCH}(\text{CH}_2\text{CHMe}_2)\text{CMe}=\text{CMe}\}\text{Cp}^*_2]$.²⁴²

g. Insertion of Diphenyl Ketene. Insertion of diphenyl ketene into the Zr–C bonds of $[\text{ZrR}_2\text{Cp}_2]$ (R = Me, Bz, Ph) gives $[\text{Zr}(\text{OCR}=\text{CPh}_2)_n(\text{R})_{2-n}\text{Cp}_2]$ (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 (γ^2). This absorption is shifted to higher wavenumbers if the ZrO₂C₂ ring is less puckered (Figure 8).²⁴⁵ Accordingly, $[\text{Zr}\{\text{OC}(\text{Bu}^t)=\text{C}(\text{Bu}^t)\text{O}\}\text{Cp}^*_2]$, which was shown to contain a planar ZrO₂C₂ ring by X-ray crystallography, exhibits a

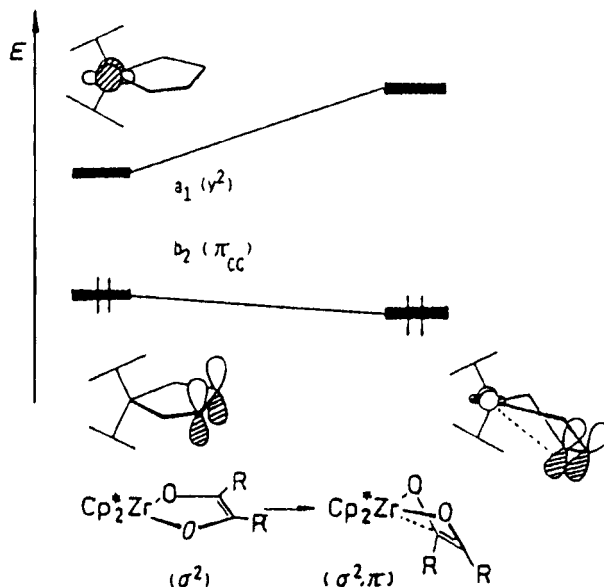


Figure 8. Energy of the frontier orbitals in planar and puckered enediolato complexes. (Reprinted from ref 245. Copyright 1985 VCH Publishers, Inc.)

maximum at 570 nm, while for $[\text{Zr}\{\text{OC}(\text{Me})=\text{C}(\text{Me})\text{O}\}\text{Cp}^*_2]$, which has a puckered ring, the absorption is observed at 495 nm.²⁴⁵

All compounds have been characterized by NMR spectroscopy. In the ¹³C 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 $[\text{ZrCl}(\text{OCR}=\text{CH}_2)\text{Cp}_2]$ (R = NPh₂,²³⁸ PPh₂²³⁹) and $[\text{ZrH}(\text{OCH}=\text{CH}_2)\text{Cp}^*_2]$ ²⁴⁹ the O–C resonance is observed between 154.2 and 169.2 ppm, while the =CH₂ resonance appears at 78.1 (X = NPh₂) or 103.0 ppm (X = PPh₂) in the former, and at 89.4 ppm in the latter. For $[\text{ZrI}(\text{OCH}=\text{CHBu}^t)\text{Cp}^*_2]$ the H–H coupling constants for the *cis* ($J(\text{HH}) = 7.9$ Hz) and *trans* ($J(\text{HH}) = 13.2$ Hz) isomer have been determined.²⁴⁹

In the IR spectrum the $\nu(\text{C}=\text{C})$ mode is observed between 1600 and 1700 cm⁻¹, and the $\nu(\text{CO})$ mode between 1200 and 1270 cm⁻¹.^{241,249}

3. Structural Data

Structural data are available for the enolato complexes $[\text{ZrCl}(\text{OCR}=\text{CH}_2)\text{Cp}_2]$ [R = NPh₂, Zr–O 1.976(3), O–C 1.337(5) Å, Zr–O–C 147.3(3)°;²³⁸ R = PPh₂, Zr–O 1.960(3), O–C 1.339(5) Å, Zr–O–C 163.6(3)°;²³⁹ R = Fe(CO)(PPh₃)Cp, Zr–O 1.948(8), O–C 1.364(14) Å²⁴⁰], (*E*)- $[\text{ZrCl}\{\text{OC}(\text{SiMe}_3)=\text{CHR}\}\text{Cp}_2]$ [R = 9-anthryl, Zr–O 1.950(4), O–C 1.360(6) Å, Zr–O–C 157.7(3)°],²⁴⁷ $[\text{ZrMe}(\text{OCMe}=\text{CPh}_2)\text{Cp}_2]$ [Zr–O 1.975(3), O–C 1.341(7) Å, Zr–O–C 150.8(3)°],⁶⁸ and $[\text{Zr}(\text{OCMe}=\text{CPh}_2)_2\text{Cp}_2]$ [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 $[\text{Zr}\{\text{OC}(=\text{CH}_2)\text{SiMe}_2\text{C}(=\text{CH}_2)\text{O}\}\text{Cp}^*_2]$ [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 $[\text{Zr}\{\text{OC}(\text{R})=\text{C}(\text{R})\text{O}\}\text{Cp}^*_2]$ (R = Me, Bu^t) show a planar ZrO₂C₂ ring for R = Bu^t [Zr–O 2.031(4), 2.048(6) Å], and a nonplanar ring for R = Me [dihedral angle ZrO₂/O₂C₂ 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 non-planar 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=CH₂)Cp₂] (R = NPh₂,²³⁸ PPh₂)²³⁹ has been exploited to form complexes with Cr(CO)₅. Crystal structures have been reported for [ZrCl{OCRCH₂Cr(CO)₅}Cp₂] (R = NPh₂,²³⁸ PPh₂)²³⁹.

[ZrCl{OC(=CH₂)PPh₂}Cp₂] reacts rapidly with benzaldehyde to form [ZrCl{OCHPhCH₂C(=O)PPh₂}Cp₂].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 (RCH₂C(=O)SBU^t) (R = Me, Et, CHMe₂), underwent syn-selective condensation with the imine 4-MeOC₆H₄CH₂N=CHC≡CSiMe₃ to give β -amino acid derivatives.²⁵²

5. Related Complexes

The reaction of zirconocene dichloride with dipotassium dithiooxalate (dto) in CH₂Cl₂ gives [(ZrClCp₂)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(μ -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(O₂CR)_{*n*}(Cl)_{2-*n*}Cp₂] [base usually NEt₃, *n* = 1 or 2; R = Prⁱ, MeC(=O)NHCHMe—;²⁵⁴ RCO₂H = 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 ([ZrCl₂Cp₂] and [ZrCl₂(η -C₅H₄Me)₂] were used as starting materials),²⁵⁸ *N*-phthaloyl amine acids *o*-C(O)C₆H₄C(O)NCHR'CO₂H (with R' = H, Me, Bz, Prⁱ, CH₂CH₂SMe),²⁵⁹ *trans*-cinnamic acid, dihydrocinnamic acid²⁶⁰]. 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(O₂CR')₃(η -C₅H₄R)] (R = H, Me, R'CO₂H = palmitic acid, stearic acid, behenic acid)²⁶⁸ (cf. section VI.E.1).

Reaction of [MCl₂Cp₂] (M = Ti, Zr) with 3-indole derivatives (i.e., 3-indoleacetic acid, 3-indolepropionic acid, 1-tryptophan, 3-indolebutyric acid) in the presence of NEt₃ 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(O₂CR)Cp₂]. However, the 1:2 reaction yields [HfCl(O₂CR)₂Cp].²⁶²

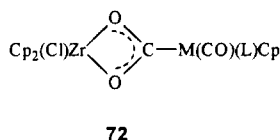
[(ZrBrCp₂)₂O] reacts with CCl₃COOH with cleavage of the Zr—O—Zr bond to give the intermediate [ZrBr(O₂CCl₃)Cp₂] which disproportionates to [ZrBr₂Cp₂] and [Zr(O₂CCl₃)₂Cp₂].²⁶³ With organic acids RCOOH (R = Me, Ph) the mixed compound [ZrBr(O₂CR)-Cp₂]₄[Zr(O₂CR)₂Cp₂] is formed.²⁶³ Treatment of [(ZrClCp₂)₂O] with excess RCO₂H gave [ZrCl(O₂CR)-Cp₂] (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(O₂CMe)(X)Cp₂] (X = Cl, O₂CMe) 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 CHCl₃/H₂O yields the dinuclear complex [{Zr(O₂CCF₃)(μ -OH)Cp₂}]₂, which contains five-coordinate Zr, in 30% yield.²⁶⁹ [Zr(η^2 -CHPh-NMe₂)(Me)Cp₂] reacts with TFA with replacement of the Me ligand by CF₃COO.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(O₂CR')(η -C₅H₄R)₂] (R = H, R' = 2-, 3-, or 4-BrC₆H₄, 2- or 4-ClC₆H₄, 2- or 4-IC₆H₄, 2- or 3-FC₆H₄, 3- or 4-NO₂C₆H₄, *p*-Tol, 4-CNC₆H₄, 2-NH₂C₆H₄, Ph,²⁷¹ R = Me, R' = nap;²⁷² R = H, Me, R' = nap, α -CH₂C₁₀H₇, PhCH=CH, *p*-ClC₆H₄OCH₂;²⁷³ R = Me, R' = nap²⁷⁴) in 67–91% yield, as well as for the synthesis of zirconocene complexes containing ferrocenylcarboxylato ligands [{ZrCl(η -C₅H₄R)₂}]_{*n*}(Y) [*n* = 1, R = H, Me, Y = FcCO₂, FcCH₂CO₂, Fc(CH₂)₃CO₂, FcC(O)-(CH₂)₂CO₂, FcC(O)(C₇H₈)CO₂ (C₇H₈ = 5,6-norbornene),²⁷⁵ *n* = 1, R = H, Y = FcC(O)(CH₂)₂CO₂;²⁷⁶ *n* = 2, R = H, Me, Y = Fe{C₅H₄C(O)(CH₂)₂CO₂}₂;²⁷⁵ *n* = 1, R = H, Me, Y = FcCO₂, FcCH₂CO₂, FcCOCH₂-CH₂CO₂;²⁷⁷]. The monothiocarbamate complex [ZrCl(SOCNMe₂)Cp₂] was prepared accordingly (cf. section VI.E.1).²⁷⁸

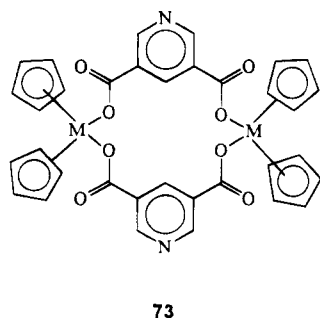
The dicarbonyl complex **72** (M = Re, L = CO) is obtained by salt elimination from zirconocene dichloride and Na[Re(CO)₂(COO)Cp].²⁷⁹ Analogously, zirconocene dichloride reacts with Na[M(CO)₂(COO)Cp] (M = Fe, Ru) at low temperature to give **72** (M = Fe, Ru, L = CO).²⁸⁰ Treatment of methyl zirconocene chloride with [Re(CO)(CO₂H)(NO)Cp] results in elimination of methane and formation of light yellow **72** (M = Re, L = NO) in 82% yield.²⁸¹ The titanocene

analogues ($M = \text{Fe}, \text{Ru}, \text{L} = \text{CO}$) are unstable above -30°C .²⁸⁰

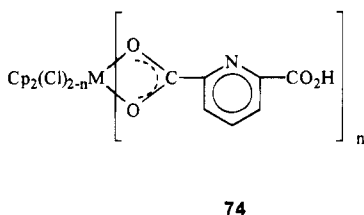


Complex **42** ($R = \text{Bu}^t$) reacts with PhCOOH to give $[\text{Zr}(\text{O}_2\text{CPh})_2(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2]$; excess of carboxylic acid yields $[\text{Zr}(\text{O}_2\text{CPh})_3\text{Cp}]$.¹⁸⁵

Utilization of aromatic dicarboxylato ligands allows the synthesis of monomeric,²⁵⁵ dimeric,²⁸² or trimeric²⁸³ 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** ($M = \text{Ti}, \text{Zr}$) quantitatively.²⁸² The crystal structure of the Ti derivative has been determined.²⁸² Both pyridine ligands in **73** can act as Lewis bases toward $[\text{M}'(\text{CO})_2\text{Cl}]$ ($M' = \text{Rh}, \text{Ir}$).²⁸²



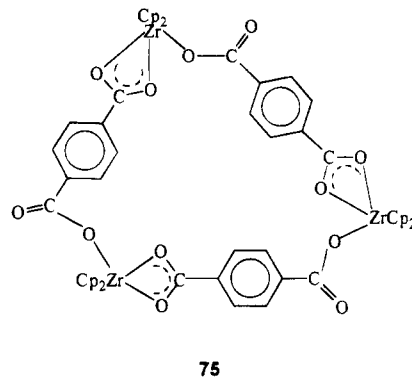
In contrast, when titanocene or zirconocene dichloride was reacted with pyridine-2,6-dicarboxylic acid and NEt_3 in varying molar ratios, the complexes **74** ($M = \text{Ti}, \text{Zr}, n = 1$ or 2) were obtained.²⁵⁵



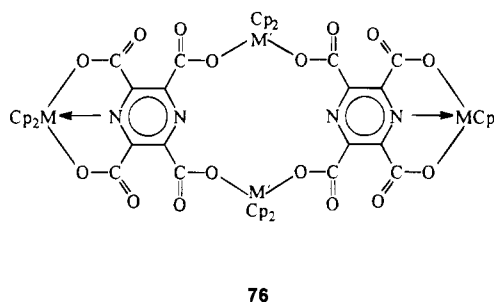
A monomeric product $[\text{Zr}\{\text{OC}(=\text{O})\text{CH}_2\text{OCH}_2\text{C}(=\text{O})\}_n\text{Cp}_2]$ was also obtained from the reaction of zirconocene dichloride with the disodium salt of oxydiacetic acid in $\text{CHCl}_3/\text{H}_2\text{O}$. Titanocene dichloride gives a mononuclear or dinuclear product, depending on the solvent employed.²⁸⁴

The trinuclear complex **75** is obtained on reacting zirconocene dichloride with disodium terephthalate in $\text{H}_2\text{O}/\text{CHCl}_3$.²⁸³

The reaction of titanocene dichloride with tetrasodium pyrazinetetracarboxylate gives the tetrametallic complex **76** ($M = M' = \text{Ti}$).²⁸⁵ Attempts to prepare the Zr analogue (**76**, $M = M' = \text{Zr}$) were unsuccessful.²⁸⁵ However, if the tetrasodium salt is reacted with equimolar amounts of titanocene and zir-



conocene dichloride, **76** ($M = \text{Zr}, M' = \text{Ti}$) is obtained.²⁸⁵



The polymeric complexes $[\text{Zr}(\mu\text{-OCOC}\equiv\text{COCO})\text{Cp}_2]_n$ and $[\text{Zr}(\mu\text{-OCOC}\equiv\text{COCO})\text{Cp}_2\text{CHCl}_3]_n$ are obtained from zirconocene dichloride and acetylenedicarboxylic acid in $\text{H}_2\text{O}/\text{CHCl}_3$ or $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$,²⁸⁶ while the analogous Ti system gave $[\text{Ti}(\mu\text{-OCOC}\equiv\text{COCO})\text{Cp}_2]_n$ ($n = 2, 4$)²⁸⁷ with tetracoordinate Ti.

$[\text{Zr}(\text{C}_2\text{H}_4(\text{PMe}_3)\text{Cp}_2)]$ reacts with carboxylic acids RCOOH , undergoing protonation of the ethylene ligand and formation of mononuclear ethyl carboxylato complexes $[\text{ZrEt}(\text{O}_2\text{CR})\text{Cp}_2]$ ($R = \text{H}, \text{Me}, \text{CF}_3$).²⁰⁶ Excess TFA gives $[\text{Zr}(\text{O}_2\text{CCF}_3)_2\text{Cp}_2]$.²⁰⁶ With bifunctional H-acidic compounds, such as dicarboxylic acids or salicylic acid, bridged dinuclear ethyl complexes $[\text{Cp}_2(\text{Et})\text{Zr}(\mu\text{-O}_2\text{CXCO}_2)\text{Zr}(\text{Et})\text{Cp}_2]$ are obtained ($X = \text{CH}_2, \text{CH}_2\text{CH}_2, \text{cis- and trans-CH=CH}, \text{CH=CMe}$).²⁸⁸ Reactions with tetrafunctional carboxylic acids (citric acid, pentaerythritol) yield tetranuclear complexes **57** (cf. section V.A.1).²⁰⁸

2. Spectroscopic Properties

The heterocarboxylates $[\text{ZrCl}(\text{O}_2\text{CR})\text{Cp}_2]$ and $[\text{Zr}(\text{O}_2\text{CR})_2\text{Cp}_2]$ ($\text{RCO}_2\text{H} = 2\text{- or }4\text{-pyridinecarboxylic acid}, 2,6\text{-pyridinedicarboxylic acid}, 2,5\text{-}2\text{-thiophenecarboxylic acid}, 2\text{-thiopheneacetic acid}, 3\text{-pyridinecarboxylic acid}, 2,5\text{-}3\text{-thiophenecarboxylic acid}, 3\text{-thiopheneacetic acid}, 2\text{-thiophenebutyric acid}, 2,5\text{-}3\text{-indoleacetic acid}, 3\text{-indolepropionic acid}, 1\text{-tryptophan}, 3\text{-indolebutyric acid}$ ²⁶¹) are brown ($M = \text{Zr}$) or yellow to brown ($M = \text{Hf}$) and exhibit one fairly intense absorption between 242 and 301 nm in their electronic spectra. The complexes $[\text{ZrCl}(\text{O}_2\text{CR})\text{Cp}_2]$, $[\text{ZrCl}(\text{O}_2\text{CR})(\eta\text{-C}_5\text{H}_4\text{Me})_2]$, $[\text{Zr}(\text{O}_2\text{CR})_2\text{Cp}_2]$, and $[\text{Zr}(\text{O}_2\text{CR})_2(\eta\text{-C}_5\text{H}_4\text{Me})_2]$ ($\text{RCO}_2\text{H} = \text{palmitic, stearic, and behenic acid}$),²⁵⁸ $[\text{ZrCl}(\text{O}_2\text{CR})\text{Cp}_2]$ ($R = 2\text{-, }3\text{-, or }4\text{-BrC}_6\text{H}_4, 2\text{- or }4\text{-ClC}_6\text{H}_4, 2\text{- or }4\text{-IC}_6\text{H}_4, 2\text{- or }3\text{-FC}_6\text{H}_4, 3\text{- or }4\text{-NO}_2\text{C}_6\text{H}_4, p\text{-Tol}, 4\text{-CNC}_6\text{H}_4, 2\text{-NH}_2\text{C}_6\text{H}_4, \text{Ph}$),²⁷¹ $R =$

H, Me, Bu^t, Ph²⁶⁴), and [Zr(Cl)_{2-n}(O₂CR)_nCp₂] (*n* = 1, 2, O₂CR = *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 $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ 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 $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ 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(O₂CR)Cp₂] (R = 2-, 3-, or 4-BrC₆H₄, 2- or 4-ClC₆H₄, 2- or 4-IC₆H₄, 2- or 3-FC₆H₄, 3- or 4-NO₂C₆H₄, *p*-Tol, 4-CNC₆H₄, 2-NH₂C₆H₄, Ph), and a bidentate coordination was suggested.²⁷¹

In **72** the ν_{as} and $\nu_{\text{s}}(\text{COO})$ 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 = CO²⁸⁰) with respect to analogous monometallic complexes.

For the bridged dinuclear products [Cp₂(Et)Zr(μ -O₂CXCO₂)Zr(Et)Cp₂] ν_{as} and $\nu_{\text{s}}(\text{COO})$ are observed at 1526–1567 and 1426–1460 cm⁻¹, respectively.²⁸⁸

The $\nu(\text{Zr—O})$ 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 CO₂H and coordinated carboxylato group.²⁵⁵

In [Zr{OC(=O)CH₂OC₆H₄-*p*-Cl}(Cl)Cp₂] a five-membered ring is observed (by IR) instead of η^2 -coordination of the carboxylato ligand.²⁷³ Observation of the $\nu(\text{ZrCl})$ mode at 250–280 cm⁻¹ in [ZrCl(L)Cp₂] (L = *N*-phthaloyl amino acids) was attributed to the presence of chloro-bridged dimers.²⁵⁹

The solution and solid-state IR spectra of [ZrCl(O₂CR)Cp₂] (R = H, Me, Bu^t, Ph) are consistent with η^2 -bonding of the carboxylato ligand [$\nu_{\text{as}}(\text{COO})$ 1493–1528 cm⁻¹, $\nu_{\text{s}}(\text{COO})$ 1410–1477 cm⁻¹], although the formate complex (R = H) is in equilibrium with unidentate η^1 -carboxylate as shown by variable-temperature ¹H and ¹³C 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(O₂CR)Cp₂] (R = 2-, 3-, or 4-BrC₆H₄, 2- or 4-ClC₆H₄, 2- or 4-IC₆H₄, 2- or 3-FC₆H₄, 3- or 4-NO₂C₆H₄, *p*-Tol, 4-CNC₆H₄, 2-NH₂C₆H₄, Ph) (6.20–6.45 ppm)^{259,271} and [ZrCl(O₂CR)(η -C₅H₄R')₂] (R' = H, Me, R = nap, α -CH₂C₁₀H₇, PhCH=CH, *p*-ClC₆H₄-OCH₂) (6.01–6.36 ppm)²⁷³ compared to zirconocene dichloride was observed in the ¹H NMR spectra.

In the ¹³C NMR spectra the chemical shift of the carboxylate C atom —CO₂— is observed between 187.1 and 213 ppm.^{280,281} In [ZrCl(L)Cp₂] (L = *N*-phthaloyl amino acids) chemical shifts are observed between 170 and 175 ppm.²⁵⁹

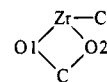
The mass spectra of some bis(cyclopentadienyl)-substituted benzoato zirconium chlorides have been reported and the main fragmentation pathways proposed.²⁸⁹

The zirconocene complexes containing ferrocenyl-carboxylato ligands are orange and sensitive to light and air.²⁷⁵ The $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ 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; C₅H₄Me, 5.80–6.23 ppm) compared with those of [ZrCl₂Cp₂] and [ZrCl₂(η -C₅H₄Me)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(O₂CR)-(η -C₅H₄Me)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 dithiocarbamate 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{O₂C-(CH₂)₂C(O)Fc}Cp₂] 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).

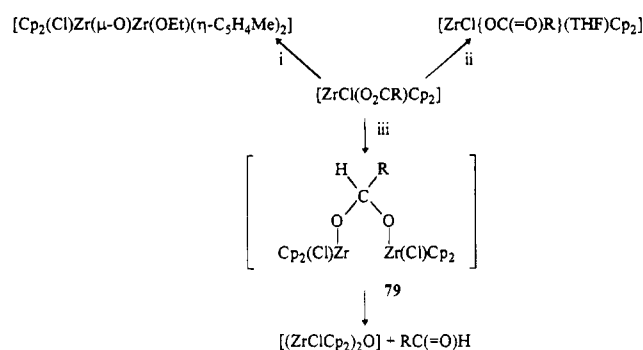


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The dimetallic tetranuclear complex **76** (M = Zr, M' = Ti) exhibits Zr—O bond lengths of 2.17(1) and 2.20(1) Å. The molecule lies on a crystallographic mirror plane.²⁸⁵

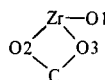
A monodentate carboxylato ligand is observed in [Zr(η^2 -CHPhNMe₂)(O₂CCF₃)Cp₂] [Zr—O 2.205(3) Å],²⁷⁰ [Zr{OC(=O)CH₂OCH₂C(=O)O}Cp₂] [Zr—O 2.156(2) Å],²⁸⁴ and [Zr(O₂CCF₃)(μ -OH)Cp₂]₂ [Zr—O 2.217-(4) Å].²⁶⁹ The Zr—O bonds are shorter than in complexes with η^2 -bonding of the carboxylato group.

The carboxylato ligand acts as a (2 + 1)-dentate ligand in the cyclic trinuclear complex **75**²⁸³ and polymeric [Zr(μ -OCOC≡COCO)Cp₂]_n and [Zr(μ -OCOC≡COCO)Cp₂-CHCl₃]_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 2₁ 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) $[\text{ZrH}(\mu\text{-H})(\eta\text{-C}_5\text{H}_4\text{Me})_2]$ ($\text{R} = \text{Me}$); (ii) THF ($\text{R} = \text{H, Me, Bu}^t, \text{Ph}$); (iii) $[\text{ZrCl}(\text{H})\text{Cp}_2]_k$ ($\text{R} = \text{H, Me, Ph}$).

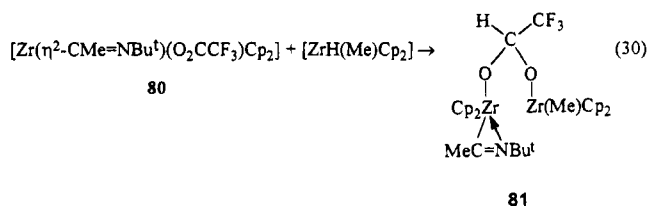
(7); $\text{Zr}-\text{O}2$, 2.261(3), 2.275(8); $\text{Zr}-\text{O}3$, 2.332(2), 2.316(8) Å].²⁸⁶



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4. Chemical Properties

Reduction of the coordinated carboxylate ligand in $[\text{ZrCl}(\text{O}_2\text{CR})\text{Cp}_2]$ to the aldehyde ($\text{R} = \text{H, Me, Ph}$) or alcohol ($\text{R} = \text{Me}$) has been reported (Scheme 23).²⁶⁴ Similarly, the dimeric complexes **72** ($\text{M} = \text{Re, L} = \text{NO}$;²⁸¹ $\text{M} = \text{Ru, L} = \text{CO}$)²⁷⁹ react with zirconocene hydride chloride to give $[\text{Cp}_2(\text{Cl})\text{Zr}-\text{OCH}_2-\text{M}(\text{CO})(\text{L})\text{Cp}]$.^{279,281} No direct evidence for the postulated $\mu\text{-}\eta^1\text{-O, O' gem-diolate}$ 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 [$\text{Zr}-\text{O}$, 2.099(3), 1.968(3) Å].²⁷⁰



The complexes $[\text{ZrCl}(\text{O}_2\text{CR})\text{Cp}_2]$ ($\text{R} = \text{Pr}^i, \text{MeC}(\text{=O})\text{NHCHMe}$) 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** ($\text{M} = \text{Fe, Ru, L} = \text{CO}$) gives $\{[\text{M}(\text{CO})_2\text{Cp}]_2\}$ and $[(\text{ZrClCp}_2)_2\text{O}]$, indicating partial deoxygenation of CO_2 .²⁸⁰

5. Related Complexes

The nitronato complexes $[\text{Zr}(\text{O}_2\text{N}=\text{CMeR})(\text{X})\text{Cp}_2]$ ($\text{R} = \text{Me}$ or $\text{H, X} = \text{Cl}$; $\text{R} = \text{Me, X} = \text{CH}_2\text{CMe}_2\text{Ph}$) were prepared from the reaction of $\text{Li}(\text{O}_2\text{N}=\text{CMeR})$ with the appropriate zirconocene derivative in 80% yield.²⁹⁰ The crystal structure of $[\text{ZrCl}(\text{O}_2\text{N}=\text{CMe}_2)\text{Cp}_2]$ shows the η^2 bonding mode of the nitronato ligand (cf. section VIII.B).²⁹⁰ The ligand "bite" is

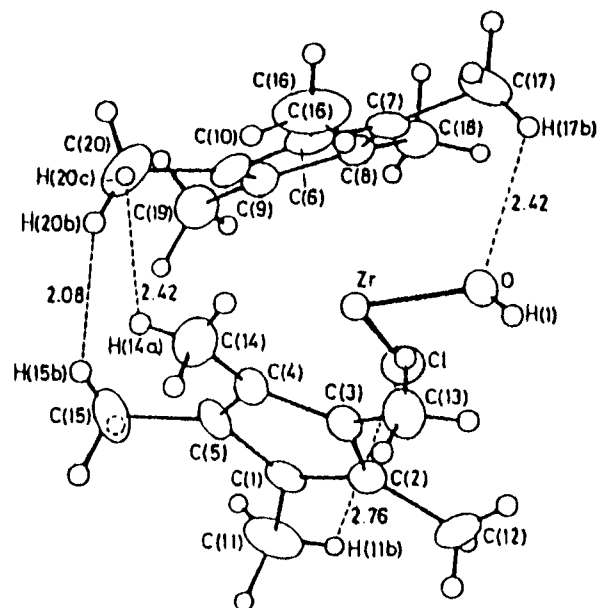


Figure 9. Molecular structure of $[\text{ZrCl}(\text{OH})\text{Cp}^*_2]$. Short intermolecular contacts are shown. (Reprinted from ref 292. Copyright 1985 Chemical Society of London.)

similar to that observed in carboxylato and dithiocarbamate complexes.

E. Metallocene Hydroxides

Monohydroxides of zirconocene derivatives $[\text{Zr}(\text{OH})(\text{X})\text{Cp}_2]$ ($\text{X} = \text{Cl, Br, I, NO}_3$;²⁹¹ C_6F_5)¹⁷⁶ and zirconocene dihydroxide¹⁷⁶ 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 $[\text{ZrMe}_2(\eta\text{-C}_5\text{R}_5)_2]$ or $[\text{ZrCl}(\text{Me})(\eta\text{-C}_5\text{R}_5)_2]$ with water affords for $\text{R} = \text{H}$ the well-known oxo-bridged dimers $[(\text{ZrXCp}_2)_2\text{O}]$ ($\text{X} = \text{Cl, Me}$), and for $\text{R} = \text{Me}$, the structurally characterized complexes $[\text{ZrCl}(\text{OH})\text{Cp}^*_2]$ [$\text{Zr}-\text{O}$, 1.950(2) Å] and $[\text{Zr}(\text{OH})_2\text{Cp}^*_2]$ [$\text{Zr}-\text{O}$, 1.975(8), 1.982(7) Å].²⁹² The former is also obtained on hydrolysis of $[\text{ZrCl}(\text{R})\text{Cp}^*_2]$ ($\text{R} = \text{Bu}$ ²⁹² or H ⁵⁵); alternatively, the dihydroxo complex is obtained from hydrolysis of $[(\text{ZrHCp}^*_2)_2\text{O}]$ or by hydrolysis of the reaction mixture of $[\text{ZrCl}_2\text{Cp}^*_2]$ and BuLi .⁵⁵ The monohydroxo complex shows the presence of significant intramolecular nonbonding contacts (Figure 9).²⁹² The mass spectrum of $[\text{Zr}(\text{OH})_2\text{Cp}^*_2]$ shows the parent ion peak and an intense signal for $[\text{Zr}(\text{=O})\text{Cp}^*_2]$.²⁹²

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

Extended Hückel MO calculations performed on the model complex $[\text{Zr}(\text{OH})_2\text{Cp}_2]$ ¹⁸⁰ are consistent with the predictions by Hoffmann and Lauher.¹³³ An energy minimum occurs when $\text{O}-\text{Zr}-\text{O}$ is 97.9° ; however, the energy varies only slightly over the range $96\text{--}101^\circ$, suggesting $d_\pi\text{-}p_\pi$ interaction between the $1a_1$ orbital of the Cp_2Zr fragment and the oxygen p orbitals.¹⁸⁰

[ZrCl₂Cp₂] reacts with TFA in CHCl₃/H₂O to give the hydroxo-bridged complex [$\{Zr(O_2CCF_3)(\mu-OH)Cp_2\}_2$] [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(C₂Ph₂)Cp₂^{*}] reacts with H₂O to give the monohydroxide [Zr(CPh=CHPh)(OH)Cp₂^{*}].⁶⁹ Similarly, **42** (R = Bu^t) reacts with stoichiometric amounts of water to give [Zr(FC)(OH)(η -C₅H₄Bu^t)₂].¹⁸⁵

Hydrolysis of [M(CO)₂Cp₂] affords [Cp₆Ti₆O₈] (M = Ti) and crude ZrO₂ (M = Zr), respectively,^{293,294} no reaction of [M(CO)₂Cp₂^{*}] (M = Ti^{293,294} or Zr²⁹⁴) with water was observed.

Complexes [(ZrXCp₂)₂O] (X = Cl, Br, OPh), [Zr(OPh)₂Cp₂] and [ZrCl(Y)Cp₂] (Y = NO₃, O₂C₁₅H₁₁ (β -diketonate)) are hydrolyzed by excess water, primarily undergoing elimination of one Cp ligand.²⁹⁵

N₂O reacts with [HfH₂Cp₂^{*}] under mild conditions to yield N₂ and [HfH(OH)Cp₂^{*}] quantitatively. Competitive oxidation of the hydrido and aryl ligands in [HfH(Ph)Cp₂^{*}] occurs with N₂O at 80 °C, affording [Hf(OH)(Ph)Cp₂^{*}] and [HfH(OPh)Cp₂^{*}] (3:2).²¹¹ Independently, [Hf(OH)(Ph)Cp₂^{*}] has been prepared from [HfH(Ph)Cp₂^{*}] and water.²¹¹

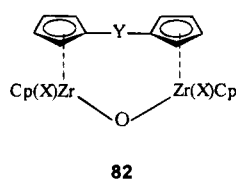
F. Oxo-Bridged Metallocene Dimers

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.

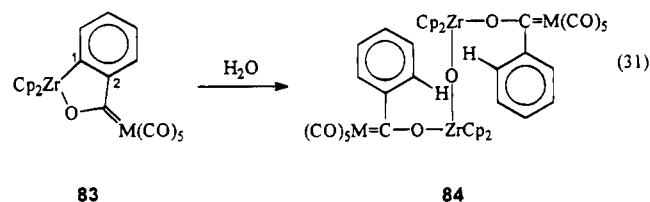
a. Hydrolysis. Hydrolysis of metallocene dialkyls or dihalides [MX₂(η -C₅H₄R)₂] (M = Hf, R = H, X = *o*-, *m*-, or *p*-Tol, Ph;²⁹⁶ M = Zr, R = H, X = Cl;^{297,298} M = Hf, R = H, Me, X = 4-ClC₆H₄, 4-MeOC₆H₄, 3,4-Me₂C₆H₃;²⁹⁹ M = Zr, R = Bu^t, X = Me^{300,301}) and of [MCl₂{(η -C₅H₄)₂Y}] (M = Zr, Y = (SiMe₂)_n, n = 2, 3;^{297,165} M = Ti, Zr, Hf, Y = Me₂SiOSiMe₂, (SiMe₂)_n, n = 2, 3¹⁶⁵) or solvolysis of [ZrX₂Cp₂] (X = Cl, *o*-Tol)³⁰² with ethanol yields the corresponding oxo-bridged dimetallic derivatives in high yield. [ZrEt(O₂CR)Cp₂] (R = H, Me, CF₃) is hydrolyzed to [{Zr(O₂CR)Cp₂]₂O}.²⁰⁶ Kinetic studies have been reported for the hydrolysis of [ZrCl₂Cp₂].^{303,304}

Hydrolysis of the dinuclear complexes [(ZrCl₂Cp)₂Y] (Y = SiMe₂, CH₂)³⁰⁵ and [(ZrMe₂Cp)₂(η^5 : η^5 -C₁₀H₈)]³⁰⁶ gives **82** (X = Cl, Y = SiMe₂, CH₂; X = Me, no Y). The structurally characterized Cl derivative **82** (X = Cl, no Y) was obtained from oxidation of [{Zr(μ -Cl)Cp]₂(η^5 : η^5 -C₁₀H₈)] 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

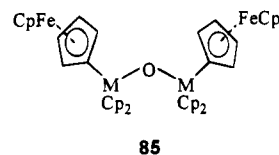


[MH₂Cp^{*}]₂ (M = Zr, Hf) react in a clean stepwise manner with water to afford [MH(OH)Cp^{*}]₂, [(MHCp^{*})₂O], and finally [M(OH)₂Cp^{*}]₂H₂O with evolution of H₂.⁵⁵ The dihydrides react with [M(OH)(X)Cp^{*}]₂ (X = Cl, OH, H) to give [Cp^{*}₂(X)M—O—M(H)Cp^{*}]₂ (M = Zr, Hf).⁵⁵

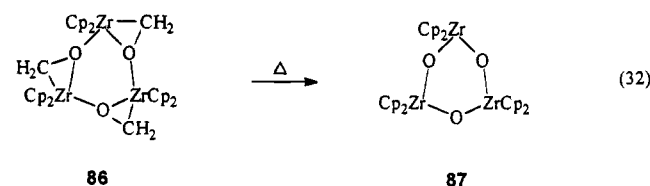
Hydrolysis of **83** gives **84** (M = Mo, W) (eq 31).³⁰⁸ Similarly, [Zr(C₂H₄)(PMe₃)Cp₂] reacts with water with protonation of the ethylene ligand and formation of [(ZrEtCp₂)₂O];²⁰⁶ [ZrEt(OH)Cp₂] is proposed as intermediate.



b. Oxidation. Oxidation of dimethylzirconocene, [(Zr(μ -Cl){(η -C₅H₄)₂SiMe₂)₂], or **42** (R = H) with oxygen (air) gave [(ZrMeCp₂)₂O] (10% yield),³⁰⁹ [(ZrCl{(η -C₅H₄)₂SiMe₂)₂O}] (identified in solution as intermediate),³¹⁰ and **85** (M = Zr, Hf, ca. 30% yield),³¹¹ respectively.



Ph₃PO or CO₂ have been used as oxidizing agents for [{Zr(μ -Cl)Cp]₂{(η -C₅H₄)₂SiMe₂}]₂. O atom abstraction gives **82** (X = Cl, Y = SiMe₂).³¹² Similarly, [{Zr(μ -O)Cp₂]₃] (**87**) was first prepared from [Zr(CO)₂Cp₂] and CO₂.³¹³ Complex **87** was also obtained on thermalolysis of tris(η^2 -formaldehyde)zirconocene (**86**) (eq 32).³¹⁴



Reaction of the Zr(III) complexes [{Zr(μ -Cl)Cp]₂(η^5 : η^5 -C₁₀H₈)] and [Zr(μ -Cl)Cp₂]₂ with [ReO₃Cp^{*}] gives **82** (X = Cl, no Y) and [{Zr(μ -O)Cp₂]₃] (**87**), respectively.³¹⁵

c. Others. Zirconocene dichloride reacts with [WO₃Cp^{*}]⁻ to give the heterobimetallic μ -oxo complex [Cp^{*}WO₃Zr(Cl)Cp₂] in 69% yield.³¹⁶

Photolysis of [Cp₂(Cl)Zr(OCHRCHR')W(CO)₃Cp] (R = R' = H; R = Me, Ph, R' = H; R = R' = Ph) gives [Cp₂(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 $\nu(\text{ZrOZr})$ mode is observed at lower wavenumbers (735, 702 cm^{-1}).³¹⁵ The trimeric complex $[\{\text{Zr}(\mu\text{-O})\text{Cp}_2\}_3]$ exhibits a broad band at 750 cm^{-1} .³¹⁵ In $[\text{Cp}_2(\text{Cl})\text{Zr}-\text{O}-\text{W}(\text{CO})_3\text{Cp}]$ the $\nu(\text{ZrOW})$ mode is observed at 789 cm^{-1} .²³⁴

The FIR and Raman spectra of $[(\text{MFCp}_2)_2\text{O}]$ (M = Zr, Hf) have been reported.³¹⁸

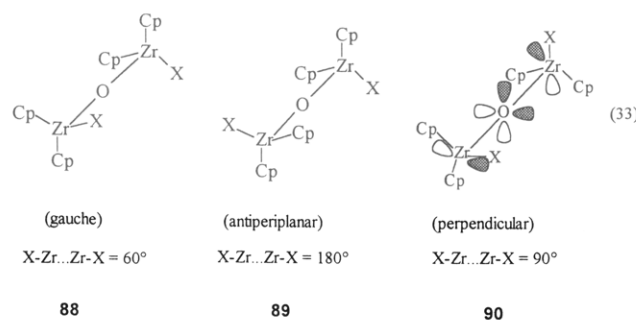
¹⁷O NMR spectra have been reported for $[(\text{MHCp}^*_2)\text{O}]$ (M = Hf, $\delta = 503$, M = Zr, $\delta = 581$ ppm) and $[\{\text{Cp}^*_2(\text{X})\text{Zr}-\text{O}-\text{Zr}(\text{H})\text{Cp}^*_2\}]$ (X = OH, $\delta = 532$, X = Cl, $\delta = 576$ ppm).⁵⁵

The complexes $[\{\text{Zr}(\text{OR})\text{Cp}_2\}_2\text{O}]$ (R = 3- or 4-ClC₆H₄, *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: $[(\text{ZrRCp}_2)_2\text{O}]$ [(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 = SiMe₂, Zr—O 1.944(2) Å, Zr—O—Zr 178.6(1)[°],³⁰⁵ X = Cl, Y = CH₂, Zr—O 1.938(5) Å, Zr—O—Zr 174.3(2)[°],³⁰⁵ X = Cl, Y = (SiMe₂)₂, Zr—O 1.949(3), 1.946(3) Å, Zr—O—Zr 169.8(2)[°],²⁹⁷ X = Cl, Y = (SiMe₂)₃, Zr—O 1.9561(8) Å, Zr—O—Zr 165.2(3)[°],²⁹⁷]. Structural data are also available for the heterodinuclear complex $[\text{Cp}_2(\text{Cl})\text{Zr}-\text{O}-\text{W}(\text{CO})_3\text{Cp}]$ (Zr—O—W 175.7[°]).²³⁴

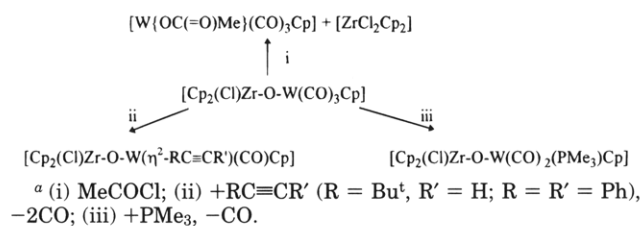
The relatively short Zr—O bond lengths, typically ca. 1.95 Å, indicate the presence of partial double-bond character. Thus, while the conformers **88** and **89** should be sterically favored (eq 33), structures are



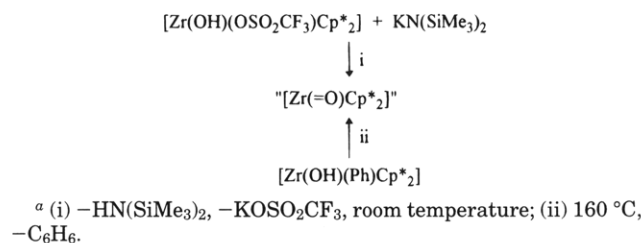
encountered which show a geometry between the extremes **88** and **90**. In **90**, π -interaction of the bridging oxygen lone pairs with the single available metallocene acceptor orbital stabilizes a linear heteroallene-type structure with an angle (X—Zr...Zr—X) of ca. 90°. The only structural exception 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.

The crystal structure of $[\{\text{Zr}(\mu\text{-O})\text{Cp}_2\}_3]$ shows a six-membered, nearly planar ring with Zr—O 1.959(3) Å, O—Zr—O 142.5(2)[°].³¹³

Scheme 24^a

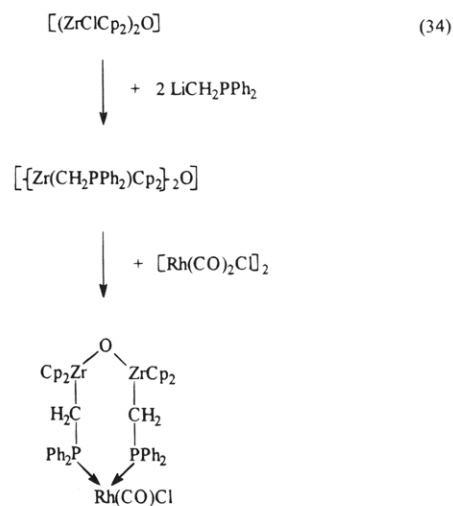


Scheme 25^a



4. Chemical Properties

Introduction of a functionalized alkyl ligand in oxo-bridged zirconocene complexes and further reaction with $[\text{Rh}(\text{CO})_2\text{Cl}]$ have been studied (eq 34).³²⁷



Reactions of $[\text{Cp}_2(\text{Cl})\text{Zr}-\text{O}-\text{W}(\text{CO})_3\text{Cp}]$ with acetyl chloride, alkynes, and PMe₃ have been carried out (Scheme 24).²³⁴ As expected, MeLi reacts with $[\text{Cp}_2(\text{Cl})\text{Zr}-\text{O}-\text{W}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ with substitution of the chloro ligand. The products are thermally more stable than the starting material.²³⁴

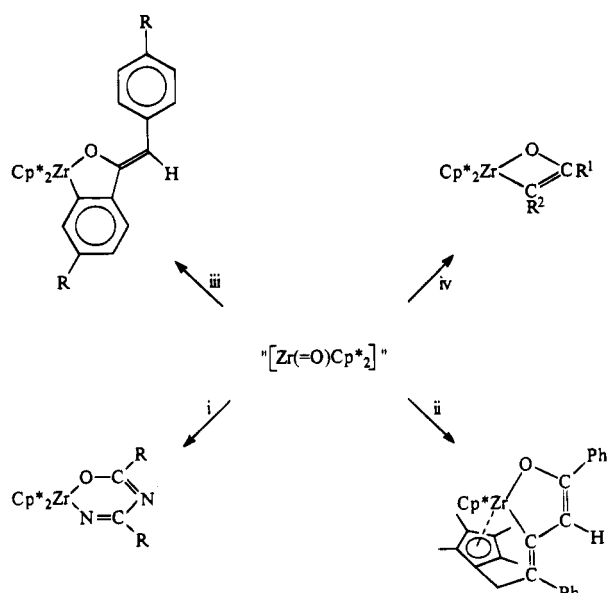
The oxo bridge is cleaved by protic reagents. Thus, $[(\text{ZrRCp}_2)_2\text{O}]$ reacts with acids HX to yield $[\text{ZrR}(\text{X})\text{Cp}_2]$ (R = Cl, Br, OPh, X = Cl; R = Cl, X = F; R = Br, X = NO₃).²⁶³

G. Zirconocene Oxide $[\text{Zr}(=\text{O})\text{Cp}^*_2]$; Generation and Trapping

Unstable $[\text{Zr}(=\text{O})\text{Cp}^*_2]$ 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, R¹C≡CR² (R = H or Me; R¹ = R² = Ph; R¹ = R² = Tol); (iv) R¹C≡CR² (R¹ = R² = Ph; R¹ = Me, R² = 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

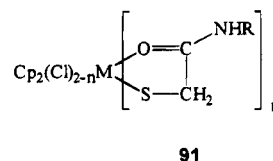
A. Metallocene(IV) Thiolates, Selenates, and Tellurates

1. Synthesis, Spectroscopic, and Chemical Properties

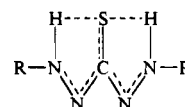
Several of the methods used for the preparation of metallocene(IV) alkoxides and aryloxides are suitable for the synthesis of the corresponding thiolates and selenates. The following synthetic routes have been employed: (a) the triethylamine method, (b) salt elimination, (c) insertion of chalcogens into 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)₂Cp₂] (E = S, Se)³³¹ and [M(SH)₂Cp₂] (M = Ti, Zr)³³² and has been employed for the synthesis of the thiolatoacetamide complexes **91** from [MCl₂Cp₂] and RHNC(=O)CH₂-SH (*n* = 1, 2, M = Hf,³³³ M = Zr,³³⁴ R = Ph, *o*-, *m*-, or *p*-Tol, nap, 3,5-Me₂C₆H₃). 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,

low, orange, or brown and extremely sensitive to hydrolysis.^{333,334}

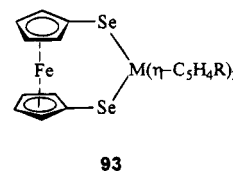


The same preparative method was employed for the synthesis of zirconocene dithizonato complexes. Depending on the stoichiometry of the starting materials [zirconocene dichloride/1,5-diarylthiocarbazono (**92**, R = Ph, *o*- or *p*-Tol, 2- or 4-ClC₆H₄)/triethylamine] the monosubstituted (1/1/1), disubstituted (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



[ZrCl₂Cp₂] reacts with S-containing Schiff bases R=NN=C(SH)SMe [R = PhCH, PhCMe, Ph₂C, C₅H₈, C₆H₁₀, C₆H₄(OH)CH, C₁₀H₈, (OH)CH, MeC₆H₄(OH)-CMe, MeCC(OH)CHCR' (R' = Me, Ph)] in the presence of NEt₃ to yield the corresponding mono- and disubstituted complexes.³³⁶ Similarly, [ZrCl₂Cp₂] reacts with thiosemicarbazones in THF in the presence of NEt₃ or BuNH₂ to give [ZrCl(L)Cp₂] or [ZrL₃-Cp] (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 metalladiselenoferrocenophanes **93** (M = Zr, Hf, R = Bu^t; M = Zr, R = H) from [Fe(η -C₅H₄SeH)₂] and the appropriate metallocene dichloride in boiling toluene in the presence of NEt₃ 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

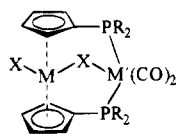


The reaction of [MCl₂Cp₂] (M = Ti, Zr) with substituted thiophenols RSH (R = 4-FC₆H₄, 2,3,5,6-F₄C₆H, C₆F₅) in the absence or presence of a base (NEt₃ or NaNH₂) gave the mono- or disubstituted product, depending on the stoichiometry.³³⁹ Often, mixtures of both compounds were obtained. The nonlinear optical properties have been studied.³³⁹

b. Salt Elimination. While the triethylamine method affords titanocene³⁴⁰ and zirconocene thiolates $[\text{Zr}(\text{EPh})_2\text{Cp}_2]$ ($\text{E} = \text{S}, \text{Se}$) and $[\text{Zr}(\eta^2\text{-}1,2\text{-S}_2\text{R})\text{-Cp}_2]$ ($\text{R} = \text{C}_6\text{H}_4, 4\text{-MeC}_6\text{H}_3, \text{C}(\text{CN})=\text{C}(\text{CN})$)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 $[\text{Hf}(\text{SR})_2\text{Cp}_2]$ ($\text{R} = \text{Ph}, o\text{- or } p\text{-Tol}, 4\text{-NH}_2\text{C}_6\text{H}_4$) 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 biselenato complexes $[\text{M}(\text{SeR}')_2(\eta\text{-C}_5\text{H}_4\text{R})_2]$ in 40–70% yield ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{H}, \text{Bu}^t, \text{R}' = \text{Ph}$;³⁴² $\text{M} = \text{Zr}, \text{R} = \text{Me}, \text{R}' = \text{Bz}, \text{Ph}$;³⁴³ $\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Bu}^t, \text{R}' = p\text{-Tol}$; $\text{M} = \text{Hf}, \text{R} = \text{H}, \text{R}' = p\text{-Tol}$;³⁴⁴ $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{R} = \text{H}, \text{Bu}^t, \text{R}' = \text{Ph}, p\text{-Tol}$ ³⁴⁵). As MeSeLi is not accessible by the reaction of MeLi with selenium, the methyl selenates were prepared via insertion of Se into a $\text{M}-\text{C}$ 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 $[\text{Zr}(\text{SR})_2(\eta\text{-C}_5\text{H}_4\text{R}')_2]$ ($\text{R} = \text{Bz}, \text{R}' = \text{Me}, \text{Bu}^t$) are prepared accordingly from zirconocene dichloride and a mixture of dibenzyl disulfide with LiBET_3H in 89–94% yield.³⁴³

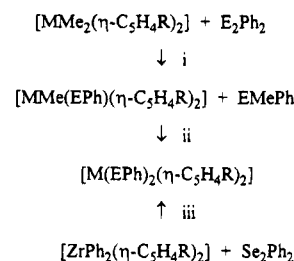
Reaction of the metallocene dichlorides with equimolar amounts of lithium phenylselenate (from PhSeH and BuLi) gave the monoselenato complexes $[\text{MCl}(\text{SePh})\text{Cp}_2]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) in 34–76% yield.³⁴⁶ The zirconium and hafnium complexes are yellow and air sensitive. The products were characterized by ¹H NMR, IR, and mass spectroscopy. The chemical shift of the cyclopentadienyl ligands decreases in the following order $\text{Ti} > \text{Zr} > \text{Hf}$.³⁴⁶

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



94

Phosphine sulfides were introduced into metallocene(IV) complexes by the reaction of $[\text{MCl}_2\text{Cp}_2]$ with LiSPR_2 ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Cy}, \text{Ph}$).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 $[\{\text{M}(\mu\text{-S})\text{Cp}_2\}_2]$ (50–60% yield) (cf. section VI.B.1).¹³⁵ If lithium phosphine selenide is used in the reaction, the corresponding metallocene selenides $[\{\text{M}(\mu\text{-Se})\text{Cp}_2\}_2]$ are formed immediately in over 90% yield.¹³⁵ The phosphine sulfide complexes show a singlet in the ³¹P NMR

Scheme 27^a

^a (i) Heptane; (ii) UV; (iii) UV, $\text{E} = \text{Se}$.

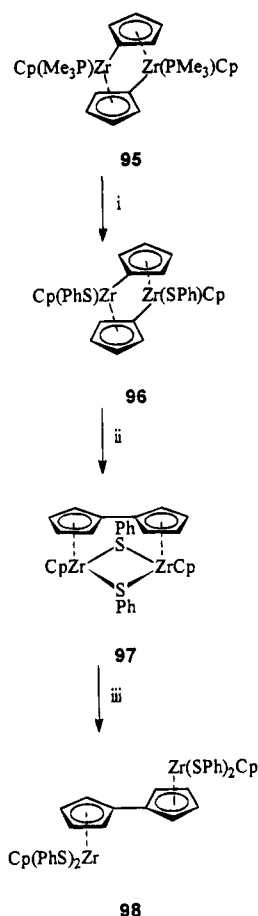
spectrum (25–26 ppm, $\text{M} = \text{Zr}$; 63.5–64.5 ppm, $\text{M} = \text{Hf}$).¹³⁵

c. Insertion of Chalcogens into $\text{M}-\text{C}$ Bonds. Chalcogens readily insert into zirconium- and hafnium-methyl bonds to give $[\text{M}(\text{EMe})_2(\eta\text{-C}_5\text{H}_4\text{R})_2]$ ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{H}, \text{Bu}^t, \text{E} = \text{Se}$;^{342,345} $\text{M} = \text{Zr}, \text{R} = \text{H}, \text{E} = \text{S}, \text{Te}$ ³⁴³). The rate of insertion decreases in the sequence $\text{S} > \text{Se} > \text{Te}$, 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 $[\text{M}(\text{SeR}')_2(\eta\text{-C}_5\text{H}_4\text{R})_2]$ ($\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{H}, \text{R}' = \text{Ph}$; $\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{H}, \text{Bu}^t, \text{R}' = \text{Me}$) exhibit parent ion peaks in the mass spectrum.^{342,345} For the Zr derivatives ($\text{R} = \text{H}, \text{Bu}^t, \text{R}' = \text{Me}, \text{Ph}$) fragmentation with loss of R' is observed, while for the Hf complexes loss of SeR' is favored.³⁴² In the IR spectrum no $\nu(\text{M}-\text{Se})$ mode was assignable.³⁴²

$[\text{HfPh}_2(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2]$ cleanly inserts Se with formation of $[\text{Hf}(\text{SePh})_2(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2]$, while $[\text{HfPh}_2\text{Cp}_2]$ failed to give a clean reaction product.³⁴⁵ $[\text{ZrPh}_2(\eta\text{-C}_5\text{H}_4\text{R})_2]$ ($\text{R} = \text{H}$,³⁴⁵ Me ³⁴³) inserts Se to give $[\text{Zr}(\text{SePh})_2(\eta\text{-C}_5\text{H}_4\text{R})_2]$, while $[\text{ZrPh}_2(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2]$ gives the metallacycle $[\text{Zr}(1,2\text{-Se}_2\text{C}_6\text{H}_4)(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2]$ (cf. section VI.A.2).³⁴⁵ The reaction mixtures ($\text{R} = \text{H}, \text{Me}$) 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 ($\text{M} = \text{Zr}, \text{R} = \text{H}, \text{Bu}^t, \text{E} = \text{Se}$; $\text{M} = \text{Zr}, \text{R} = \text{H}, \text{E} = \text{S}$;³⁴⁸ $\text{M} = \text{Zr}, \text{R} = \text{Bu}^t, \text{M} = \text{Hf}, \text{R} = \text{H}$ 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 $\text{S}_\text{H}2$ substitution at the metal center was proposed as the mechanism.³⁴⁸ Similarly, irradiation of $[\text{MR}'_2(\eta\text{-C}_5\text{H}_4\text{R})_2]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{R} = \text{H}, \text{R}' = \text{Ph}$; $\text{M} = \text{Zr}, \text{Hf}, \text{R} = \text{Bu}^t, \text{R}' = \text{Ph}$; $\text{M} = \text{Hf}, \text{R} = \text{H}, \text{Bu}^t, \text{R}' = p\text{-Tol}$;⁴⁹ $\text{M} = \text{Zr}, \text{R} = \text{Bu}^t, \text{H}, \text{R}' = \text{Ph}$ ¹⁸⁵) in the presence of Se_2Ph_2 gives $[\text{M}(\text{SePh})_2(\eta\text{-C}_5\text{H}_4\text{R})_2]$ and $\text{R}'\text{-R}'$.³⁴⁵

Oxidation of **95** with Ph_2S_2 afforded the thermally unstable zirconium(III) complex **96**, which undergoes reductive coupling of the two bridging $\eta^1, \eta^5\text{-C}_5\text{H}_4$

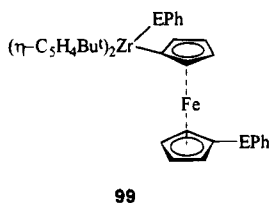
Scheme 28^a

^a (i) S₂Ph₂, -2PMe₃; (ii) Δ; (iii) S₂Ph₂.

rings to give a *cis*-fulvalenezirconium(III) complex **97** in boiling THF.^{306,83} Further oxidation of **97** with Ph₂S₂ gave the bright yellow zirconium(IV) complex **98** (Scheme 28).^{306,83}

Similarly, oxidative addition of disulfides (S₂R₂, R = Et, Ph) to [Zr(CO)₂Cp₂] gives [Zr(SR)₂Cp₂] in 57 and 84% yield, respectively.³⁴⁹ Reaction of [Zr(SPh)₂Cp₂] with the dicarbonyl complex gave the red, dimeric zirconocene(III) complex [$\{\text{Zr}(\mu\text{-SPh})\text{Cp}_2\}_2$] in 64% yield.³⁴⁹

Irradiation of **42** (R = Bu^t) in the presence of E₂-Ph₂ (E = S, Se) yields **99**.¹⁸⁵



With protic reagents [Zr(C₂H₄)(PMe₃)Cp₂] undergoes protonation of the ethylene ligand. Thus, ethanedithiol yields [Cp₂(Et)Zr(μ-SCH₂CH₂S)-Zr(Et)Cp₂]²⁸⁸ and Bu^tSH gives [ZrEt(SBu^t)Cp₂].²⁰⁶ Reaction of the latter with HX (X = HC(=O)O, ac) or ROH (R = Me, Et, Ph) gives [ZrEt(X)Cp₂] and [ZrEt(OR)Cp₂], respectively.²⁰⁶

The electronic structures of the complexes [M(ER)₂(η-C₅H₄R')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-Se₂C₆H₄, R' = Bu^t) and [ZrMe(SePh)(η-C₅H₄Bu^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

⁷⁷Se and ¹³C NMR data are available for [M(SeR)₂(η-C₅H₄R')₂] (M = Zr, Hf, R = Ph, *p*-Tol, R' = H, Bu^t) as well as their titanium analogues.³⁴⁴ In the ⁷⁷Se 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 ⁷⁷Se resonance in [Zr(SeMe)₂Cp₂] (267.2 ppm).³⁴⁴

e. Thermal Rearrangement of α-Zirconocenyl Thioethers. Zirconocene thiolates [Zr{CHR'(SiMe₃)}(SR)-Cp₂] were obtained by thermal rearrangement of α-zirconocenyl thioethers [Zr{CH(SR)(SiMe₃)}(R')-Cp₂] in toluene (R = Ph, R' = Ph, *p*-Tol, 4-MeOC₆H₄, 4-ClC₆H₄,³⁵¹ 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}₂Cp₂] in toluene afforded [Zr(SPh)₂Cp₂] 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)₂Cp₂] (M = Zr, R = Ph;²¹⁸ M = Hf, R = Bu^t)³⁵ have been obtained by solvolysis of [ZrCp₄] and [Hf(NMe₂)₂Cp₂], respectively, with the appropriate thiol. Similarly, the reaction of dimethylzirconocene with alkyl thiols in the presence of trimethylphosphine gave [ZrMe(SCH₂R)Cp₂] (R = Me, Ph,^{354,355} 4-CF₃C₆H₄, 4-ClC₆H₄, 4-MeOC₆H₄, 4-Me₂NC₆H₄)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(η²-SCHR)(PMe₃)-Cp₂].^{354,355} Dibenzyl zirconocene reacts with benzenethiol with formation of [Zr(SPh)₂Cp₂] 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(CH₂)_nSH (n = 2–4), *o*- or *m*-(HSCH₂)₂C₆H₄ were reacted with dimethylzirconocene dimeric complexes [Cp₂Zr(μ-SRS)₂ZrCp₂] (R = (CH₂)_n, n = 2–4; *o*- or *m*-CH₂C₆H₄CH₂) 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(CH₂)_nSSiMe₃ (n = 2, 3) with dimethylzirconocene or zirconocene hydride chloride in 60–67% and 50–55% yield, respectively.³⁵⁸ The molecular structures of [Cp₂Zr(μ-SRS)₂ZrCp₂] [R =

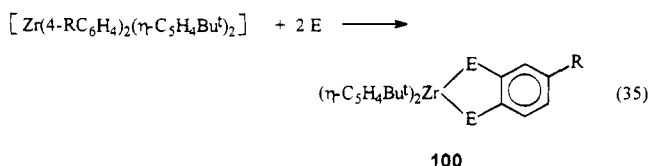
$(\text{CH}_2)_2$, Zr—S 2.56(1), 2.676(8) Å,³⁵⁸ R = $(\text{CH}_2)_3$, Zr—S 2.480(2) to 2.518(2) Å^{357,358}] were determined. These compounds [R = $(\text{CH}_2)_n$, $n = 2$ or 3] act as macrocyclic metalloligands. Thus, the reaction with AgBPh₄ led to encapsulation of the silver ion (30–45% yield). The structures of the resulting cationic complexes have been determined [R = $(\text{CH}_2)_2$, Zr—S 2.560(5) to 2.617(5) Å, Ag—S 2.479(5) to 2.514(5) Å,³⁵⁸ R = $(\text{CH}_2)_3$, 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, R₂C=S (4,4'-dimethoxythiobenzophenone, 4,4'-dimethylthiobenzophenone, 4-methoxythiobenzophenone, thiobenzophenone, 4,4'-bis(dimethylamino)thiobenzophenone, thiocamphor, adamantanethione, 3-thioxoandrost-1,4-dien-17-one), undergo hydrozirconation at room temperature with [$\{\text{ZrCl}(\text{H})\text{Cp}_2\}_n$] to give yellow [$\text{ZrCl}(\text{SCHR}_2)\text{Cp}_2$].³⁵⁹ The products were generated in situ for use in organic synthesis.³⁵⁹

2. Dichalcogenophenylene Metallocenes

Related complexes, reported in 1968, include [$\text{Zr}(1,2\text{-S}_2\text{-4-MeC}_6\text{H}_3)\text{Cp}_2$] and [$\text{Zr}(1,2\text{-S}_2\text{C}_6\text{H}_4)\text{Cp}_2$]³³¹ and the enedithiolates [$\text{Zr}\{\text{SC}(\text{R})=\text{C}(\text{R})\text{S}\}\text{Cp}_2$] (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 = NMe₂, Br³⁶⁴) 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



A more general route to dichalcogenophenylene metallocenes [$\text{M}(1,2\text{-E}_2\text{C}_6\text{H}_4)(\eta\text{-C}_5\text{H}_4\text{R})_2$] 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 S³⁴¹). [$\text{Hf}(1,2\text{-S}_2\text{-4-MeC}_6\text{H}_3)\text{Cp}_2$] was prepared accordingly.³⁴¹ These complexes are more air stable than the corresponding dithiolato complexes. The related *cis*-1,2-enedithiolato complex [$\text{Hf}\{\text{S}_2\text{C}_2(\text{CN})_2\}\text{Cp}_2$] was obtained by the same method in 78% yield.³⁴¹

The mixed *o*-thiatelluraphenylene zirconocene complexes, [$\text{Zr}(1\text{-S-2-TeC}_6\text{H}_4)(\eta\text{-C}_5\text{H}_4\text{R})_2$] (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

Table 4. Activation Parameters for [$\text{M}(1,2\text{-E}_2\text{-4-R'C}_6\text{H}_3)(\eta\text{-C}_5\text{H}_4\text{R})_2$]

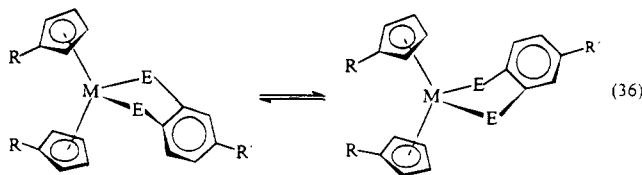
M	E	R	R'	ΔG^\ddagger (kJ/mol)	T (°C)	ref
Zr	S	H	H or Me		< -80	331
Hf	S	H	H	44.8	-64	341
Hf	S	H	Me	46.8	-54	341
Zr	Se	H	H		< -80	365
Hf	Se	H	H		-75	365
Hf	Te	H	H	48	-50	366
Zr	S	Bu ^t	H	44	-45(Cp)	363
Zr	Se	Bu ^t	H	48	-35(Cp)	363
Zr	Te	Bu ^t	H	51	-30(Cp)	363
				49	-40(Bu ^t)	363
Zr	S	Bu ^t	OMe	48	-30(Cp)	363
Zr	Se	Bu ^t	OMe	49	-30(Cp)	363
				49	-50(Bu ^t)	363

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

When metallocene dichlorides [$\text{MCl}_2(\eta\text{-C}_5\text{H}_4\text{R})_2$] 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, SiMe₃) the dimeric chelate complexes [$\{(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Zr}\}_2(\mu\text{-1,2,4,5-S}_4\text{C}_6\text{H}_2)$] (M = Ti, Zr, Hf, R = H,³⁶⁸ SiMe₃³⁶⁹) were obtained in 35–67% yield.

b. Spectroscopic Properties. ⁷⁷Se NMR data are available for **100** [E = Se¹, Se², (R = H) 562.9 ppm; (R = Me) 574.5 (Se¹), 568.8 ppm (Se²)].^{344,362}

Variable-temperature ¹H NMR indicates that the five-membered ME₂C₂ 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 [$\text{Hf}\{\text{S}_2\text{C}_2(\text{CN})_2\}\text{Cp}_2$] shows only one resonance for the Cp protons even at -90 °C.³⁴¹

Negative chemical ionization (NCI) mass spectra have been recorded for [$\text{Zr}(\text{EPH})_2(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2$] (E = Se, Te), which show very little fragmentation.³⁷⁰ Complexes [$\{(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Zr}\}_2(\mu\text{-1,2,4,5-S}_4\text{C}_6\text{H}_2)$] (R = H) are insoluble in common organic solvents, but molecular ions were observed in the mass spectrum.³⁶⁸ For the more soluble derivatives (R = SiMe₃, M = Ti,³⁶⁸ Zr, Hf³⁶⁹) 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 MS₂C₂ 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-Se₂C₆H₄)(η-C₅H₄Bu^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-S₂C₆H₄)Cp₂]³⁷¹ (46°), the ethylene-1,2-dithiolato complex [Ti{SC(H)=C(H)S}—Cp₂]³⁷² (46.1°) and the tetrathiolato complex [Cp₂Ti(S₂C=CS₂)TiCp₂]³⁷³ (46°), while comparable molybdocene and tungstocene complexes show much smaller angles (2.6–9°).^{374–376}

The molecular structure of [Zr(1-S-2-TeC₆H₄)(η-C₅H₄Bu^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 [(η-C₅H₄R)₂Zr]₂(μ-1,2,4,5-S₄C₆H₂) (M = Ti, Hf, R = SiMe₃) shows the presence of the chair conformation in the solid state.³⁶⁹ The dihedral angle (MS₂/S₂C₂) 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

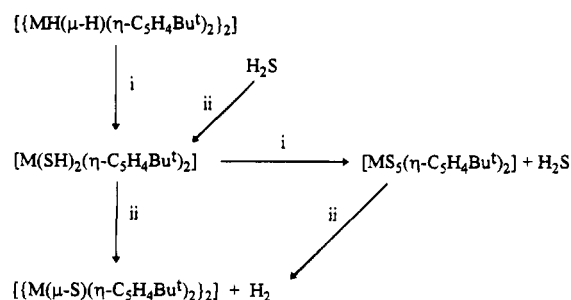
Several routes have been employed for the synthesis of chalcogenido-bridged bimetallic complexes: (a) classical metathetical reactions of metallocene dichlorides and chalcogenides, (b and c) reaction of a highly reactive organometallic species with elemental chalcogen, (d) replacement of chalcogen-containing 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(μ-E)(η-C₅H₄R)₂]₂] (M = Zr, Hf, R = H, Bu^t, E = S, Se;^{379,301} M = Zr, Hf, R = Me, E = S, Se³⁷⁹). The required anhydrous nucleophilic species, E²⁻, 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 (LiSePR₂, R = Cy, Ph) the complexes [(M(μ-Se)Cp₂)]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 bimetallic cyclic compounds [(M(μ-E)(η-C₅H₄R)₂]₂, in 40–79% yield (M

Scheme 29^a

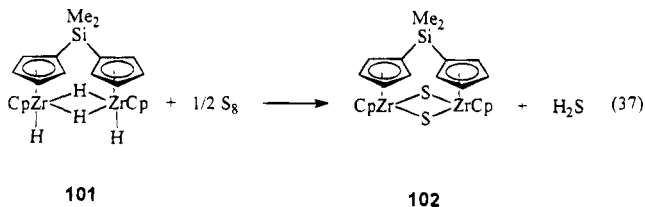


^a (i) S; (ii) [(MH(μ-H)(η-C₅H₄Bu^t)₂]₂.

= 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

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 H₂ and H₂S) were detected by ¹H NMR.³⁸¹ The bissulfanido complexes [M(SH)₂(η-C₅H₄Bu^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

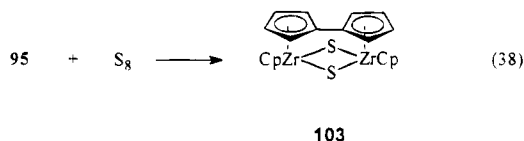
When the dinuclear zirconocenophane complex **101** was reacted with sulfur, only the sulfido-bridged product **102** was obtained in 39% yield (eq 37).³¹² Alternatively, **102** was obtained on refluxing a solution of [(ZrMe₂Cp)₂(η-C₅H₄)₂SiMe₂] and sulfur for 12 h.³¹² The sulfido bridges in **102** resist cleavage with PMe₃, MeNC, and pyridine.³¹²



c. **From Metallocene(II) Precursors.** [Zr(butadiene)(η-C₅H₄R)₂] (R = Bu^t, 1,1-dimethylpentyl) reacted with stoichiometric amounts of sulfur, gray selenium, or tellurium to give the complexes [(Zr(μ-E)(η-C₅H₄Bu^t)₂)]₂ (E = S, Se³⁸² Te^{300,383}) and [(Zr(μ-Te)(η-C₅H₄R)₂)]₂ (R = 1,1-dimethylpentyl)³⁸³ in 35–50% yield.

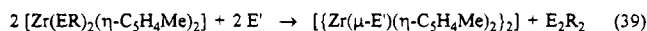
Oxidation of **95** with elemental sulfur resulted in reductive coupling of the two bridging η¹,η⁵-C₅H₄ rings to give the *cis*-fulvalenezirconium(IV) complex **103** in 40% yield (eq 38).³⁰⁶ The bright-red complex

103 was also obtained from the reaction of $[\{\text{ZrMe}_2\text{-Cp}\}_2(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)]$ or $[\{\text{Zr}(\mu\text{-SPh})\text{Cp}\}_2(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)]$ with sulfur.³⁰⁶

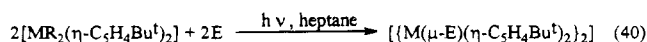


The reaction of $[\text{Zr}(\text{CO})_2(\eta\text{-C}_5\text{R}_5)_2]$ ($\text{R} = \text{H, Me}$) with H_2S or H_2Se in toluene at 80°C over 3–8 days in a 1:1 ratio gave air-stable $[\{\text{Zr}(\mu\text{-S})(\eta\text{-C}_5\text{R}_5)_2\}_2]$ (79%, $\text{R} = \text{H}$; 46%, $\text{R} = \text{Me}$)²⁹³ and $[\{\text{Zr}(\mu\text{-Se})(\eta\text{-C}_5\text{R}_5)_2\}_2]$ (50–62% yield, $\text{R} = \text{H, Me}$)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; $\text{E} = \text{Se, R} = \text{Bz, Ph, E}' = \text{S}$; $\text{E} = \text{Se, R} = \text{Bz, E}' = \text{Se}$; $\text{E} = \text{S, R} = \text{Bz, E}' = \text{S}$).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



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 ($\text{M} = \text{Zr, Hf, R} = \text{Me, Ph, E} = \text{Se}$,^{379,384} S ;³⁷⁹ $\text{M} = \text{Zr, R} = \text{Ph, E} = \text{Se}$,^{344,345} $\text{M} = \text{Hf, R} = p\text{-Tol, E} = \text{Se}$ 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 $[\{\text{M}(\text{SePh})_2(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2]$.³⁸⁴



Thermally induced dimerization of metallocene dithiols $[\text{M}(\text{SH})_2(\eta\text{-C}_5\text{H}_4\text{R})_2]$ with loss of hydrogen sulfide gives $[\{\text{M}(\mu\text{-S})(\eta\text{-C}_5\text{H}_4\text{R})_2\}_2]$ and was observed to occur fairly readily when $\text{R} = \text{H}$ ($\text{M} = \text{Zr, Hf}$),³⁸⁵ while the reaction of the species with $\text{R} = \text{Bu}^t$ needed more drastic conditions (boiling toluene, 30 h).³⁸¹

Monitoring of the thermolysis of the cationic complex $[\text{Zr}(\text{SBU}^t)(\text{THF})\text{Cp}_2][\text{BPh}_4]$ in THF- d^8 at 97°C by ^1H NMR showed the formation of $[\{\text{Zr}(\mu\text{-S})\text{Cp}_2\}_2]$ and products due to decomposition of $[\text{Bu}^t][\text{BPh}_4]$.³⁸⁶

Thermolysis of $[\text{Zr}\{\eta^2\text{-S}_2\text{CP}(\text{SiMe}_3)_2\}(\text{Cl})\text{Cp}_2]$ gives $[\{\text{Zr}(\mu\text{-S})\text{Cp}_2\}_2]$.¹³⁴ The same product is obtained from

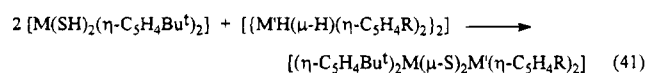
$[\text{Zr}\{\text{P}(\text{SiMe}_3)_2\}_2\text{Cp}_2]$ or $[\text{ZrMe}\{\text{P}(\text{SiMe}_3)_2\}\text{Cp}_2]$ and elemental sulfur in low yield.¹³⁴

2. Mixed Species

a. Mixed-Chalcogenido Ligands. UV irradiation of the oxo-bridged complex $[\{\text{ZrMe}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2\text{O}]$ in the presence of sulfur or gray selenium in toluene gave the mixed chalcogenido-bridged complexes $[\{\text{ZrMe}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2(\mu\text{-O})(\mu\text{-E})]$ ($\text{E} = \text{S}$,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

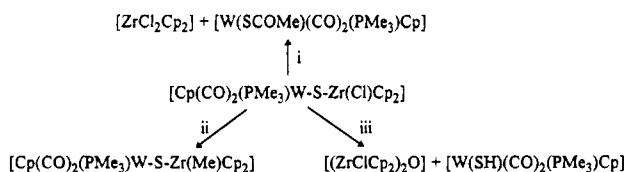
Controlled hydrolysis of $[\{\text{Zr}(\mu\text{-Te})(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2]$ with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ afforded the green complex $[\{\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2(\mu\text{-O})(\mu\text{-Te})]$ in 60% yield.³⁰⁰ At ambient temperature 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 $\text{M-C}_5\text{H}_4\text{Bu}^t$ rotation was estimated to be $\Delta G^\ddagger(206\text{ K}) \approx 40.2 \pm 1.5\text{ kJ mol}^{-1}$.³⁰⁰ Similar dynamic NMR spectra were observed for the selenido analogue ($\Delta G^\ddagger(222\text{ K}) \approx 46.1 \pm 1.5\text{ kJ mol}^{-1}$).³⁰⁰

b. Heterobimetallic and Unsymmetrical Complexes. A facile synthesis of sulfido-bridged bimetallic species or unsymmetrically substituted complexes is shown in eq 41 ($\text{M} = \text{M}' = \text{Zr, R} = \text{H}$; $\text{M} = \text{Hf, M}' = \text{Zr, R} = \text{H, Bu}^t$; $\text{M} = \text{Zr, M}' = \text{Hf, R} = \text{H, Bu}^t$).³⁴³ The products are red, blue, or green, have high melting points ($>210^\circ\text{C}$), 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 $\text{M} = \text{M}' = \text{Zr}$ and $\text{R} = \text{H}$.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



The thermal stability of some derivatives (eq 41; $\text{M} = \text{M}' = \text{Zr, R} = \text{H}$; $\text{M} = \text{Hf, M}' = \text{Zr, R} = \text{H, Bu}^t$) 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 $[\{\text{Zr}(\mu\text{-S})(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2]$, $[\{\text{Zr}(\mu\text{-S})\text{Cp}_2\}_2]$ 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 $\text{M}=\text{S}$ double bond, which dimerize to give the observed products.³⁴³

The tungsten–zirconium complex *cis*- $[\text{Cp}(\text{CO})_2\text{-}(\text{PMe}_3)\text{W-S-Zr}(\text{Cl})\text{Cp}_2]$, which contains a single unsupported $\text{M-S-M}'$ linkage, was prepared by introducing 1 equiv of propylene sulfide into a mixture of $\text{Li}[\text{W}(\text{CO})_2(\text{PMe}_3)\text{Cp}]$ and $[\text{ZrCl}_2\text{Cp}_2]$. One

Scheme 30^a

^a (i) MeCOCl; (ii) MeLi; (iii) 0.5 H₂O.

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 [$\{\text{M}(\mu\text{-Te})(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2$] 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 [$\{\text{Zr}(\mu\text{-Te})(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2$], 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—C₅H₄—Bu^t rotation could not be determined.³⁰⁰

⁷⁷Se NMR data are available for [$\{\text{Zr}(\mu\text{-Se})(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2$] (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 M₂E₂ 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 [$\{\text{Zr}(\mu\text{-Te})(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2$]].³⁰⁰ The presence of a SiMe₂ group bridging two cyclopentadienyl ligands has only a minor effect on the central Zr₂S₂ core (dihedral angle 4.1°).³¹² The geometry of the Zr₂S₂ core of the fulvalene complex [$\{\text{Zr}(\mu\text{-S})\text{Cp}\}_2(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)$]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, [$\{\text{Zr}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2(\mu\text{-O})(\mu\text{-Te})$] exhibits a considerably distorted arrangement.³⁰⁰

The heterobimetallic complex *cis*-[Cp(CO)₂(PMe₃)-W—S—Zr(Cl)Cp₂] 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 [Zr(SCPh=CPh)Cp*₂] [Zr—S 2.505-(1) Å] and [Zr(=S){4-Bu^t(NC₅H₄)₂Cp*₂}] [Zr—S 2.316 Å] were structurally characterized.

D. Metallocene(IV) Complexes with Polychalcogenido Ligands

1. Synthesis

The complexes [MS₅Cp₂] (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)₂Cp₂] 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 Li₂S₂/3S 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, [MS₅(η-C₅H₄Bu^t)₂] (M = Zr, Hf) was formed when (i) [MPh₂(η-C₅H₄Bu^t)₂] is photolyzed in the presence of excess sulfur,³⁷⁹ (ii) when [MH(μ-H)(η-C₅H₄Bu^t)₂] is treated with excess sulfur (cf. Scheme 29),^{380,381} or (iii) when [Zr(butadiene)(η-C₅H₄Bu^t)₂] is reacted with excess sulfur (cf. section VI.B.1.c).³⁸² Alternatively, the pentasulfido complexes [MS₅Cp₂] (M = Ti, Zr, Hf) (50–60% yield),³³² [MS₅(η-C₅H₄Bu^t)₂] (M = Zr, Hf) (48–71% yield),³⁷⁹ and [ZrS₅{(η-C₅H₄)₂SiMe₂}] (14% yield)³⁸⁸ are accessible by treatment of the appropriate metallocene dichloride with a mixture of LiBEt₃H and sulfur (2:5). The pentasulfido complex [ZrS₅(η-C₅H₄Bu^t)₂] reacts with the starting material (metallocene dihydride or butadiene complex) to give [$\{\text{Zr}(\mu\text{-S})(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2\}_2$].^{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, Na₂Se_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



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

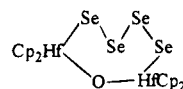
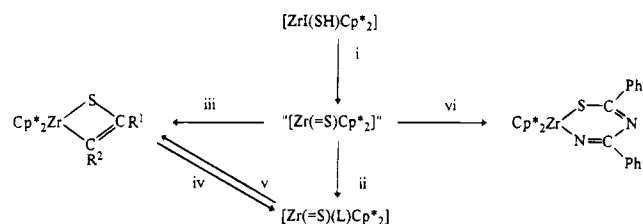


Table 5. Selected Structural Parameters for Chalcogenido-Bridged Dimetallic Complexes

compound	M-E (Å)	E-M-E (deg)	M-E-M (deg)	ref(s)
[{Zr(μ -Te)(η -C ₅ H ₄ Bu ^t) ₂ } ₂]	2.855(1)	89.14(1)	90.86(1)	300,383
[{Zr(μ -S)Cp ₂ } ₂]	2.487(2), 2.480(2)	89.5(2)	90.5(2)	134
[{Zr(μ -S)Cp ₂ } ₂]	2.490(3), 2.482(3)	89.6(1)	90.4(1)	293
[{Zr(μ -S)Cp ₂ } ₂ (η^5 - η^5 -C ₁₀ H ₈)]	2.490(1)	87.85(1)	86.60(3)	306
[{Zr(μ -S)Cp ₂ } ₂ (η -C ₅ H ₄) ₂ SiMe ₃]	2.488(1)	89.87(4)	90.06(4)	312
[{Zr(η -C ₅ H ₄ Bu ^t) ₂ } ₂ (μ -O)(μ -Te)]	2.880(1) (E=Te)	84.4(3)	72.1(1) (E=Te)	300
	1.967(7) (E=O)		119.2(2) (E=O)	
<i>cis</i> -[Cp(CO) ₂ (PMe ₃)W-S-Zr(Cl)Cp ₂]	2.418(1)		132.42(4)	387

Scheme 31^a

^a (i) +KN(SiMe₃)₂, room temperature, -KI, -HN(SiMe₃)₂; (ii) L, L = py, 4-*tert*-butylpyridine; (iii) EtC≡CET, R¹ = R² = Et; (iv) +L, L = py, 4-*tert*-butylpyridine, -R¹C≡CR², R¹ = R² = Et, R¹ = R² = Ph, R¹ = R² = *p*-Tol; (v) +R¹C≡CR², R¹ = R² = Et, R¹ = R² = Ph, R¹ = R² = *p*-Tol, 85 °C, -L, L = py, 4-*tert*-butylpyridine; (vi) PhCN.

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 [MS₃Cp*₂] was observed when the bis(pentamethylcyclopentadienyl)metal dichlorides were reacted with sulfur in the presence of LiBEt₃H (M = Ti, Zr, Hf)³⁸⁵ or with Li₂S₂/S₈ (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 2LiBEt₃H/5S has been shown to contain the polysulfide ions S_x²⁻ (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 [ZrS₅(η -C₅H₄R)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(μ -Se)(η -C₅H₄Me)₂}₂] with excess sulfur gave the corresponding zirconocene pentasulfide.³⁴³

The reaction of zirconocene dichloride with Na₂S₅ and (NH₄)₂S₅ is reported to give the polymeric products [{ZrS₃Cp_n}_n] and [{Zr₂S₇Cp₂}_n], respectively.³⁹² Also, treating [Zr(SH)₂Cp₂] with sulfur gave the polymeric product [{ZrS₅Cp_n}_n]. The products do not contain ZrCp₂ groups.³⁹²

2. Spectroscopic Properties

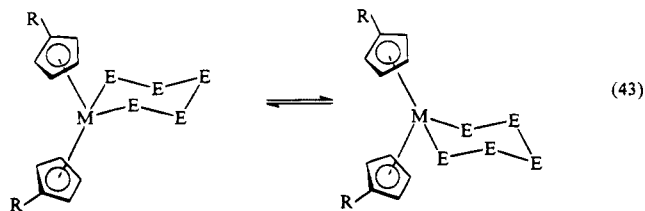
a. Mass Spectra. The pentasulfido, pentaselenido, and trisulfido complexes show a molecular ion peak in the mass spectrum. While the first two show

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

	ΔG^\ddagger (kJ mol ⁻¹)	ref(s)
	[MS ₅ Cp ₂]	
M = Zr	(227 K) 48.6	385,332
M = Hf	(257 K) 58.0	385,332
	[MS ₅ (η -C ₅ H ₄ Bu ^t) ₂]	
M = Zr	(243 K) 51.6 (C ₅ H ₄)	379
	(239 K) 52.7 (Bu ^t)	
M = Hf	(283 K) 61.2 (C ₅ H ₄)	379
	(277 K) 61.3 (Bu ^t)	
	[MSe ₅ Cp ₂]	
M = Zr	49.9	385
M = Hf	61.6	385
	[MS ₃ Cp* ₂]	
M = Zr	39.3	385,391
M = Hf	<30	385

metastable ion peaks corresponding to loss of S₂ or Se₂, the trisulfido complexes do not.³⁸⁵

b. Variable-Temperature NMR Studies. It was shown earlier that the complexes [MS₅Cp₂] undergo chair-to-chair ring flipping (eq 43).^{332,393,394} Thus, at



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 ΔG^\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 (ΔG^\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 [TiS₅Cp₂] has been known since 1971³⁹⁵ (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, Hf³⁸⁹). 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(η²-S₂-

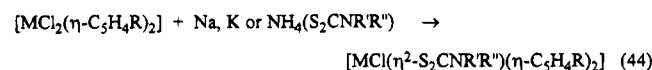


Table 7. Abbreviations Used in Eq 44

M	R	R'	R''	ref(s)
Zr,Hf	H,Me	Bz	Bz	401
Zr	Me	H	Ph, <i>o</i> -, <i>m</i> -, <i>p</i> -Tol, 2-, 3-, 4-ClC ₆ H ₄ , 4-MeOC ₆ H ₄ , 2-, 4-EtOC ₆ H ₄ , 4-BrC ₆ H ₄ , 4-IC ₆ H ₄	402
Zr ^a	H,Me	H	P(=S)OEt ₂	403
Hf	H	H	cyclopentyl or cycloheptyl	404
Hf	H	Et	<i>m</i> -Tol	404
Zr	H	H	cyclopentyl or cyclohexyl	405
Zr	H	Et	<i>m</i> -Tol	405
Zr ^a	H,Me	H	P(=O)(OEt) ₂	406
Zr	H	Cy	Me,Et,Pr ⁱ	407
Zr	H	H	<i>o</i> -, <i>m</i> -, <i>p</i> -Tol, Ph, 2-, 3-, 4-ClC ₆ H ₄ , 4-MeOC ₆ H ₄ , 4-EtOC ₆ H ₄ , 4-BrC ₆ H ₄ , 4-IC ₆ H ₄	408
Zr	H	Me	Me	409, 410
Zr	H	Bz	Bz	411
Zr	H	NR'R''	= pyrrolidino, piperidino	412
Zr	<i>b</i>	Me	Me	413
Zr	<i>b</i>	Et	Et	413
Zr	<i>b</i>	Pr ⁱ	Pr ⁱ	413
Zr	<i>b</i>	H	Ph, <i>o</i> -, <i>m</i> -, <i>p</i> -Tol, 2-, 3-, 4-ClC ₆ H ₄ , 4-BrC ₆ H ₄ , 4-IC ₆ H ₄ , 4-MeOC ₆ H ₄	414

^a Also Zr(η⁵-indenyl)₂. ^b η⁵-Fluorenyl instead of Cp.

CNR'₂(X)(η-C₅H₄R)₂] (R = H, Me, X = Cl, R' = Me, Et;³⁹⁹ R = H, X = Me, R' = Me, Et⁴⁰⁰) were prepared accordingly. The zirconocene silyl complexes [MCl(SiMe₃)Cp₂] (M = Zr, Hf) reacted with NaS₂CNEt₂

to give a silyl dithiocarbamato complex (cf. section II.D.3).¹² The monothiocarbamato complex [ZrCl(SOCNMe₂)Cp₂] was prepared according to eq 44 from zirconocene dichloride and the appropriate sodium salt.²⁷⁸

Substituted dithiocarbamato complexes can be obtained by reacting the appropriate zirconocene derivative [ZrCl(X)Cp₂] with sodium dithiocarbamate. Thus, complexes [Zr(η²-S₂CNMe₂)(X)Cp₂] (X = CH₂-SiMe₃, CH₂CMe₂Ph, 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, HS₂CNH(NHPh)-H₂NNHPh, also reacted with [ZrCl₂L₂] (L = Cp, η-C₅H₄Me, η⁵-indenyl, η⁵-pyrrolyl) with formation of [ZrCl{η²-S₂CNH(NHPh)}L₂], which contains a dithiocarbamato group.⁴¹⁵

Insertion of CS₂ into the Zr—P bond of [Zr{P(SiMe₃)₂}(X)Cp₂] (X = Cl, Me) yielded [Zr{η²-S₂CP(SiMe₃)₂}(X)Cp₂]. The ligand can be regarded as the P-analogue of a dithiocarbamato ligand (cf. section IV.A.4).⁹⁷

[ZrCl₂Cp₂] reacts with dipotassium dithiooxalate (dto) to give [(ZrClCp₂)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}

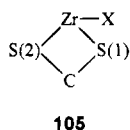
The related complexes [Zr(η²-S₂COR)₃Cp] (R = Me, Et) have been prepared from [ZrCl₂Cp₂] and sodium alkyl xanthates.⁴¹⁸

2. Structural Data

Crystal structures have been determined for [Zr(η²-S₂CNR₂)(X)Cp₂] (X = Cl, R = Et;⁴¹⁰ X = OPh, R = Me;⁴¹⁹ X = Cl, R = Bz,^{401,411} X = SiMe₃, R = Et¹²), the related [ZrCl{η²-S₂CP(SiMe₃)₂}Cp₂],⁹⁷ and the monothiocarbamato complex [ZrCl(SOCNMe₂)Cp₂].²⁷⁸

For the dithiocarbamato complexes, the endocyclic parameters of the ZrS₂X 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 NC₂ 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.



In $[\text{ZrCl}(\text{SOCNMe}_2)\text{Cp}_2]$ [$\text{Zr}-\text{S}$ 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 $\text{Zr}-\text{O}$ bond [2.249(4) Å] is long, indicating considerable crowding.²⁷⁸

3. Spectroscopic Properties

The alkyl- and arylthiocarbamate 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 non-electrolytes (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 dithiocarbamate ligand. One medium to strong band in the range 960–1020 cm^{-1} [$\nu(\text{C}-\text{S})$] indicates the presence of a four-membered ZrS_2C ring. The strong thioureide band [$\nu(\text{C}-\text{N})$] in the range 1495–1525 cm^{-1} is characteristic for dithiocarbamate complexes. This absorption lies between that for $\nu(\text{C}-\text{N})$ (1200–1350 cm^{-1}) and $\nu(\text{C}=\text{N})$ (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 $\nu(\text{Zr}-\text{S})$. $\nu(\text{Zr}-\text{Cl})$ lies in the range 360–390 cm^{-1} .

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

In the monothiocarbamate complex $[\text{ZrCl}(\text{SOCNMe}_2)\text{Cp}_2]$ the $\nu(\text{CN})$ and $\nu(\text{CO})$ modes are observed at 1568, $\nu(\text{CS})$ at 939, and $\nu(\text{ZrO})$ and $\nu(\text{ZrS})$ 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 $\text{Ti} > \text{Zr} > \text{Hf}$ for $[\text{MCl}(\eta^2-\text{S}_2\text{CNBz}_2)(\eta-\text{C}_5\text{H}_4\text{R})_2]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{R} = \text{H}, \text{Me}$).⁴⁰¹ The peak for the $\text{N}-\text{H}$ 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 dithiocarbamate protons in the ^1H NMR spectra at 30 °C.³⁹⁹ This geometry is unprecedented and unlikely for steric

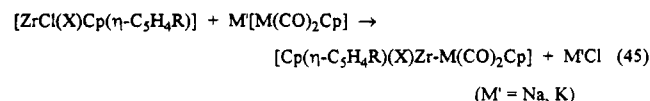
reasons, and it was shown that the complexes are fluxional at 30 °C leading to the observance of single resonances.^{409,410} The fluxionality of $[\text{Zr}(\eta^2-\text{S}_2\text{CNMe}_2)(\text{X})\text{Cp}_2]$ ($\text{X} = \text{Cl}, ^{409,410} \text{Br}, \text{I}, \text{Me}, \text{Bz}, \text{OPh}, \text{CH}_2-\text{SiMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}, 4\text{-pyridyloxy}, 2,6\text{-dimethylphenoxy}$)⁴⁰⁹ and the *N,N*-dimethylthiocarbamates $[\text{Zr}(\text{SOCNMe}_2)(\text{X})\text{Cp}_2]$ ($\text{X} = \text{Cl}, 4\text{-pyridyloxy}$) 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 ($\Delta G^\ddagger(298 \text{ K}) = 50\text{--}80 \text{ kJ mol}^{-1}$). The kinetic data are also similar to those of organic dithiocarbamates. Thus, an exchange mechanism involving rotation about the $\text{C}-\text{N}$ bond was assumed. Preliminary rupture of one $\text{Zr}-\text{S}$ bond was not ruled out.^{409,410,413,414}

c. Electronic Spectra. The electronic spectra of dithiocarbamate 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 $\text{Zr}-\text{M}$ or $\text{Hf}-\text{M}$ Bonds ($\text{M} = \text{Transition Metal}$)

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, $\text{X} = \text{Cl}, \text{Me}, \text{OBU}^t, \text{R} = \text{H}, \text{M} = \text{Ru}, \text{Fe}$;⁴²⁰ $\text{X} = \text{Me}, \text{Cl}, \text{octyl}, \text{R} = \text{H}, \text{M} = \text{Fe}$;⁴²¹ $\text{X} = \text{OBU}^t, \text{R} = \text{PPh}_2, \text{M} = \text{Fe}$;⁴²² yields range from 58 to 83%). The derivatives $\text{X} = \text{Me}, \text{OBU}^t, \text{R} = \text{H}, \text{M} = \text{Ru}$ were also obtained from the reaction of the corresponding chloro complex with MeLi or KOBU^t , respectively.⁴²⁰

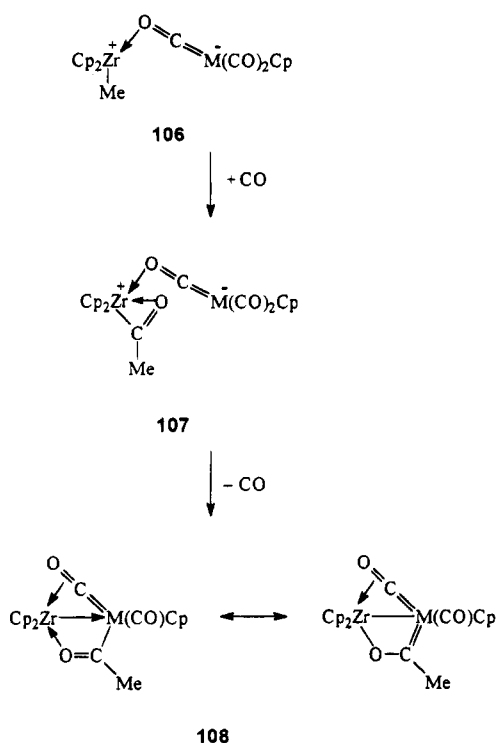


Reactions with carbonyl complexes can result in $\text{M}-\text{M}'$ or $\text{M}-\text{O}-\text{C}-\text{M}'$ linkage, whereby the bonding mode is determined by steric effects. Thus, the low steric requirements of the $\text{M}(\text{CO})_2\text{Cp}$ fragments ($\text{M} = \text{Fe}, \text{Ru}$) allow $\text{M}-\text{M}'$ bond formation,⁴²⁰⁻⁴²² whereas with the more crowded $\text{M}(\text{CO})_3\text{Cp}^-$ anion, $\text{Zr}-\text{O}$ bonding to give **106** is favored ($\text{M} = \text{Mo}$,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}

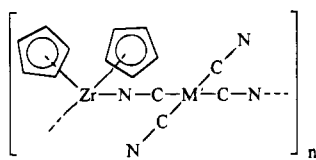
The metallacycle $[\text{Zr}\{\text{C}(\text{SiMe}_3)=\text{CPhCPh}=\text{C}(\text{SiMe}_3)\}\text{Cp}_2]$ reacts with $[\text{WH}(\text{CO})_3\text{Cp}]$ at 70 °C in toluene to give the adduct $[\text{Cp}_2\text{Zr}\{\text{C}(\text{SiMe}_3)=\text{CHPh}\}\{\text{OC}-\text{W}(\text{CO})_2\text{Cp}\}]$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

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

Scheme 32

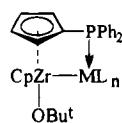


(II) is reported to produce two bimetallic complexes with Zr—Fe bonds.⁴²⁹



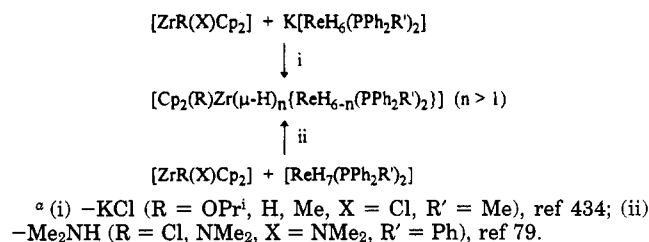
109

When [ZrCl(OBu^t)Cp(η-C₅H₄PPh₂)] 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

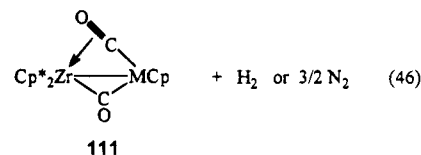
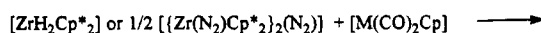
Reaction of [ZrI₂Cp₂] with 2 equiv of K[Ru(CO)₂Cp] gave the orange disubstitution product [Cp₂Zr{Ru(CO)₂Cp}₂] in 90% yield.²³¹ The monosubstituted product was observed as an intermediate by ¹H NMR.²³¹ The corresponding reaction with [ZrCl₂Cp₂] was much slower, and significant amounts of [Ru(CO)₂Cp]₂ were formed.²³¹ However, the Fe analogue [Cp₂ZrCl{Fe(CO)₂Cp}] was obtained by reacting [ZrCl₂Cp₂] with Na[Fe(CO)₂Cp].⁴²¹ The more soluble alkyl derivatives [Cp₂ZrR{Fe(CO)₂Cp}] (R = Me, octyl) have been prepared analogously.⁴²¹ The Fe complex

Scheme 33^a

is not accessible via the reaction of [ZrI₂Cp₂] 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 [ZrI₂Cp*₂] with 2 equiv of Na[Fe(CO)₂Cp] or of [{Zr(N₂)Cp*₂]₂(N₂)] 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.

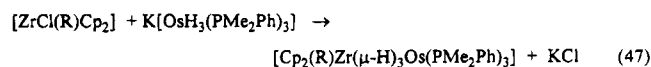
When the dianion Fe(CO)₄²⁻ was reacted with [ZrR(X)Cp₂] (R = Me, X = Cl; R = octyl, X = BF₄) the disubstituted Fe(CO)₄ complexes *cis*-[Fe(CO)₄(ZrRCp₂)₂] were obtained.⁴³⁰ The reaction of Na₂[Fe(CO)₄] with hafnocene dichloride or diiodide gave the dark-brown dimeric complex [Cp₂Hf{Fe(CO)₄}]₂, which contains a four-membered Hf—Fe—Hf—Fe ring.⁴³¹

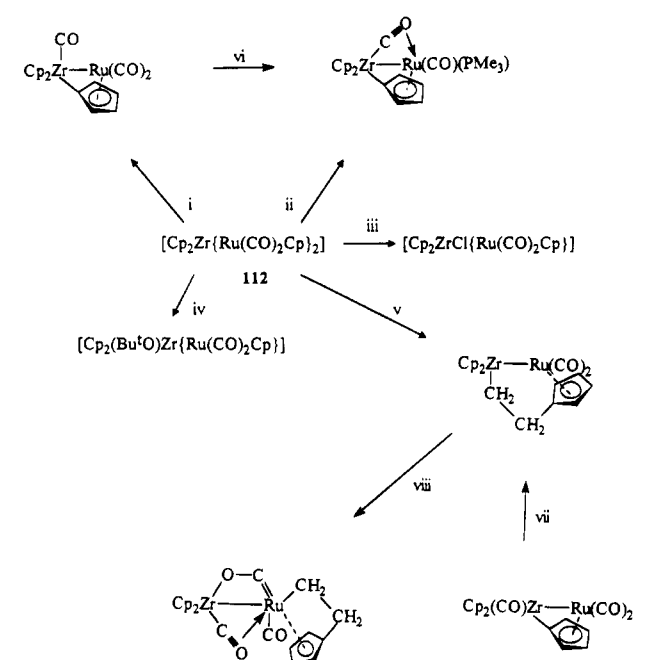
Zirconocene dihydride or the dinitrogen complex react with cyclopentadienylmetal dicarbonyl with formation of metal—metal bonded carbonyl-bridged species **111** (eq 46, M = Co, 95% yield;⁴³² M = Rh, 44% yield;⁴³³ M = RuH, 59% yield⁴³³). No reaction



was observed with [MH(CO)(PMe₃)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 H₂ is then prevented.⁴³³

Hydrido-bridged complexes with a Zr—M bond were obtained in 70% yield as shown in eq 47 (R = Cl, H,⁴³⁴ R = H⁴³⁵) 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



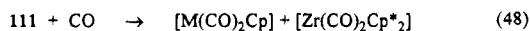
Scheme 34^a

^a (i) +CO, $-\text{[RuH(CO)}_2\text{Cp]}$, ref 436; (ii) +PMe₃, $-\text{[RuH(CO)}_2\text{Cp]}$, ref 436; (iii) $[\text{ZrCl}_2\text{Cp}_2]$, ref 231; (iv) $[\text{Cp}_2(\text{Bu}^t\text{O})\text{Zr}\{\text{Fe}(\text{CO})_2\text{Cp}\}]$, $-\text{[Fe(CO)}_2\text{Cp}]_2$ (possibly resulting from decomposition of $[\text{Cp}_2\text{Zr}\{\text{Ru}(\text{CO})_2\text{Cp}\}\{\text{Fe}(\text{CO})_2\text{Cp}\}]$), ref 231; (v) +CH₂=CH₂, $-\text{[RuH(CO)}_2\text{Cp]}$, ref 436; (vi) +PMe₃, ref 436; (vii) H₂C=CH₂, ref 436; (viii) CO, ref 437.

B. Chemical Properties

The trimetallic complex **112** reacts with CO, PMe₃, or ethylene to give dimetallic complexes (Scheme 34).⁴³⁶ Also, the Ru(CO)₂Cp groups exchange with the chloro or Fe(CO)₂Cp ligands of $[\text{ZrCl}_2\text{Cp}_2]$ or $[\text{Cp}_2(\text{Bu}^t\text{O})\text{Zr}\text{—}\text{Fe}(\text{CO})_2\text{Cp}]$ (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



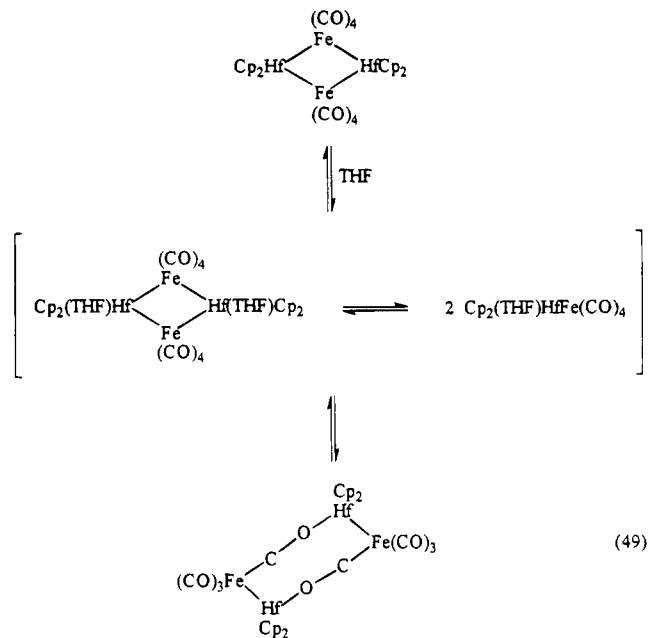
The complexes $[\text{Cp}_2(\text{R})\text{Zr}(\mu\text{-H})_n\{\text{ReH}_{6-n}(\text{PPh}_2\text{R}')_2\}]$ ($n > 1$) (R = Cl, R' = Ph; R = H, R' = Me) and $[\text{Cp}_2(\text{H})\text{Zr}(\mu\text{-H})_3\text{Os}(\text{PMe}_2\text{Ph})_3]$ failed to react with CO.⁷⁹ CO₂ inserts into the terminal Zr—H bond, yielding the corresponding formate complexes.⁷⁹

The dimeric hafnocene—iron tetracarbonyl complex reacts rapidly with HCl to give hafnocene dichloride and Fe₃(CO)₁₂. On dissolution in THF, isomerization to an isocarbonyl complex is observed (eq 49).⁴³¹

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

C. Spectroscopic Properties

The two $\nu(\text{CO})$ 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 $[\text{K}\{\text{M}(\text{CO})_2\text{Cp}\}]$ (M = Fe,^{231,421} Ru²³¹), as expected for compounds with a Zr—M bond. The ¹³C NMR spectra of $[\text{Cp}_2\text{ZrX}\{\text{Ru}(\text{CO})_2\text{Cp}\}]$ (X = Cl, Me, OBU^t)⁴²⁰ show one CO signal, whereas $[\text{Cp}_2\text{Zr}\{\text{Ru}(\text{CO})_2\text{Cp}\}_2]$ exhibits two



CO signals at -60°C and a single broad peak at 51°C .²³¹ The temperature-dependent dynamic process ($\Delta G^\ddagger = 56.2 \pm 2.0 \text{ kJ mol}^{-1}$) 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

The Zr—Fe and Zr—Ru bonded complexes exhibit a parent ion peak in the mass spectrum.^{420,421}

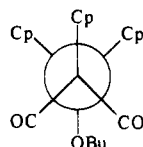
In $[\text{Cp}_2\text{Hf}\{\text{Fe}(\text{CO})_4\}]_2$ ⁴³¹ and $\text{cis-}[\text{Fe}(\text{CO})_4(\text{ZrRCP}_2)_2]$ (R = Me, octyl)⁴³⁰ four terminal CO bands are observed, consistent with the local C_{2v} symmetry of the Fe(CO)₄ fragment. The shift of $\nu(\text{CO})$ from 1788 cm⁻¹ in Fe(CO)₄²⁻ 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 $\nu(\text{Hf—Fe})$ modes, the presence of two bands indicating a dimeric molecule.⁴³¹ The complexes $[\text{Cp}_2\text{ZrX}\{\text{Fe}(\text{CO})_2\text{Cp}\}]$ exhibit the $\nu(\text{Zr—Fe})$ band at 187 (X = Me) and 181 cm⁻¹ (X = Cl), respectively.⁴²¹

The carbonyl-bridged complexes **111** (M = Rh,⁴³³ RuH,⁴³³ Co⁴³²) exhibit absorptions at 1670–1700 and 1710–1750 cm⁻¹ for the two bridging carbonyl groups.

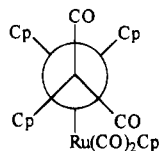
D. Structural Data

The zirconocene—ruthenium complexes $[\text{Cp}_2\text{Zr}(\text{OBU}^t)\{\text{Ru}(\text{CO})_2\text{Cp}\}]$ ⁴²⁰ and $[\text{Cp}_2\text{Zr}\{\text{Ru}(\text{CO})_2\text{Cp}\}_2]$ ²³¹ contain direct, unbridged zirconium to late transition metal bonds. In the former, the OBU^t and Ru(CO)₂Cp 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 $[\text{Cp}_2\text{Zr}\{\text{Ru}(\text{CO})_2\text{Cp}\}_2]$, 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 [Cp₂ZrI{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_{z²} 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(N₃)Cp₂].⁴⁴⁰ The IR spectrum shows the ν_{as} and ν_s (N₃) modes at 2080 and 1270 cm⁻¹, respectively. The bisazide, [Zr(N₃)₂Cp₂], 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(OCHMeCH₂Cl)₂Cp₂] 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(N₃)₂Cp₂] 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 [ZrR₂Cp₂] (R = Me, Ph) gives the highly air sensitive yellow (R = Me) or orange (R = Ph) 1,3-triazenido complexes [ZrR{N(R)-NNPh}Cp₂] with a bidentate triazenido group.⁴⁴⁰ Analogously, [HfH₂Cp*₂] reacts smoothly with RN₃ (R = Ph, *p*-Tol) to give moderately stable [HfH{N(H)-NNR}Cp*₂], which upon thermolysis at 80 °C loses N₂ to form an arylamido complex.⁵⁷

The reaction of [MCl₂Cp(η-C₅R₅)] (M = Zr, R = H, Me; M = Hf, R = Me) with Me₃SnNSNSnMe₃ yields the sulfur diimido complexes [Cp(η-C₅R₅)M(NSN)₂MCp(η-C₅R₅)] 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(η-C₅R₅)(η-C₅R'₅)] (M = Ti, R = R' = H; M = Zr, R = H, R' = Me; M =

Table 8. Metal-Metal Distances in Complexes with M-M' Bonds

compound	M-M' (Å)	ref
[Cp ₂ Zr{Ru(CO) ₂ Cp} ₂]	Zr-Ru 2.938(1), 2.948(1)	231
[Cp ₂ Zr(OBu ⁺) ₂ {Ru(CO) ₂ Cp}]	Zr-Ru 2.910(1)	420
[Cp ₂ ZrCl(μ-H) ₃ Os(PMe ₂ Ph) ₃] ^a	Zr-Os 2.805(1)	434
[Cp ₂ (Cl)Zr(μ-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*-OsH₃P₃ unit. ^b Hydrides not located.

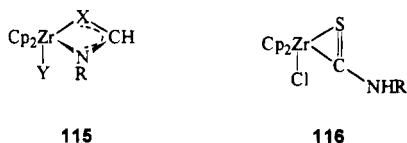
Zr, Hf, R = R' = Me) are available by salt elimination.⁴⁴⁴ Several other routes to the titanocene derivative are known.⁴⁴⁴ The complexes are pale to deep yellow and only slightly sensitive to air. Parent ion peaks are observed in the mass spectrum. In the IR spectra three absorptions (ca. 1250, 1080, 520 cm⁻¹) which are characteristic of the NSO ligand are observed.⁴⁴⁴ The crystal structure of [Zr(NSO)₂-CpCp*] [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(SiMe₃)₂ with elimination of Li(OSiMe₃) and formation of [Ti{NSN(SiMe₃)₂Cp₂}.⁴⁴⁵

The dithiocyanato complexes [M(SCN)₂(η-C₅H₄R)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' = alkyl⁴⁴⁹) were prepared by reacting the appropriate metallocene dichloride with potassium thiocyanate.

The corresponding metallocene diisocyanato complexes [M(NCO)₂Cp₂] (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

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



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

In general, metallocene nitrates are obtained from the reaction of metallocene complexes with nitric acid. Thus, $[\text{ZrCl}(\text{NO}_3)\text{Cp}_2]$ is obtained from $[\text{ZrCl}_2\text{Cp}_2]$ and HNO_3 .⁴⁵⁴ The corresponding bromide $[\text{ZrBr}(\text{NO}_3)\text{Cp}_2]$ is obtained from the reaction of $[\text{ZrBr}(\text{X})\text{Cp}_2]$ (X = OPh, Br)⁴⁵⁵ or $[(\text{ZrBrCp}_2)_2\text{O}]$ ^{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 $[\text{ZrCl}(\text{NO}_3)\text{Cp}_2]$ revealed a monomeric molecule with η^2 -bonded nitrate ligands (Zr—O 2.15(3), 2.54(3) Å).⁴⁵⁴ The analogous Hf complex $[\text{HfBr}(\text{NO}_3)\text{Cp}_2]$ is available from $[(\text{HfBrCp}_2)_2\text{O}]$ and HNO_3 .⁴⁵⁶

If dilute HNO_3 is employed, hydrolysis occurs with formation of metallocene hydroxide nitrates. Thus, $[\text{ZrCl}_2\text{Cp}_2]$ reacts with nitric acid in CHCl_3 with cleavage of a Zr—Cp bond and formation of $[\{\text{Zr}(\text{NO}_3)_2(\mu\text{-OH})\text{Cp}\}_2] \cdot 2\text{THF}$.⁴⁵⁷ The same product is obtained on hydrolysis of $[\text{Zr}(\text{NO}_3)_2\text{Cp}_2]$.⁴⁵⁸ The crystal structure shows bidentate nitrate 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 $[\text{HfCp}_4]$ reacts with HNO_3 to yield the corresponding hafnocene complex.⁴⁵⁶ However, $[\text{ZrCp}_4]$ reacts with HNO_3 to afford $[\text{Zr}(\text{NO}_3)(\text{OH})\text{Cp}_2 \cdot \text{H}_2\text{O}]$, which hydrolyzes to $[\text{Zr}(\text{NO}_3)(\text{OH})_2\text{Cp} \cdot \text{H}_2\text{O}]_4$.⁴⁵⁸ The IR spectra of solid $[\text{Zr}(\text{NO}_3)(\text{OH})\text{Cp}_2 \cdot \text{H}_2\text{O}]$ and $[\text{Zr}(\text{NO}_3)(\text{OH})_2\text{Cp} \cdot \text{H}_2\text{O}]_4$ 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 nitrate group. In solution, only bands due to covalently bonded nitrate are present for both complexes.⁴⁵⁸ IR and Raman spectra of $[\text{Zr}(\text{NO}_3)_2\text{Cp}_2]$ are different in solution and in the solid state. Molecular weight measurements in THF showed the complex to be trimeric.⁴⁵⁸

The reaction of $[\text{ZrL}_2\text{Cp}_2]$ and $[\text{ZrL}(\text{X})\text{Cp}_2]$ (LH = Ac_2CH_2 , Bz_2CH_2 , X = Cl, Br) with HNO_3 was studied. With $[\text{ZrL}_2\text{Cp}_2]$ at $-35\text{ }^\circ\text{C}$ $[\text{ZrL}_2(\text{NO}_3)\text{Cp}_2]$ was obtained, which reacts further at $20\text{ }^\circ\text{C}$ to give $[\text{ZrL}(\text{NO}_3)_2\text{Cp}]$. $[\text{ZrL}(\text{X})\text{Cp}_2]$ gives $[\text{Zr}(\text{NO}_3)(\text{X})\text{Cp}_2]$ at $-35\text{ }^\circ\text{C}$.⁴⁵⁹

$[\text{ZrCl}_2\text{L}_2]$ (L = Cp, η -indenyl) reacts with NaNO_2 in refluxing THF to give $[\text{Zr}(\text{NO}_2)_2\text{L}_2]$. Use of AgNO_2 yields the nitrito complex $[\text{Zr}(\text{ONO})_2\text{L}_2]$.⁴⁶⁰

The nitronato complexes $[\text{Zr}(\text{O}_2\text{N}=\text{CMeR})(\text{X})\text{Cp}_2]$ (X = Cl, R = Me, H; X = $\text{CH}_2\text{CMe}_2\text{Ph}$, R = Me) were prepared from $\text{Li}(\text{O}_2\text{N}=\text{CMeR})$ and the appropriate zirconocene chloride derivative. Their IR spectra suggest a symmetrical chelating mode of coordination for the alkanenitronato ligand ($\nu(\text{CN})$ 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 $[\text{ZrPh}\{\text{ON}(\text{Ph})\text{NO}\}\text{Cp}_2]$.⁴⁶¹ The chloro derivative $[\text{ZrCl}\{\text{ON}(\text{R})\text{NO}\}\text{Cp}_2]$ (R = Ph, *p*-Tol) is obtained from zirconocene dichloride and $\text{Ag}\{\text{ON}(\text{R})\text{NO}\}$, whereas with $\text{NH}_4\{\text{ON}(\text{p-Tol})\text{NO}\}$ only $[\text{Zr}\{\text{ON}(\text{p-Tol})\text{NO}\}_4]$ was formed.⁴⁶¹ The complexes are

white. IR spectra indicate the presence of a $\text{Zr}\{\text{ON}(\text{R})\text{NO}\}$ chelate ring (three strong absorptions between 1170 and 1365 cm^{-1} , one between 920 and 945 cm^{-1}).⁴⁶¹ The corresponding *N*-methyl-*N*-nitrosohydroxylaminate complexes were reported in 1972. Thus, $[\text{ZrMe}(\text{X})\text{Cp}_2]$ (X = Cl, Me) reacts with NO to give $[\text{Zr}\{\text{ON}(\text{Me})\text{NO}\}(\text{X})\text{Cp}_2]$.⁴⁶²

Di-*tert*-butyl nitroxide readily substitutes $[\text{MR}_2\text{Cp}_2]$ (M = Zr, R = Cl, Br, Me, $\text{CH}_2\text{R}'$ 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 $[\text{M}(\text{ONBu}^t_2)(\text{R})\text{Cp}_2]$.³⁵⁶

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

$[\text{Zr}(\text{HSO}_4)_2\text{Cp}_2]$ was obtained from sulfuric acid and $[(\text{ZrClCp}_2)_2\text{O}]$.⁴⁶³

The reaction of zirconocene dichloride with AgO_3SCF_3 in THF gives $[\text{Zr}(\text{O}_3\text{SCF}_3)_2(\text{THF})\text{Cp}_2]$, which has a five-coordinate bent metallocene structure, the THF group being symmetrically surrounded by $\text{CF}_3\text{-SO}_3$ 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 $[\text{Ti}(\text{O}_3\text{SCF}_3)_2\text{Cp}_2]$ proved to be efficient catalysts for Diels–Alder reactions (acceleration rates of 10^3 to $>10^5$).⁴⁶⁵ The reaction of $[\text{Zr}(\text{O}_3\text{SCF}_3)_2(\text{THF})\text{Cp}_2]$ with bipy or water gives the ionic compounds $[\text{Zr}(\text{O}_3\text{SCF}_3)(\text{bipy})\text{Cp}_2]^+\text{CF}_3\text{SO}_3^-$ ⁴⁶⁶ and $[\text{Zr}(\text{H}_2\text{O})_3\text{Cp}_2]^{2+}(\text{CF}_3\text{SO}_3^-)_2 \cdot 2\text{THF}$,⁴⁶⁷ respectively. Both products have been structurally characterized.^{466,467}

The reaction of dimethylzirconocene with 1 or 2 equiv of $\text{H}_2\text{C}(\text{SO}_2\text{CF}_3)_2$ yields $[\text{ZrMe}\{\text{HC}(\text{SO}_2\text{CF}_3)_2\}\text{Cp}_2]$ and $[\text{Zr}\{\text{HC}(\text{SO}_2\text{CF}_3)_2\}_2\text{Cp}_2]$, respectively.¹⁷⁸ The methyl hafnocene analogue was prepared accordingly.³⁰⁹ Analogously, the complexes $[\text{ZrMe}_{2-n}(\text{X})_n\text{Cp}_2]$ ($n = 1$ or 2 , X = $\text{PhC}(\text{SO}_2\text{CF}_3)_2$, $\text{N}(\text{SO}_2\text{CF}_3)_2$, CF_3SO_3 , $\text{HC}(\text{SO}_2)_2(\text{CF}_2)_3$; $n = 2$, X = $\text{CH}_2=\text{CHCH}_2\text{C}(\text{SO}_2\text{CF}_3)_2$) were prepared.¹⁷⁸ The complexes are nonelectrolytes in dichloromethane. In acetonitrile solvolysis occurs with formation of $[\text{ZrMe}(\text{CH}_3\text{CN})_2\text{Cp}_2]^+$ (monosubstituted complex) and $[\text{Zr}(\text{CH}_3\text{CN})_3\text{Cp}_2]^{2+}$ (disubstituted complex).¹⁷⁸ THF is polymerized by these compounds.¹⁷⁸ The X-ray analysis of $[\text{Zr}\{\text{HC}(\text{SO}_2\text{CF}_3)_2\}_2\text{Cp}_2]$ shows a bidentate [Zr—O 2.243(2), 2.259(2) Å] and a monodentate [Zr—O 2.237(2) Å] $\text{CH}(\text{SO}_2\text{CF}_3)$ 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 $-100\text{ }^\circ\text{C}$ 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

⁹¹Zr 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(SO₂CF₃)₂}Cp₂] inserts CO into the Zr–Me bond to give the corresponding η²-acetyl derivative. ¹⁹F NMR spectra suggest the presence of a monodentate oxygen-bonded CH(SO₂CF₃)₂ ligand.¹⁷⁸

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