refinement converged at $R = 0.035$ and $R_w = 0.043$ (weighting scheme: $w^{-1} = \sigma^2(F_o) + 0.0023F_o^2$). There was only one peak higher than 1 e/Å^3 in the final difference map (2.3 e/Å^3) which was located at 0.83 Å from the heavy atom. All calculations were performed using SHELX-76.[33]

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Supplementary Material Available: Tables of anisotropic thermal parameters and complete distances and angles (2 pages); a listing of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Unprecedented Coordination of a Si–Cl Bond to a Transition Metal: Synthesis and Structure of $[rac\text{-}\mathrm{C_2H_4(indenyl)_2}\overline{\mathrm{Zr\{CH(SiMe_2Cl}}\mathrm{)(SiMe_3)\}][Al_2Cl_{6.5}Me_{0.5}]}$ Formed by Reversible Si–C Bond Activation

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Reaction of $\mathrm{Cp'_2Zr\{CH(SiMe_3)_2\}Cl}$ with a 2-fold excess of $\mathrm{AlCl_3}$ affords the novel Si–C bond activation products $[\mathrm{Cp'_2}\overline{\mathrm{Zr\{CH(SiMe_2Cl}}\mathrm{)(SiMe_3)\}][Al_2Cl_nMe_{7-n}]}$ ($\mathrm{Cp'_2} = rac\text{-}\mathrm{C_2H_4(indenyl)_2}$ (**1**), $\mathrm{(C_5H_5)_2}$ (**2**)); the Lewis acid adducts $\mathrm{Cp'_2Zr\{CH(SiMe_3)_2\}Cl{\cdot}AlCl_3}$ are obtained with 1 equiv of $\mathrm{AlCl_3}$. In contrast, $\mathrm{Cp'_2Zr(CH_2SiMe_3)Cl}$ ($\mathrm{Cp'_2} = rac\text{-}\mathrm{C_2H_4(indenyl)_2}$, $\mathrm{(C_5Me_5)_2}$) undergoes rapid alkyl–chloride exchange with $\mathrm{AlCl_3}$, giving $\mathrm{Cp'_2ZrCl_2{\cdot}(Me_3SiCH_2)AlCl_2}$. The structure of $[rac\text{-}\mathrm{C_2H_4(indenyl)_2}\overline{\mathrm{Zr\{CH(SiMe_2Cl}}\mathrm{)(SiMe_3)\}][Al_2Cl_{6.5}Me_{0.5}]}$ (**1**) has been determined by X-ray crystallography. Crystal data: $\mathrm{C_{26.5}H_{33.5}Al_2Cl_{7.5}Si_2Zr}$, M_r 819.3, monoclinic, $P2_1/n$, $a = 9.419$ (2) Å, $b = 23.134$ (5) Å, $c = 17.418$ (4) Å, $Z = 4$, final $R = 0.053$ for 5215 "observed" reflections. The unusual chelating alkyl ligand shows the first example of Si–Cl bond coordination to a transition metal (Zr–Cl = 2.573 (1) Å; Si–Cl = 2.266 (2) Å; Zr–Cl–Si = 80.4 (1)°). The Si–C bond activation reaction leading to **1** is reversible, as shown by formation of $rac\text{-}\mathrm{C_2H_4(indenyl)_2Zr\{CH(SiMe_3)_2\}Cl}$ on reaction of **1** with a 2-fold excess of $\mathrm{AlMe_3}$. Sterically and electronically saturated **1** is inert toward unsaturated substrates. Treatment of **1** with Lewis bases affords $rac\text{-}\mathrm{C_2H_4(indenyl)_2Zr\{\eta^1\text{-}CH(SiMe_2Cl)(SiMe_3)\}Cl}$ (**3**).

Introduction

The hypothesis that a cationic complex, $[\mathrm{Cp'_2MR}]^+$, is the active species in alkene polymerization catalysts, based on group 4 metallocenes with alkylaluminoxane[1] or alkylaluminum halide[2] cocatalysts, has recently led to the synthesis of well-characterized d^0 cocatalyst-free cationic model complexes.[3,4] A number of Lewis base adducts, $[\mathrm{Cp'_2MR(L)}]^+$,[3] have been prepared, but more electrophilic alkylmetallocene cations, more closely related to the active site in the two-component catalysts, are frequently less stable and have been less extensively studied.[4] Direct in situ study of the active two-component catalysts has been attempted using NMR,[5] UV,[6] and XPS[7] techniques but is hindered by the complexity and dynamic nature of the

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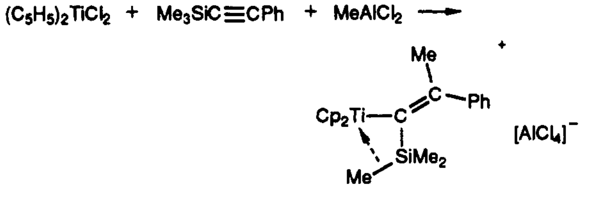
catalysts and, in the case of alkylaluminum halide cocatalysts, by catalyst instability.

The importance of alkylaluminum halides as cocatalysts suggests that halide abstraction from $Cp'_2Zr(R)Cl$ using the Lewis acid $AlCl_3$ offers a potential route to isolable Lewis-base-free cationic complexes, provided coordination of $AlCl_4^-$ and alkyl transfer from zirconium to aluminum[8] can be suppressed. However, the equilibrium in eq 1 (X = Cl)[5,6] is believed to be displaced toward the neutral species containing an η^1-coordinated anion, as exemplified by the solid-state structures of $(C_5H_5)_2MCl(AlCl_4)$ (M = Ti, Zr).[9a,b] The related structurally characterized complex $(C_5H_5)_2TiCl(AlMeCl_3)$[9c] is likely in equilibrium with ionic $[(C_5H_5)_2TiMe][AlCl_4]$ in solution; the latter species may be trapped on reaction with a bulky alkyne to give the cationic alkenyl complex shown in eq 2.[5d] Stabilization of the ionic species in eq 1 (X = alkyl) probably requires electronic and/or steric stabilization of the cation.

$$Cp'_2M(X)(Cl{-}AlCl_3) \rightleftharpoons Cp'_2M{-}X^+[AlCl_4]^- \quad (1)$$

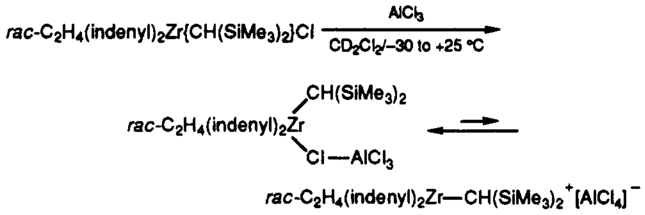


(2)

Secondary interactions, such as agostic[10] coordination of a β-[3c,4a,11] or α-C–H[12] bond of electrophilic d^0 alkyl complexes, $[Cp'_2MR]^{n+}$ (n = 0, 1), are believed to play an important role, both in the stabilization of such complexes, and in the stereospecificity of the alkene insertion reaction. Ab initio MO calculations predicting that the stabilization energy offered by the related but stronger β-Si–C–M agostic interaction in hypothetical $[Cl_2Ti\{C(SiH_2Me){=}CH_2\}]^+$, related to the product of eq 2, is ca. 15 kcal mol^{-1}[13] suggest that incorporation of an alkyl ligand, X, with β-Si–Me groups should result in displacement of the equilibrium in eq 1 toward the ionic species. Use of the bulky alkyl ligand $CH(SiMe_3)_2$ appears particularly advantageous, since it has been widely found to stabilize neutral, highly electron-deficient f-element complexes, by a combination of agostic β-Si–C–M and α-C–H–M interactions,[14] and because the steric bulk of the ligand should hinder alkyl–halide exchange with $AlCl_3$.[8]

Due to the importance of chiral metallocenes for stereospecific isotactic polypropylene formation,[1] such a metallocene, *rac*-$C_2H_4(indenyl)_2Zr(R)Cl$,[15] was chosen for initial study, together with analogous alkyl complexes having cyclopentadienyl or pentamethylcyclopentadienyl ligands. We report here that, in the reaction of $AlCl_3$ with $Cp'_2Zr\{CH(SiMe_3)_2\}Cl$, the alkyl ligand remains bonded to zirconium but unexpected "activation" of a Si–Me bond occurs to give a cationic complex containing a novel chelating silaalkyl chloride group.

Scheme I

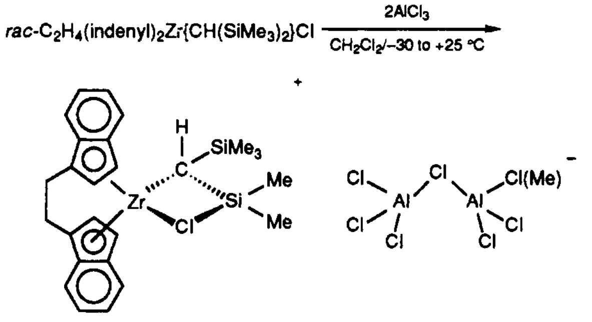


Results and Discussion

Reactions of Crowded Silaalkyl Complexes with $AlCl_3$. Silaalkyl complexes $Cp'_2Zr\{CH(SiMe_3)_2\}Cl$ (Cp'_2 = *rac*-$C_2H_4(indenyl)_2$, $(C_5H_5)_2$) may be obtained by alkylation of Cp'_2ZrCl_2 using $LiCH(SiMe_3)_2$ in ether, followed by recrystallization from toluene/hexane solution.[16,17] The reaction of $(C_5Me_5)_2ZrCl_2$ with $LiCH(SiMe_3)_2$ leads to recovery of starting materials, while the reaction with $KCH(SiMe_3)_2$ affords complex mixtures, presumably due to steric overcrowding in the putative alkyl complex.

The reaction of *rac*-$C_2H_4(indenyl)_2Zr\{CH(SiMe_3)_2\}Cl$ and $AlCl_3$ in CD_2Cl_2 was monitored by ^1H NMR spectroscopy. The diastereotopic Si*Me*$_3$ resonances remain virtually unchanged on addition of *1 equiv* of $AlCl_3$, but the ZrC*H* resonance, found at δ −0.69 ppm in the starting complex, broadens and is shifted to δ −0.53 ppm, on reaction with 0.5 equiv of $AlCl_3$, and is entirely obscured by the $SiMe_3$ resonances (at δ 0.07 and −0.13 ppm) in the 1:1 adduct. The broadening and downfield shift of the ZrC*H* resonance suggest that increased zirconium electrophilicity results in agostic α-C–H–Zr bonding, but the small effect on the Si*Me*$_3$ resonances of $AlCl_3$ addition suggests that the equilibrium in Scheme I is shifted toward the neutral adduct. Attempted crystallization of the adduct led only to low yields of the red compound 1, present (^1H NMR) as a minor component in the crude product mixture.

Complex 1 may be prepared in 60–70% isolated yield from the reaction with *2 equiv* of $AlCl_3$, followed by hexane addition and crystallization at −40 °C (eq 3). In addition to ^1H and ^{13}C NMR resonances due to the inequivalent indenyl ligands, the complex shows five Si*Me* resonances



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(3)

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in a 1:1:3 intensity ratio, consistent with loss of one methyl group from $CH(SiMe_3)_2$. Upfield resonances corresponding in intensity to half a methyl group, found at δ −0.14 and −6.2 ppm (−60 °C, broad) in the ^1H and ^{13}C NMR spectra, respectively, suggest the presence of an Al*Me* fragment. The spectroscopic evidence and elemental analysis, together with reactivity studies and X-ray analysis (vide infra), show that complex 1 is $[rac\text{-}C_2H_4(indenyl)_2Zr\{CH(SiMe_2Cl)(SiMe_3)\}][Al_2Cl_{6.5}Me_{0.5}]$, in which an unusual chelating alkyl ligand shows unpercedented silicon–halide coordination to the electron-deficient zirconium center.

The reaction leading to 1 is mirrored, albeit less cleanly, in the cyclopentadienyl system. Treatment of $(C_5H_5)_2Zr\{CH(SiMe_3)_2\}Cl$ with *equimolar* $AlCl_3$ in CD_2Cl_2 gives $(C_5H_5)_2Zr\{CH(SiMe_3)_2\}Cl\cdot AlCl_3$, in which the Zr*CH* and C_5H_5 resonances are shifted downfield from δ 2.49 to ca. 3.6 ppm and from δ 6.34 to ca. 6.6 ppm, respectively, compared to the starting complex. The comparatively small downfield shift of the broad Si*Me*$_3$ resonance (δ 0.12 to 0.14 ppm) again provides no evidence for agostic Si–C–Zr bonding in an ionic species. The reaction with *2 equiv* of $AlCl_3$ is slower than that leading to 1, and the crude isolated product 2 often contains some $(C_5H_5)_2Zr\{CH(SiMe_3)_2\}Cl\cdot AlCl_3$ and $(C_5H_5)_2ZrCl_2\cdot AlCl_3$. Use of 2 or 3 equiv of $AlCl_3$, followed by reprecipitation and hexane washing of the oily solid, allows isolation of $[(C_5H_5)_2Zr\{CH(SiMe_2Cl)(SiMe_3)\}][Al_2Cl_7]$ (2) as a yellow tacky solid, shown by NMR spectroscopy to be >95% pure. The cation in 2 is analogous to that in 1 and shows the expected ^1H and ^{13}C NMR resonances due to five ligand methyl groups and inequivalent cyclopentadienyl ligands.

In contrast to the reaction of complexes containing the $CH(SiMe_3)_2$ ligand with $AlCl_3$, reaction of $Cp'_2Zr(CH_2SiMe_3)Cl$ (Cp'_2 = $rac\text{-}C_2H_4(indenyl)_2$, $(C_5Me_5)_2$) (obtained by alkylation of Cp'_2ZrCl_2) with equimolar $AlCl_3$ leads to alkyl group transfer to aluminum (eq 4), despite

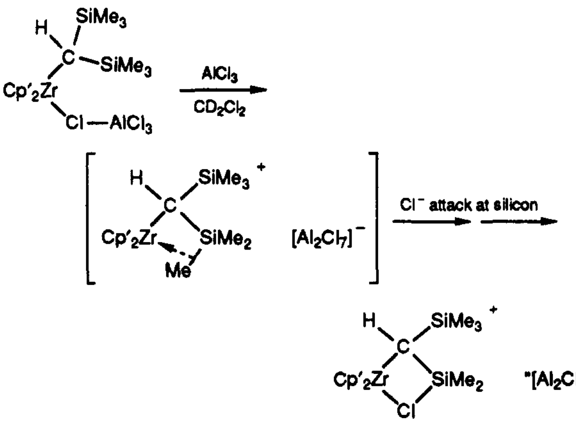
$$Cp'_2Zr(CH_2SiMe_3)Cl \xrightarrow[CD_2Cl_2/-30\text{ to }+25\ ^\circ C]{AlCl_3} Cp'_2ZrCl_2\cdot(Me_3SiCH_2)AlCl_2 \quad (4)$$

$$Cp' = rac\text{-}C_2H_4(indenyl)_2,\ (C_5Me_5)_2$$

the sterically crowded nature of the metallocenes. The resulting $(Me_3SiCH_2)AlCl_2$ forms a labile adduct with the metallocene dichloride, as shown by the downfield shift in the indenyl and C_5Me_5 resonances from δ 6.55/6.24 and 1.96 ppm, respectively, in Cp'_2ZrCl_2, to δ 6.68/6.29 and 1.99 ppm, respectively, in the adduct. Alkyl ligand coordination to aluminum is confirmed by the observation of a broad upfield methylene resonance at δ −0.48 (bis(indenyl)) or −0.41 ppm (C_5Me_5). Addition of THF gives Cp'_2ZrCl_2 and $(Me_3SiCH_2)AlCl_2(THF)$, in which the broad methylene resonance is found at δ −0.69 ppm. In contrast to our results, a previous report of the reaction of $(C_5H_5)_2Zr(R)Cl$ with $AlCl_3$ suggested that the $RAlCl_2$ generated does not form an adduct with $(C_5H_5)_2ZrCl_2$, although $(C_5H_5)_2ZrCl_2\cdot AlCl_3$ is formed with >1 equiv of $AlCl_3$.[8]

That Lewis acid adduct formation between $Cp'_2Zr(R)Cl$ and $AlCl_3$ is favored over alkyl–halide exchange if R is the bulky ligand $CH(SiMe_3)_2$, but not if R is CH_2SiMe_3, is believed to be due to the inaccessibility of a μ-alkyl intermediate (Zr–R–Al) for the bulky alkyl ligand. As already noted, NMR study of the reaction of $Cp'_2Zr\{CH(SiMe_3)_2\}Cl$ with 1 equiv of $AlCl_3$ suggests that the equilibrium between neutral and ionic species is displaced toward the neutral adduct, despite the potential for agostic stabilization of a cationic species. Formation of such a putative cation on addition of a *second equivalent* of $AlCl_3$ may promote Si–Me bond activation to give unexpected complexes 1 and 2.

Scheme II



1, 2

Although the redistribution reactions of methylchlorosilanes (e.g. of Me_4Si and $SiCl_4$ giving Me_nSiCl_{4-n}, n = 1–3) catalyzed by $AlCl_3$ are well-known,[18] high temperatures are generally required (>250 °C). Since there is no reaction between $SiMe_4$ and $AlCl_3$ in CD_2Cl_2 at 25 °C, coordination of the silaalkyl ligand to electron-deficient zirconium appears to be the major determining factor in the reaction leading to 1 and 2. The dramatic transformation may have its origins in the reaction of the second equivalent of $AlCl_3$ with "coordinated $[AlCl_4]^-$" in $Cp'_2Zr(R)Cl\cdot AlCl_3$ to give poorly ligating $[Al_2Cl_7]^-$.[19] Although the exact mode of methyl–chloride exchange leading to 1 and 2 is unknown, it appears likely that agostic coordination of a Si–Me bond[13,14] to zirconium in the putative $[Cp'_2Zr\{CH(SiMe_3)_2\}]^+[Al_2Cl_7]^-$ results in weakening of the bond analogous to the effect of agostic C–H–M bonding in weakening C–H bonds; the increased electrophilicity of silicon leads to nucleophilic chloride attack (from $Al_2Cl_7^-$ or $AlCl_4^-$) at silicon as shown in Scheme II. Methyl–chloride exchange might occur via nucleophilic displacement of Me^- at silicon by Cl^- to give $Cp'_2Zr\{CH(SiMe_3)(SiMe_2Cl)\}Me$, followed by methyl transfer from zirconium to aluminum, or via a concerted process.

Although β-alkyl migration/elimination[20] is now accepted as an analogous decomposition pathway to the β-hydrogen-transfer process for metal alkyl complexes, the activation of a β-silicon–carbon bond in β-silaalkyl complexes has very few precedents.[21] There is, however, at least one reported example of the activation of a β-Si–C bond by halide attack in a cationic complex, related to the formation of 1 and 2. The reaction of $(C_5H_5)Ru(Br)(CH_2SiMe_3)(\eta^3\text{-}C_3H_5)$ with AgF, giving $(C_5H_5)Ru(Me)(CH_2SiMe_2F)(\eta^3\text{-}C_3H_5)$, is believed[21b] to proceed via bromide abstraction, followed by fluoride attack at silicon in the resulting cation, to give the transitory zwitterionic $(C_5H_5)Ru^+(CH_2SiMe_3F^-)(\eta^3\text{-}C_3H_5)$, containing 5-coordinate

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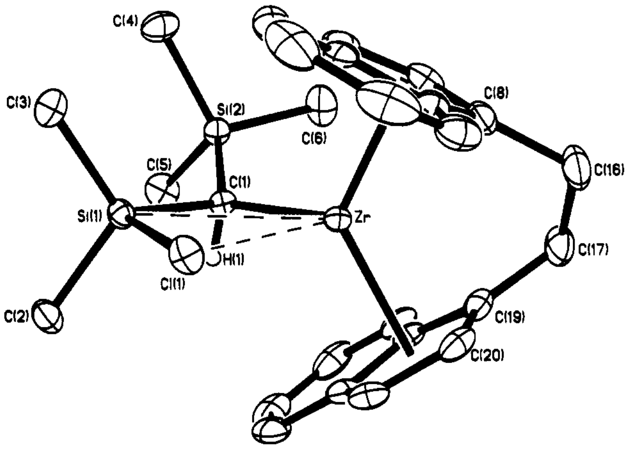

Figure 1. Molecular geometry of the cation in 1 with 30% probability ellipsoids. Indenyl and methyl group hydrogens have been omitted for clarity.

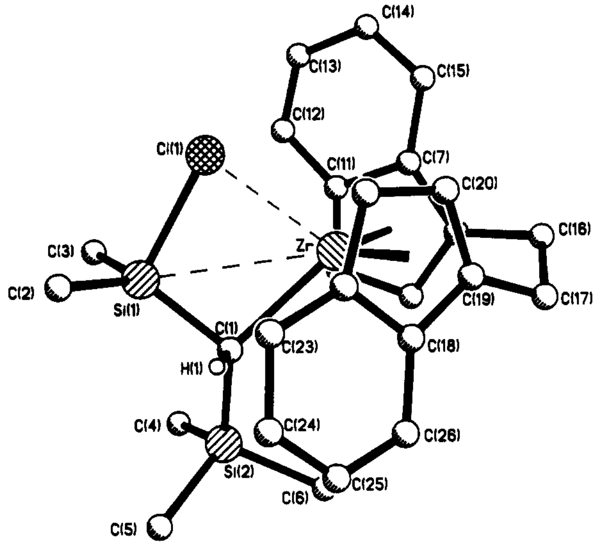

Figure 2. Alternative ORTEP view of the cation in 1. Indenyl and methyl group hydrogens have been omitted for clarity.

silicon, followed by methyl transfer to the metal.

In contrast to the ruthenium case, the end destination of the displaced methyl group in the reaction leading to 1 is the anion. It is therefore surprising that the counteranion in *crystalline* 1 is a ca. 1:1 mixture of $[AlCl_7]^-$ and $[Al_2Cl_6Me]^-$. Since the yield of crystalline 1 is never more than ca. 70%, it is likely that the "lost" half-methyl group remains in the soluble product fraction, as is also the case for complex 2 containing $[Al_2Cl_7]^-$ as anion.

Solid-State Structure of [*rac*-C_2H_4(indenyl)$_2$Zr{CH($SiMe_2Cl$)($SiMe_3$)}][$Al_2Cl_{6.5}Me_{0.5}$] (1). Compound 1 consists of distinct cations and anions separated by normal van der Waals contacts, the structures of which are illustrated in Figures 1–3. Crystal data are given in Table I, bond distances and angles in Tables II and III, respectively, and atomic coordinates in Table IV.

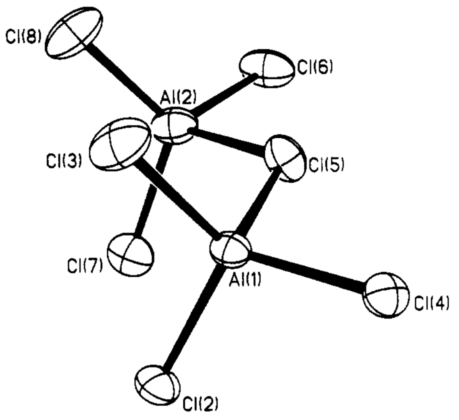

Figure 3. Molecular geometry of the $[Al_2Cl_{6.5}Me_{0.5}]^-$ anion in 1 with 30% probability ellipsoids.

Table I. Crystallographic Data for Complex 1

formula: $C_{26.5}H_{33.5}Al_2Cl_{7.5}Si_2Zr$
fw: 819.3
cryst syst: monoclinic
space group: $P2_1/n$ (No. 14)
cryst dimens: 0.28 × 0.40 × 0.60 mm
$a = 9.419$ (2) Å
$b = 23.134$ (5) Å
$c = 17.418$ (4) Å
$\beta = 110.66$ (2)°
$V = 3551.3$ (13) Å^3
$Z = 4$
$D_{exptl} = 1.53$ g cm^{-3}
$T = -43$ °C
$\lambda = 0.71069$ Å (Mo Kα)
$\mu = 10.1$ cm^{-1} (graphite monochromator)
Nicolet R3m/V: 2θ range 4.0–50.0°
$0 \le h \le 11, 0 \le k \le 27, -20 \le l \le 20$
no. of rflns: 6841
no. of indep rflns: 6251
no. of rflns ($I > 2\sigma(I)$): 5215
$R = 0.053$; $R_w = 0.077$ (5215 rflns)
$w^{-1} = \sigma_c^2(F_o) + 0.0007F_o^2$
$S = 1.999$

Table II. Bond Lengths (Å)

Zr–Cl(1)	2.573 (1)	Zr–Si(1)	3.132 (1)
Zr–C(1)	2.300 (5)	Zr–C(7)	2.537 (5)
Zr–C(8)	2.485 (5)	Zr–C(9)	2.457 (7)
Zr–C(10)	2.496 (7)	Zr–C(11)	2.576 (5)
Zr–C(18)	2.529 (5)	Zr–C(19)	2.439 (6)
Zr–C(20)	2.482 (7)	Zr–C(21)	2.543 (7)
Zr–C(22)	2.609 (5)	Cl(1)–Si(1)	2.266 (2)
Cl(2)–Al(1)	2.111 (3)	Cl(3)–Al(1)	2.095 (3)
Cl(4)–Al(1)	2.112 (2)	Cl(5)–Al(1)	2.230 (2)
Cl(5)–Al(2)	2.341 (3)	Cl(6)–Al(2)	2.119 (3)
Cl(7)–Al(2)	2.108 (3)	Cl(8)–Al(2)	2.049 (6)
Si(1)–C(1)	1.820 (5)	Si(1)–C(2)	1.848 (6)
Si(1)–C(3)	1.846 (6)	Si(2)–C(1)	1.885 (6)
Si(2)–C(4)	1.879 (7)	Si(2)–C(5)	1.860 (6)
Si(2)–C(6)	1.866 (7)	C(1)–H(1)	0.922 (70)
C(7)–C(8)	1.431 (7)	C(7)–C(11)	1.445 (8)
C(7)–C(15)	1.425 (9)	C(8)–C(9)	1.394 (9)
C(8)–C(16)	1.512 (8)	C(9)–C(10)	1.415 (8)
C(10)–C(11)	1.423 (9)	C(11)–C(12)	1.420 (9)
C(12)–C(13)	1.322 (13)	C(13)–C(14)	1.410 (12)
C(14)–C(15)	1.356 (9)	C(16)–C(17)	1.532 (8)
C(17)–C(19)	1.499 (9)	C(18)–C(19)	1.429 (7)
C(18)–C(22)	1.443 (9)	C(18)–C(26)	1.418 (8)
C(19)–C(20)	1.413 (9)	C(20)–C(21)	1.409 (9)
C(21)–C(22)	1.416 (8)	C(22)–C(23)	1.416 (8)
C(23)–C(24)	1.384 (11)	C(24)–C(25)	1.387 (12)
C(25)–C(26)	1.360 (9)		

The cation contains the chiral [ethylenebis(indenyl)]zirconium skeleton and the C,Cl-bonded chelating alkyl group CH($SiMe_2Cl$)($SiMe_3$). The Zr–C(1) bond length of 2.300 (5) Å in 1 is normal for bonding to an sp^3 carbon and only slightly less than the corresponding distance in {(Me_3C)C_5H_4}$_2$Zr{CH($SiMe_3$)$_2$}Cl (2.324 (8) Å).[22] The Zr–Cl(1) bond length of 2.573 (1) Å is ca. 0.12 Å greater than the terminal Zr–Cl bond length in {(Me_3C)C_5H_4}$_2$Zr{CH($SiMe_3$)$_2$}Cl (2.452 (2) Å) but only slightly less than the bridging Zr–Cl bond length in (C_5H_5)$_2$ZrCl($AlCl_4$) (2.605

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Table III. Bond Angles (deg)

Cl(1)–Zr–Si(1)	45.5 (1)	Cl(1)–Zr–C(1)	80.4 (1)	Zr–Si(1)–C(3)	118.3 (2)	Cl(1)–Si(1)–C(3)	99.2 (2)
Si(1)–Zr–C(1)	35.1 (1)	Cl(1)–Zr–C(7)	97.0 (1)	C(1)–Si(1)–C(3)	121.0 (3)	C(2)–Si(1)–C(3)	112.9 (3)
S(1)–Zr–C(7)	123.8 (1)	C(1)–Zr–C(7)	136.6 (2)	C(1)–Si(2)–C(4)	114.5 (3)	C(1)–Si(2)–C(5)	108.3 (3)
Cl(1)–Zr–C(8)	130.1 (1)	Si(1)–Zr–C(8)	144.1 (1)	C(4)–Si(2)–C(5)	107.9 (3)	C(1)–Si(2)–C(6)	113.0 (3)
C(1)–Zr–C(8)	130.2 (2)	C(7)–Zr–C(8)	33.1 (2)	C(4)–Si(2)–C(6)	105.7 (4)	C(5)–Si(2)–C(6)	107.0 (3)
Cl(1)–Zr–C(9)	134.6 (1)	Si(1)–Zr–C(9)	117.5 (2)	Cl(2)–Al(1)–Cl(3)	114.7 (1)	Cl(2)–Al(1)–Cl(4)	110.3 (1)
C(1)–Zr–C(9)	97.5 (2)	C(7)–Zr–C(9)	54.2 (2)	Cl(3)–Al(1)–Cl(4)	113.4 (1)	Cl(2)–Al(1)–Cl(5)	106.1 (1)
C(8)–Zr–C(9)	32.7 (2)	Cl(1)–Zr–C(10)	102.6 (1)	Cl(3)–Al(1)–Cl(5)	108.3 (1)	Cl(4)–Al(1)–Cl(5)	103.0 (1)
Si(1)–Zr–C(10)	89.4 (1)	C(1)–Zr–C(10)	83.4 (2)	Cl(5)–Al(2)–Cl(6)	97.7 (1)	Cl(5)–Al(2)–Cl(7)	104.7 (1)
C(7)–Zr–C(10)	54.6 (2)	C(8)–Zr–C(10)	55.0 (2)	Cl(6)–Al(2)–Cl(7)	112.9 (2)	Cl(5)–Al(2)–Cl(8)	105.2 (2)
C(9)–Zr–C(10)	33.2 (2)	Cl(1)–Zr–C(11)	82.4 (1)	Cl(6)–Al(2)–Cl(8)	114.7 (2)	Cl(7)–Al(2)–Cl(8)	118.4 (2)
Si(1)–Zr–C(11)	93.2 (1)	C(1)–Zr–C(11)	104.9 (2)	Zr–C(1)–Si(1)	98.3 (2)	Zr–C(1)–Si(2)	131.6 (3)
C(7)–Zr–C(11)	32.8 (2)	C(8)–Zr–C(11)	54.6 (2)	Si(1)–C(1)–Si(2)	118.7 (3)	Zr–C(1)–H(1)	104.3 (44)
C(9)–Zr–C(11)	54.1 (2)	C(10)–Zr–C(11)	32.5 (2)	Si(1)–C(1)–H(1)	88.0 (38)	Si(2)–C(1)–H(1)	106.9 (45)
Cl(1)–Zr–C(18)	123.8 (1)	Si(1)–Zr–C(18)	111.5 (1)	Zr–C(7)–C(8)	71.5 (3)	Zr–C(7)–C(11)	75.1 (3)
C(1)–Zr–C(18)	89.8 (2)	C(7)–Zr–C(18)	124.7 (2)	C(8)–C(7)–C(11)	107.7 (5)	Zr–C(7)–C(15)	120.6 (4)
C(8)–Zr–C(18)	97.9 (2)	C(9)–Zr–C(18)	101.4 (2)	C(8)–C(7)–C(15)	133.2 (5)	C(11)–C(7)–C(15)	119.1 (5)
C(10)–Zr–C(18)	131.2 (2)	C(11)–Zr–C(18)	152.2 (2)	Zr–C(8)–C(7)	75.4 (3)	Zr–C(8)–C(9)	72.5 (3)
Cl(1)–Zr–C(19)	134.0 (2)	Si(1)–Zr–C(19)	144.1 (1)	C(7)–C(8)–C(9)	107.5 (5)	Zr–C(8)–C(16)	116.2 (4)
C(1)–Zr–C(19)	121.3 (2)	C(7)–Zr–C(19)	91.7 (2)	C(7)–C(8)–C(16)	126.4 (6)	C(9)–C(8)–C(16)	126.1 (5)
C(8)–Zr–C(19)	69.3 (2)	C(9)–Zr–C(19)	85.9 (2)	Zr–C(9)–C(8)	74.8 (4)	Zr–C(9)–C(10)	74.9 (4)
C(10)–Zr–C(19)	118.8 (2)	C(11)–Zr–C(19)	122.5 (2)	C(8)–C(9)–C(10)	110.0 (5)	Zr–C(10)–C(9)	71.9 (4)
C(18)–Zr–C(19)	33.4 (2)	Cl(1)–Zr–C(20)	102.8 (2)	Zr–C(10)–C(11)	76.8 (4)	C(9)–C(10)–C(11)	107.6 (6)
Si(1)–Zr–C(20)	135.2 (2)	C(1)–Zr–C(20)	139.0 (2)	Zr–C(11)–C(7)	72.1 (3)	Zr–C(11)–C(10)	70.6 (3)
C(7)–Zr–C(20)	84.1 (2)	C(8)–Zr–C(20)	78.9 (2)	C(7)–C(11)–C(10)	107.2 (5)	Zr–C(11)–C(12)	123.5 (4)
C(9)–Zr–C(20)	107.2 (2)	C(10)–Zr–C(20)	133.5 (2)	C(7)–C(11)–C(12)	118.8 (6)	C(10)–C(11)–C(12)	134.0 (6)
C(11)–Zr–C(20)	116.0 (2)	C(18)–Zr–C(20)	54.1 (2)	C(11)–C(12)–C(13)	119.6 (7)	C(12)–C(13)–C(14)	122.5 (7)
C(19)–Zr–C(20)	33.4 (2)	Cl(1)–Zr–C(21)	79.3 (1)	C(13)–C(14)–C(15)	121.2 (7)	C(7)–C(15)–C(14)	118.8 (6)
Si(1)–Zr–C(21)	102.8 (1)	C(1)–Zr–C(21)	112.8 (2)	C(8)–C(16)–C(17)	110.1 (5)	C(16)–C(17)–C(19)	109.6 (5)
C(7)–Zr–C(21)	109.1 (2)	C(8)–Zr–C(21)	111.3 (2)	Zr–C(18)–C(19)	69.9 (3)	Zr–C(18)–C(22)	76.8 (3)
C(9)–Zr–C(21)	139.0 (2)	C(10)–Zr–C(21)	163.7 (2)	C(19)–C(18)–C(22)	108.0 (5)	Zr–C(18)–C(26)	120.2 (4)
C(11)–Zr–C(21)	134.1 (2)	C(18)–Zr–C(21)	54.1 (2)	C(19)–C(18)–C(26)	132.4 (6)	C(22)–C(18)–C(26)	119.6 (5)
C(19)–Zr–C(21)	55.3 (2)	C(20)–Zr–C(21)	32.5 (2)	Zr–C(19)–C(17)	115.4 (4)	Zr–C(19)–C(18)	76.8 (3)
Cl(1)–Zr–C(22)	91.4 (1)	Si(1)–Zr–C(22)	91.3 (1)	C(17)–C(19)–C(18)	128.1 (6)	Zr–C(19)–C(20)	75.0 (3)
C(1)–Zr–C(22)	86.3 (2)	C(7)–Zr–C(22)	137.2 (2)	C(17)–C(19)–C(20)	125.4 (5)	C(18)–C(19)–C(20)	106.5 (5)
C(8)–Zr–C(22)	123.9 (2)	C(9)–Zr–C(22)	134.0 (2)	Zr–C(20)–C(19)	71.6 (4)	Zr–C(20)–C(21)	76.1 (4)
C(10)–Zr–C(22)	161.0 (2)	C(11)–Zr–C(22)	166.0 (2)	C(19)–C(20)–C(21)	110.2 (5)	Zr–C(21)–C(20)	71.4 (4)
C(18)–Zr–C(22)	32.6 (2)	C(19)–Zr–C(22)	54.7 (2)	Zr–C(21)–C(22)	76.6 (4)	C(20)–C(21)–C(22)	107.4 (5)
C(20)–Zr–C(22)	53.1 (2)	C(21)–Zr–C(22)	31.9 (2)	Zr–C(22)–C(18)	70.7 (3)	Zr–C(22)–C(21)	71.5 (3)
Zr–Cl(1)–Si(1)	80.4 (1)	Al(1)–Cl(5)–Al(2)	118.5 (1)	C(18)–C(22)–C(21)	107.6 (5)	Zr–C(22)–C(23)	123.3 (4)
Zr–Si(1)–Cl(1)	54.1 (1)	Zr–Si(1)–C(1)	46.6 (2)	C(18)–C(22)–C(23)	119.9 (5)	C(21)–C(22)–C(23)	132.5 (6)
Cl(1)–Si(1)–C(1)	100.4 (2)	Zr–Si(1)–C(2)	125.3 (2)	C(22)–C(23)–C(24)	117.8 (7)	C(23)–C(24)–C(25)	121.8 (6)
Cl(1)–Si(1)–C(2)	101.0 (2)	C(1)–Si(1)–C(2)	116.9 (2)	C(24)–C(25)–C(26)	122.5 (6)	C(18)–C(26)–C(25)	118.4 (6)

(2) Å).[23] The equatorial location of C(1) and Cl in 1 is clearly consistent with lone-pair donation from chlorine to one of the two available LUMOs in the Cp'_2Zr fragment.[24] Such equatorial plane bonding may be compared to the much weaker interaction of a C–H σ-bond with zirconium found, for example, in the structurally characterized hydrocarbyl complex $(C_5Me_5)_2Zr^+\{(C_6H_4)B^-(C_6H_5)_3\}$.[4a]

Chelation has a dramatic effect on the geometry of the alkyl ligand. Coordination of the chlorine in 1 results in significant bending of the $SiMe_2Cl$ fragment toward the metal with a concomitant bending away of the $SiMe_3$ group, with Zr–C(1)–Si(1) and Zr–C(1)–Si(2) angles of 98.3 (2) and 131.6 (3)°, respectively. The lengthening of the Si(1)–Cl(1) bond on coordination is reflected in the bond length of 2.266 (2) Å compared to normal Si–Cl bond lengths near 2.075 Å.[25] In addition, the C(1)–Si(1) distance of 1.820 (5) Å is ca. 0.07 Å less than the C(1)–Si(2) distance of 1.885 (6) Å in 1 and compares to normal C–Si single-bond distances in the range 1.87–1.91 Å.[26] The acute Zr–Cl(1)–Si(1) angle (80.4 (1)°) and the rather small Zr–Si(1) separation (3.132 (1) Å, compared to 2.813 (2) Å in $(C_5H_5)_2Zr(SiPh_3)Cl$[27] and 2.935 (2) Å in $[rac\text{-}C_2H_4(\text{indenyl})_2ZrC(SiMe_3){=}CMe_2]^+$,[4g] which shows agostic Zr–C–Si bonding) appear to result from the geometrical constraints of ligand chelation.

1 is the first structurally characterized compound in which a silicon-bound chlorine is bonded to a transition metal. Although several complexes containing η^1-coordinated iodoalkanes and iodoarenes[28,29] have been well characterized, coordination of bromo-, chloro-, and fluorocarbons generally requires the added stability provided by chelation.[28,30] The acute Zr–Cl(1)–Si(1) angle in 1 compares to M–Hal–C angles in the range 90–110° in complexes containing coordinated halocarbons.[28] The greater polarization of the Si–Cl bond compared to that of the C–Cl bond suggests that silicon-bound chlorine should be a better electron donor to an electron-deficient metal than carbon-bound chlorine, and the fact that such Si–Cl–M bonding has not previously been observed prob-

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Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times 10^3$)

	x	y	z	U(eq)[a]
Zr	1959 (1)	1875 (1)	1917 (1)	23 (1)
Cl(1)	224 (1)	985 (1)	1692 (1)	37 (1)
Cl(2)	4944 (2)	813 (1)	8110 (1)	57 (1)
Cl(3)	1558 (2)	664 (1)	8541 (1)	74 (1)
Cl(4)	3552 (2)	1980 (1)	8875 (1)	48 (1)
Cl(5)	1679 (2)	1535 (1)	6918 (1)	54 (1)
Cl(6)	34 (2)	1478 (1)	4865 (1)	79 (1)
Cl(7)	3201 (2)	588 (1)	5823 (1)	72 (1)
Cl(8)[b]	−365 (5)	296 (2)	6035 (3)	94 (2)
Si(1)	2452 (2)	540 (1)	1850 (1)	28 (1)
Si(2)	5543 (2)	1120 (1)	1883 (1)	29 (1)
Al(1)	2976 (2)	1212 (1)	8178 (1)	38 (1)
Al(2)	1083 (3)	883 (1)	5822 (1)	60 (1)
C(1)	3738 (5)	1155 (2)	2116 (3)	25 (2)
C(2)	2581 (7)	23 (2)	2681 (4)	41 (2)
C(3)	1930 (7)	191 (3)	834 (4)	43 (2)
C(4)	5317 (8)	798 (3)	855 (4)	50 (3)
C(5)	6939 (7)	672 (3)	2685 (4)	46 (2)
C(6)	6433 (8)	1842 (3)	1902 (5)	54 (3)
C(7)	260 (6)	2463 (2)	714 (3)	33 (2)
C(8)	1609 (7)	2789 (2)	1120 (3)	37 (2)
C(9)	2818 (7)	2492 (3)	1018 (3)	41 (2)
C(10)	2291 (7)	1979 (3)	564 (3)	42 (2)
C(11)	687 (7)	1962 (2)	348 (3)	38 (2)
C(12)	−469 (10)	1583 (3)	−134 (3)	59 (3)
C(13)	−1901 (10)	1691 (4)	−234 (4)	70 (3)
C(14)	−2338 (8)	2168 (4)	135 (4)	62 (3)
C(15)	−1299 (7)	2551 (3)	600 (4)	46 (2)
C(16)	1716 (9)	3342 (3)	1599 (4)	57 (3)
C(17)	2807 (8)	3261 (3)	2484 (4)	49 (2)
C(18)	3461 (6)	2286 (2)	3314 (3)	33 (2)
C(19)	2435 (7)	2711 (2)	2827 (3)	36 (2)
C(20)	960 (7)	2523 (3)	2744 (3)	41 (2)
C(21)	1025 (7)	1978 (3)	3113 (3)	41 (2)
C(22)	2576 (7)	1833 (2)	3499 (3)	36 (2)
C(23)	3316 (8)	1359 (3)	3993 (3)	49 (2)
C(24)	4886 (9)	1350 (3)	4282 (4)	62 (3)
C(25)	5724 (8)	1783 (3)	4090 (4)	57 (3)
C(26)	5066 (7)	2249 (3)	3624 (3)	44 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Cl(8) site occupied by 0.47 (1) Cl and 0.53 (1) C.

ably reflects only the scarcity of hydrocarbyl ligands containing Si–Cl bonds.

The isoelectronic nature of complex 1 and the Tebbe reagent $(C_5H_5)_2TiCH_2AlClMe_2$[31] allows examination of the effect of replacing aluminum by silicon. The most striking difference between the structurally characterized zirconium analogue of the Tebbe reagent $(C_5H_5)_2ZrCH(CH_2CMe_3)AlCl(CH_2CHMe_2)_2$[32] and 1 is the ca. 0.14 Å shorter Zr–C$_\alpha$ bond (2.158 (2) Å) in the former complex, which suggests that significant Zr=C bonding occurs only in the Tebbe analogue.[32] Further, the endocyclic C–Al distance in the Tebbe analogue is ca. 0.11 Å longer than the terminal C–Al bond distances, whereas in 1 the corresponding C(1)–Si(1) bond is ca. 0.07 Å shorter than the exocyclic bonds. In contrast, the Zr–Cl bond distance of 2.576 (1) Å in the Tebbe analogue is almost identical with that in 1. The differences in Zr–C and relative endo-/exocyclic C–Al/Si distances in the otherwise structurally similar complexes suggest that, in contrast to the partial alkylidene character of the Tebbe analogue, the structure of 1 is intermediate between form A and silene/chloride form B in Figure 4. The C(1)–Si(1) separation of 1.820 (5) Å compares to C–Si separations in the range 1.78 (2)–1.810 (6) Å in three η^2-silene complexes.[26]

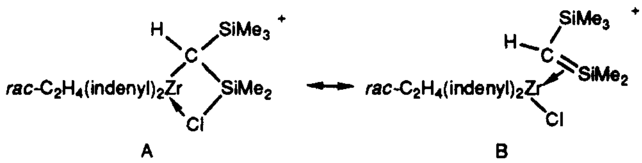
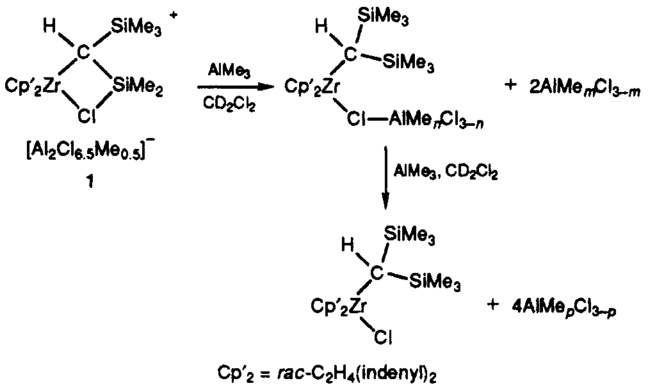


Figure 4. Alternative representations of the ligand bonding in the cation of complex 1.

Scheme III



The asymmetry of the ethylenebis(indenyl) ligand in 1 influences the orientation of the SiMe$_3$ and H substituents on C(1) in a manner similar to that in which the 1-alkene substituent in the proposed isospecific polymerization active site $[Cp'_2M(R)(alkene)]^+$ is constrained to point away from the indenyl or tetrahydroindenyl 6-ring.[1,33] The bulky SiMe$_3$ group in 1 is constrained to point away from an indenyl 6-ring, while the smaller H(1) points toward a 6-ring. The chiral *rac*-C$_2$H$_4$(indenyl)$_2$M fragment has previously been structurally characterized only in the case of the hafnium dichloride complex.[1b] The Zr–C bond distances for the indenyl 5-rings, in the range 2.439 (6)–2.609 (5) Å, are consistent with slipped η^5-coordination, and the average distance, 2.515 (7) Å, is effectively identical with the corresponding average distance in [*rac*-C_2H_4(tetrahydroindenyl)$_2$Zr(CH$_2$Ph)(NCMe)][BPh$_4$] (2.518 (9) Å).[15] Sterically demanding η^2-benzyl coordination in the latter complex results in the bending away of the tetrahydroindenyl 6-rings from over the equatorial coordination sites (λ coordination).[34] In contrast, the reduced steric crowding in 1 allows undistorted coordination of the bis(indenyl) ligand, in which the 6-rings point toward the equatorial coordination sites (δ coordination).[34]

The anion, $[Al_2Cl_{6.5}Me_{0.5}]$, shows disordered occupancy of position 8 by a methyl group and chlorine, resulting in the small Al(2)–Cl(8) distance of 2.049 (6) Å, compared to the other terminal Al–Cl bond distances in the range 2.095 (3)–2.119 (3) Å. The anion shows rather asymmetric Al–(μ-Cl) bonding, with Al(1)–Cl(5) and Al(2)–Cl(5) bond distances of 2.230 (2) and 2.341 (3) Å, respectively. The rather large Al–(μ-Cl)–Al angle (118.5 (1)°) in 1 is characteristic of the eclipsed form of $[Al_2Cl_7]^-$;[35] in two previously reported structures containing the staggered form the corresponding angles are 112.1 and 110.8.°.[35,36]

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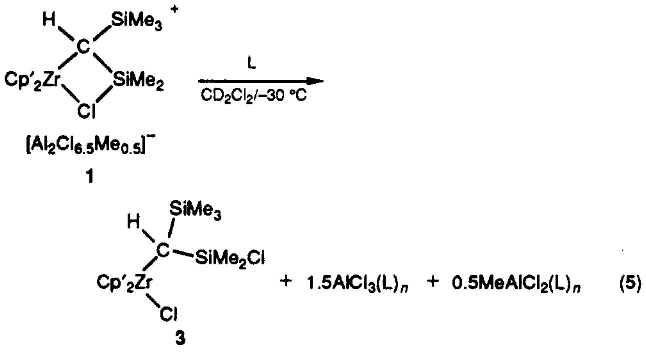
Solution Reactivity Studies for Complex 1. The two-step reaction leading to 1 may be reversed by addition of $AlMe_3$ to a solution of the complex in CD_2Cl_2. *One equivalent* of $AlMe_3$ results in a change in the ligand methyl resonances from a 1:1:3 intensity pattern to a 3:3 pattern. The similarity of the ^1H NMR spectrum to that of *rac*-C_2H_4(indenyl)$_2$Zr{CH($SiMe_3$)$_2$}Cl·$AlCl_3$ suggests that the new species is *rac*-C_2H_4(indenyl)$_2$Zr{CH($SiMe_3$)$_2$}Cl·$AlMe_nCl_{3-n}$ (Scheme III). Addition of a *second equivalent* of $AlMe_3$ cleanly affords *rac*-C_2H_4(indenyl)$_2$Zr{CH($SiMe_3$)$_2$}Cl, free from coordinated Lewis acid. The formation of a Lewis-acid-free adduct in this case results from the decreased Lewis acidity of $AlMe_nCl_{3-n}$ as *n* increases. The weakened Si–Cl bond seen in the structure of 1 is clearly unusually susceptible to metathesis with Al–Me bonds.

A similar reversible, but limited, methyl transfer from aluminum back to silicon occurs on dissolution of 1 (with $[Al_2Cl_{6.5}Me_{0.5}]^-$ as anion) in aromatic solvents. ^1H NMR spectroscopy shows that in toluene-d_8/C_6D_5Cl solution (2:1 ratio) 25% of the product (50% of the maximum possible) is present as *rac*-C_2H_4(indenyl)$_2$Zr{CH($SiMe_3$)$_2$}Cl·$AlMe_nCl_{3-n}$. As expected, the formation of this neutral Lewis acid adduct is favored by lower polarity solvents, and solutions of 1 in C_6D_5Cl or CD_2Cl_2 contain ca. 10% and <5% of the neutral species, respectively.

Attempted displacement of the Si–Cl–Zr bonding interaction in 1 by coordination of a donor ligand affords, instead, the neutral zirconocene complex 3 shown in eq 5.



L = THF, MeCN, NEt_3; Cp'_2 = *rac*-C_2H_4(indenyl)$_2$

The most convenient route to the complex is the reaction with THF, although treatment of 1 with 2 equiv of NEt_4Cl also gives 3, in addition to $[NEt_4][AlCl_4]$ and $[NEt_4][AlCl_3Me]$. Recrystallization from CH_2Cl_2/hexane solution gives analytically pure 3. The complex, in which the alkyl ligand is believed to be η^1-coordinated, shows the expected five ligand methyl resonances (1:1:3 ratio) and fingerprint indenyl resonances (^1H and ^{13}C NMR) very similar to those of *rac*-C_2H_4(indenyl)$_2$Zr{CH($SiMe_3$)$_2$}Cl. Two possible mechanisms of formation of 3 are direct chloride attack at zirconium or chloride attack at silicon followed by, or simultaneous with, displacement of the bridging chloride to zirconium.

Attempts to synthesize an aluminum halide free analogue of complex 1, by halide abstraction from 3 using $AgBPh_4$ in CD_3CN, led only to recovery of the starting complex. The lack of reactivity is presumably related to the sterically crowded environment at zirconium.

The steric crowding in 1, as well as the strong Si–Cl coordination, was expected to suppress reactivity with unsaturated molecules in comparison to the reactivity of more sterically and electronically unsaturated cations.[3,4] Indeed, when C_2H_4 is bubbled through a CD_2Cl_2 solution of the complex in an NMR tube, very slow decomposition takes place over several hours at 25 °C, but there is no further evidence for alkene reactivity. Solutions of 1 in CH_2Cl_2 under 15 bar of C_2H_4 also fail to give any polyethylene or identifiable (GC) ethylene oligomers after 2 h at 25 °C. Similarly, no reaction is observed between 1 and 2-butyne in CD_2Cl_2 at 25 °C.

Conclusions

The dramatic difference in reactivity with $AlCl_3$ between complexes containing the CH($SiMe_3$)$_2$ and CH_2SiMe_3 ligands found in this study shows the important effect of extreme steric crowding in giving unusual reactivity. The inaccessibility of μ-alkyl bonding for the bulkier alkyl ligand prevents alkyl group transfer to aluminum and allows instead the observation of unusual Si–C bond activation via the putative intermediate [Cp'_2Zr{CH($SiMe_3$)$_2$}][Al_2Cl_7], in which agostic Si–C–Zr bonding may increase the susceptibility of silicon for nucleophilic attack.

The unprecedented coordination of a silicon-bound chlorine to zirconium in products 1 and 2 may be compared to chelate bonding of carbon–halogen or aluminum–halogen bonds to electrophilic metals. In contrast to the labile nature of such bonding in the carbon analogues, and of β-C–H–M agostic bonding in formally isoelectronic d^0 $[Cp'_2MR]^{n+}$, the Si–Cl–Zr bond shows no evidence of dissociation in solution. Unlike the zirconium analogue of the Tebbe reagent, which shows partial alkylidene character, the crystal structure of closely related 1 is suggestive of partial Si–C multiple-bond character. The lack of reactivity of 1 with unsaturated substrates may be ascribed to steric as well as electronic saturation at zirconium.

Experimental Section

All experiments were performed under nitrogen in a Braun MB 200-G drybox or under argon using standard Schlenk techniques. Solvents were dried by refluxing over and distilling from standard reagents. Deuterated solvents were dried over 4-Å molecular sieves. $LiCH_2SiMe_3$[37] and LiCH($SiMe_3$)$_2$,[38] as well as (C_5Me_5)$_2$$ZrCl_2$[39] and ($C_5H_5$)$_2$Zr{CH($SiMe_3$)$_2$}Cl,[17] were prepared according to literature methods. *rac*-C_2H_4(indenyl)$_2$$ZrCl_2$, containing less than 5% of the meso isomer, was synthesized by following the improved synthesis of Collins and co-workers.[16] All other reagents were purchased from commercial sources and used without further purification.

^1H NMR (200.00-MHz) spectra were recorded on a Varian XL-200 instrument, and ^{13}C NMR (75.43-MHz) spectra were recorded on a Varian VXR-300 instrument. NMR data are listed in parts per million downfield from TMS for proton and carbon. Spectra were obtained in CD_2Cl_2 at 25 °C unless otherwise noted. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany.

***rac*-C_2H_4(indenyl)$_2$Zr{CH($SiMe_3$)$_2$}Cl.** A solution of LiCH($SiMe_3$)$_2$ (0.31 g, 1.89 mmol) in ether (40 mL) was added to a suspension of *rac*-C_2H_4(indenyl)$_2$$ZrCl_2$ (0.80 g, 1.91 mmol) in ether (40 mL), and the reaction mixture was stirred for 24 h at 25 °C. The resulting mixture was then reduced to dryness in vacuo and the yellow residue extracted with a mixture of toluene and hexane. Cooling to −40 °C gave a fluffy yellow solid, which was collected by centrifugation and washed with hexane (three crops, 0.84 g, 82%). Recrystallization from toluene/hexane afforded an analytically pure sample. ^1H NMR: δ 7.6–7.1 (m, 9, ind), 6.59, 6.29, 6.10 (d, 1, ind-C_5), 3.8–3.2 (m, 4, –CH_2CH_2–), 0.07, −0.12 (s, 9,

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Si*Me*$_3$), −0.69 (s, 1, ZrC*H*). ^{13}C NMR (CDCl$_3$): δ 128.5, 126.7, 126.6, 126.5, 126.0, 125.9, 125.4, 125.3, 125.0, 123.5, 123.4, 121.4, 120.1, 116.8, 113.0, 111.6, 110.5, 102.0 (ind), 58.1 (d, $^1J_{CH}$ = 98 Hz, ZrCH), 27.7, 26.2 (−CH$_2$CH$_2$−), 6.7, 5.2 (Si*Me*$_3$). Anal. Calcd for $C_{27}H_{35}ClSi_2Zr$: C, 59.79; H, 6.51; Cl, 6.54; Si, 10.36. Found: C, 59.66; H, 6.40; Cl, 6.68; Si, 10.20.

rac-C_2H_4(indenyl)$_2$Zr(CH_2SiMe_3)Cl. A suspension of *rac*-C$_2$H$_4$(indenyl)$_2$ZrCl$_2$ (0.20 g, 0.48 mmol) in CH$_2$Cl$_2$ (5 mL) was cooled to −78 °C, and 1.27 mL of a 1.0 M solution of Me$_3$SiCH$_2$MgCl (1.27 mmol) in ether was added. When the mixture was warmed to 25 °C and stirred for 4 days, a pale yellow solution was obtained, which was reduced to dryness in vacuo. Extraction of the residue with a toluene/hexane mixture, followed by cooling to −40 °C, gave 0.10 g of product as pale yellow crystals (45%). ^{1}H NMR (C$_6$D$_6$): δ 7.5–6.8 (m, 8, ind-C$_6$), 6.64, 6.36, 5.90, 5.46 (d, 1, ind-C$_5$), 3.1–2.6 (m, 4, −C*H*$_2$C*H*$_2$−), 0.33 (d, $^2J_{CH}$ = 11.5 Hz, 1, CH_AH$_B$SiMe$_3$), 0.17 (s, 9, CH$_A$H$_B$Si*Me*$_3$), −1.72 (d, 1, CH$_A$$H_B$SiMe$_3$).

(C_5Me_5)$_2$Zr(CH_2SiMe_3)Cl. A mixture of (C$_5$Me$_5$)$_2$ZrCl$_2$ (0.31 g, 0.72 mmol) and LiCH$_2$SiMe$_3$ (0.072 g, 0.77 mmol) in ether (8 mL), to which 2 drops of THF had been added, was stirred for 36 h at 25 °C. The solvent was then removed to vacuo and the residue extracted with a toluene/hexane mixture. The extract was reduced to dryness in vacuo, redissolved in the minimum amount of toluene/hexane mixture, and cooled to −40 °C to give 0.17 g of pale yellow crystals of product (49%). ^{1}H NMR: δ 1.91 (s, 30, C$_5$*Me*$_5$), 0.04 (s, 2, C*H*$_2$SiMe$_3$), −0.08 (s, 9, CH$_2$Si*Me*$_3$).

[rac-C_2H_4(indenyl)$_2\overline{Zr\{CH(SiMe_2Cl}$)(SiMe$_3$)}][$Al_2Cl_{6.5}Me_{0.5}$] (1). A solution of *rac*-C$_2$H$_4$(indenyl)$_2$Zr{CH(SiMe$_3$)$_2$}Cl (0.35 g, 0.64 mmol) in CH$_2$Cl$_2$ (10 mL) at −30 °C was added to solid AlCl$_3$ (0.175 g, 1.31 mmol) in a 30-mL reaction bottle at the same temperature. The reaction mixture was warmed to 25 °C over 10 min and then further stirred for 25 min. Hexane (8 mL) was added to the solution, which was then filtered through Celite to remove a small amount of unreacted AlCl$_3$. Cooling to −40 °C gave red crystalline product (two crops, 0.36 g, 68%). Recrystallization from CH$_2$Cl$_2$/hexane solution gave an analytically pure sample. ^{1}H NMR: δ 7.95 (d, 1, ind-C$_6$), 7.7–7.3 (m, 8, ind), 7.06, 6.28, 6.13 (d, 1, ind-C$_5$), 4.3–3.6 (m, 4, −C*H*$_2$C*H*$_2$−), 0.73, 0.50 (s, 3, Si*Me*$_2$Cl), 0.07 (s, 9, Si*Me*$_3$), −0.14 (s, Al*Me*); the ZrCH resonance is obscured. ^{1}H NMR (C$_7$D$_8$/C$_6$D$_5$Cl (2:1); δ(Ph*Me*) = 2.10 ppm): major species (75%), δ 7.46 (d, 1, ind), 7.2–6.8 (m, 8, ind), 6.57, 5.82, 5.57 (d, 1, ind-C$_5$), 3.7–2.7 (m, 4, −C*H*$_2$C*H*$_2$−), 0.26, 0.14 (s, 3, Si*Me*$_2$Cl), −0.16 (s, 9, Si*Me*$_3$), −0.53 (s, Al*Me*); minor species (25%), δ 6.63, 6.46, 5.63 (d, 1, ind-C$_5$), 0.05, 0.15 (s, 9, Si*Me*$_3$); other resonances were obscured. ^{13}C NMR: −25 °C, δ 127.8, 127.6, 127.4, 127.3, 127.2, 126.9, 126.3, 126.2, 125.1, 124.7, 124.6, 123.2, 121.7, 121.0, 117.8, 117.3, 111.8, 103.1 (ind), 61.1 ($^1J_{CH}$ = 101 Hz, ZrCH), 29.5, 26.9 (−CH$_2$CH$_2$−), 3.6 (Si*Me*$_3$), 3.4, 0.6 (Si*Me*$_2$Cl); −60 °C, δ −6.2 (Al*Me*). Anal. Calcd for $C_{26.5}H_{33.5}Al_2Cl_{7.5}Si_2Zr$: C, 38.85; H, 4.12; Cl, 32.45; Si, 6.86. Found: C, 38.99; H, 4.18; Cl, 32.65; Si, 6.73.

Reaction of Equimolar rac-C_2H_4(indenyl)$_2$Zr{CH($SiMe_3$)$_2$}Cl and $AlCl_3$. A solution of *rac*-C$_2$H$_4$(indenyl)$_2$Zr{CH(SiMe$_3$)$_2$}Cl (5.0 mg, 0.009 mmol) in CD$_2$Cl$_2$ at −30 °C was added to solid AlCl$_3$ (1.4 mg, 0.010 mmol) at −30 °C. When the stirred mixture was warmed to 25 °C, an orange solution of *rac*-C$_2$H$_4$(indenyl)$_2$Zr{CH(SiMe$_3$)$_2$}Cl·AlCl$_3$ was obtained. ^{1}H NMR: δ 8.0–7.0 (m, 9, ind), 6.58, 6.37, 6.10 (d, 1, ind-C$_5$), 3.9–3.1 (m, 4, −C*H*$_2$C*H*$_2$−), 0.07, −0.13 (s, 9, Si*Me*$_3$); the ZrC*H* resonance is obscured by a Si*Me*$_3$ resonance.

[(C_5H_5)$_2\overline{Zr\{CH(SiMe_2Cl}$)($SiMe_3$)}][$Al_2Cl_7$] (2). A solution of (C$_5H_5$)$_2$Zr{CH(SiMe$_3$)$_2$}Cl (0.16 g, 0.39 mmol) in CH$_2$Cl$_2$ (5 mL) at −30 °C was added to solid AlCl$_3$ (0.15 g, 1.12 mmol) at the same temperature. The mixture was warmed slowly to 25 °C and further stirred for 10 min. The solution was filtered through Celite, and hexane (6 mL) was then added to the filtrate. Cooling to −30 °C gave a pale yellow oil, which was then redissolved in CH$_2$Cl$_2$. Addition of hexane and cooling gave an oil, which solidified on washing with hexane (3 × 10 mL) and stirring vigorously. After this residue was dried in vacuo, 140 mg of yellow solid 2 was obtained (55% yield) and shown by NMR spectroscopy to be >95% pure. Attempted crystallization did not succeed, and two independently prepared samples gave incorrect and widely different elemental analyses, presumably due to the thermal instability of the complex. ^{1}H NMR: δ 6.80, 6.79 (s, 5, C$_5$*H*$_5$), 3.83 (br, 1, ZrC*H*), 0.91, 0.75 (s, 3, Si*Me*$_2$Cl), 0.19 (s, 9, Si*Me*$_3$). ^{13}C NMR (15 °C): δ 118.4, 117.2 (C$_5$H$_5$), 59.3 ($^1J_{CH}$ = 101 Hz, ZrCH), 4.7, 3.6 (Si*Me*$_2$Cl), 3.4 (Si*Me*$_3$).

Reaction of Equimolar (C_5H_5)$_2$Zr{CH($SiMe_3$)$_2$}Cl and $AlCl_3$. A stirred mixture of (C$_5$H$_5$)$_2$Zr{CH(SiMe$_3$)$_2$}Cl (10.0 mg, 0.024 mmol) and AlCl$_3$ (3.5 mg, 0.026 mmol) in CD$_2$Cl$_2$ (0.8 mL) was warmed from −30 to +25 °C over 5 min to give a pale yellow solution. ^{1}H NMR spectroscopy showed that the major species present (75%) is (C$_5$H$_5$)$_2$Zr{CH(SiMe$_3$)$_2$}Cl·AlCl$_3$: δ 6.58 (s, 10, C$_5$*H*$_5$), 3.57 (br, 1, ZrC*H*), 0.14 (s, 18, Si*Me*$_3$). Other products are complex 2 (20%) and (C$_5$H$_5$)$_2$ZrCl$_2$·AlCl$_3$ (5%): δ 6.71 (br, 10, C$_5$*H*$_5$) (for reference, see (C$_5$H$_5$)$_2$Zr{CH(SiMe$_3$)$_2$}Cl, ^{1}H NMR δ 6.34 (br, 10, C$_5$*H*$_5$), 2.49 (s, 1, ZrC*H*), 0.12 (br, 18, Si*Me*$_3$), and (C$_5$H$_5$)$_2$ZrCl$_2$, ^{1}H NMR δ 6.49 (br, 10, C$_5$H$_5$)).

Reaction of rac-C_2H_4(indenyl)$_2$Zr(CH_2SiMe_3)Cl with $AlCl_3$. Reaction of *rac*-C$_2$H$_4$(indenyl)$_2$Zr(CH$_2$SiMe$_3$)Cl (7.0 mg, 0.015 mmol) and AlCl$_3$ (2.0 mg, 0.015 mmol) in CD$_2$Cl$_2$ (−30 to +25 °C) gave an orange solution, shown by ^{1}H NMR spectroscopy to be *rac*-C$_2$H$_4$(indenyl)$_2$ZrCl$_2$·(Me$_3$SiCH$_2$)AlCl$_2$: δ 7.8–7.1 (m, 8, ind), 6.68, 6.29 (d, 2, ind-C$_5$), 4.0–3.7 (m, 4, −C*H*$_2$C*H*$_2$−), 0.06 (s, 9, CH$_2$Si*Me*$_3$), −0.48 (br, 2, C*H*$_2$SiMe$_3$).

Addition of excess THF to the reaction mixture led to a yellow solution, shown by ^{1}H NMR spectroscopy to be mostly *rac*-C$_2$H$_4$(indenyl)$_2$ZrCl$_2$ and (Me$_3$SiCH$_2$)AlCl$_2$(THF): δ 7.7–7.1 (m, 8, ind), 6.54, 6.22 (d, 2, ind-C$_5$), 3.9–3.6 (m, 4, −C*H*$_2$C*H*$_2$−), 0.05 (s, 9, CH$_2$Si*Me*$_3$), −0.69 (br, 2, C*H*$_2$SiMe$_3$).

Reaction of (C_5Me_5)$_2$Zr(CH_2SiMe_3)Cl with $AlCl_3$. Reaction of (C$_5$Me$_5$)$_2$Zr(CH$_2$SiMe$_3$)Cl (10.0 mg, 0.021 mmol) and AlCl$_3$ (3.0 mg, 0.022 mmol) in CD$_2$Cl$_2$ (−30 to +25 °C) gave a yellow solution, shown by ^{1}H NMR spectroscopy to be (C$_5$Me$_5$)$_2$ZrCl$_2$·(Me$_3$SiCH$_2$)AlCl$_2$: δ 1.99 (s, 30, C$_5$*Me*$_5$), 0.07 (s, 9, CH$_2$Si*Me*$_3$), −0.41 (br, 2, C*H*$_2$SiMe$_3$). Addition of excess THF gave (C$_5$Me$_5$)$_2$ZrCl$_2$ and (Me$_3$SiCH$_2$)AlCl$_2$(THF) as the major products. ^{1}H NMR: δ 1.96 (s, 30, C$_5$*Me*$_5$), 0.05 (s, 9, CH$_2$Si*Me*$_3$), −0.69 (br, 2, C*H*$_2$SiMe$_3$).

Reaction of Complex 1 with $AlMe_3$. Addition of 1.5 μL of AlMe$_3$ (0.013 mmol) to a solution of 1 (10.0 mg, 0.012 mmol) in CD$_2$Cl$_2$ resulted in the following ^{1}H NMR spectrum: δ 7.7–7.1 (m, 9, ind), 6.66, 6.53, 6.12 (d, 1, ind-C$_5$), 3.9–3.3 (m, 4, −C*H*$_2$CH$_2$−), 0.07, −0.12 (s, 9, Si*Me*$_3$), −0.28 (br, Al*Me*). Addition of a further 1.5 μL of AlMe$_3$ resulted in the following spectrum: δ 7.6–7.1 (m, 9, ind), 6.59, 6.30, 6.10 (d, 1, ind-C$_5$), 3.8–3.2 (m, 4, −C*H*$_2$C*H*$_2$−), 0.08, −0.12 (s, 9, Si*Me*$_3$), −0.33 (br, Al*Me*), −0.69 (s, 1, ZrC*H*).

rac-C_2H_4(indenyl)$_2\overline{Zr\{CH(SiMe_2Cl}$)($SiMe_3$)}Cl (3). Addition of THF (50 μL, 0.62 mmol) to a solution of complex 1 (0.16 g, 0.20 mmol) in CH$_2$Cl$_2$ at −30 °C gave an instantaneous color change from red to yellow. After the mixture was warmed to 25 °C, the solvent was removed in vacuo and the residue was extracted with toluene (3 mL). Addition of 3 mL of hexane to the toluene extract gave a white precipitate of Me$_n$AlCl$_{3-n}$(THF) (n = 0, 1), which was removed by filtration through Celite. Cooling the supernatant solution to −30 °C gave 0.070 g of yellow crystals of 3 (62%). Recrystallization of the complex from CH$_2$Cl$_2$/hexane solution gave an analytically pure sample. ^{1}H NMR: δ 7.7–7.1 (m, 9, ind), 6.53, 6.34, 6.09 (d, 1, ind-C$_5$), 3.9–3.3 (m, 4, −C*H*$_2$C*H*$_2$−), 0.34, 0.30 (s, 3, Si*Me*$_2$Cl), 0.14 (s, 9, Si*Me*$_3$), −0.50 (s, 1, ZrC*H*). ^{13}C NMR (C$_6$D$_6$, 10 °C): δ 126.0, 125.5, 125.2, 123.5, 123.3, 121.6, 121.0, 117.8, 114.0, 112.0, 111.3, 102.4 (ind), 52.6 ($^1J_{CH}$ = 97 Hz, CH), 27.6, 26.2 (−CH$_2$CH$_2$−), 8.7, 7.8 (Si*Me*$_2$Cl), 7.0 (Si*Me*$_3$); one indenyl resonance was obscured by the solvent peak. Anal. Calcd for $C_{26}H_{32}Cl_2Si_2Zr$: C, 55.48; H, 5.73; Cl, 12.60; Si, 9.98. Found: C, 55.43; H, 5.68; Cl, 12.82; Si, 9.83.

Single-Crystal X-ray Diffraction Analysis of [rac-C_2H_4(indenyl)$_2\overline{Zr\{CH(SiMe_2Cl}$)($SiMe_3$)}][$Al_2Cl_{6.5}Me_{0.5}$] (1). A single crystal of 1 (approximate dimensions 0.28 × 0.40 × 0.60 mm), obtained from dichloromethane/hexane solution, was mounted in a thin-walled glass capillary under N$_2$ and held in place with silicone grease. All diffraction measurements were made at low temperature (230 K) on a Nicolet P3m diffractometer fitted with an LT-1 crystal cooling device, using graphite-monochromated Mo Kα X-radiation. Unit cell dimensions were determined from 15 centered reflections in the range 29.0 < 2θ < 30.0°. A total of 7270 diffracted intensities, including check reflections, were measured in a unique quadrant of reciprocal space for $4.0 < 2\theta < 50.0°$ by Wyckoff ω scans. Three check reflections remeasured after every 100 ordinary data showed a decay of 4% and variation of 5% over the period of data collection, the latter apparently associated with intermittent buildup of ice around the crystal; an appropriate correction was therefore applied. Of the 6841 intensity data collected, 6251 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences; of these, 5215 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of the indexed crystal faces; maximum and minimum transmission coefficients were 0.775 and 0.671, respectively. Lorentz and polarization corrections were applied. The structure was solved by conventional heavy-atom (Patterson and Fourier) methods. All non-hydrogen atoms were assigned anisotropic displacements and all hydrogen atoms fixed isotropic displacement parameters. All non-hydrogen atoms and the hydrogen atom H(1) were refined without positional constraints. All other hydrogen atoms were constrained to idealized geometries (C-H = 0.96 Å, H-C-H = 109.5°). One chlorine atom of the anion showed abnormally large displacement parameters as well as a uniquely short Cl-Al distance. Refinement of its occupancy revealed that this site was occupied approximately equally by carbon and chlorine atoms. Separation of the positions of carbon and chlorine atoms led to unstable refinement without identifying distinct positions for these atoms and was therefore abandoned. Accordingly, the atomic site composition was refined, giving final occupancies of 0.47 (1) and 0.53 (1) for the chlorine and carbon atoms at this position (Cl(8)). Full-matrix least-squares refinement of this model (371 parameters) converged to final residual indices $R = 0.053$, $R_w = 0.077$, and $S = 1.999$. Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0007$ was chosen to minimize the variation in S as a function of $|F_o|$. Final difference electron density maps showed no features outside the range +1.2 to −1.11 e Å^{-3}, the largest of these being close to the chlorine atoms of the anion. Attempts to model these electron density features led to physically unreasonable models. All calculations were carried out on a Nicolet R3m/V structure determination system using programs of the SHELXTL-PLUS package.[40] Complex neutral-atom scattering factors were taken from ref 41.

Supplementary Material Available: Listings of anisotropic displacement parameters and hydrogen atomic parameters for complex 1 (2 pages); a listing of observed and calculated structure factors for 1 (23 pages). Ordering information is given on any current masthead page.

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Synthetic, Structural, and Reactivity Studies of Dirhenium Carbonyl Complexes of 17α-Ethynylestradiol and Phenylacetylene: Variable-Temperature ^{13}C NMR Spectra and X-ray Crystal Structure of $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{C–R})\text{Re}_2(\text{CO})_7(\text{MeCN})$

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$\text{Re}_2(\text{CO})_9(\text{MeCN})$ and $\text{Re}_2(\text{CO})_8(\text{MeCN})_2$ have been investigated for the synthesis of dirhenium complexes of alkynes. Only $\text{Re}_2(\text{CO})_8(\text{MeCN})_2$ reacts with 17α-ethynylestradiol and phenylacetylene to produce the complexes $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{C—R})\text{Re}_2(\text{CO})_7(\text{MeCN})$ (1, R = α-ethynylestradiol; 2, R = Ph). Compound 1 was characterized by X-ray diffraction methods: space group $P2_1/n$, $Z = 4$, $a = 7.4262$ (7) Å, $b = 16.146$ (2) Å, $c = 17.060$ (3) Å, $\beta = 101.13$ (1)°. A total of 3301 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure to $R = 0.023$ and $R_w = 0.025$ (258 least-squares parameters). 1 and 2 have been found to react with CO gas, pyridine, and PPh_3 by replacement of the MeCN ligand. The ^{13}C NMR spectra of the complexes $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{C—R})\text{Re}_2(\text{CO})_7(\text{L})$, where L = MeCN or pyridine, reveal a fluxional process involving the carbonyls at the metal bearing the L ligand; the triphenylphosphine compounds, L = PPh_3, do not exhibit this fluxionality. A barrier of 15.7 ± 0.4 kcal mol^{-1} was obtained for the fluxional process in compound 1. The apical CO in complex 3 or 6 is very labile; it can be easily substituted by MeCN, pyridine, PPh_3, and $n\text{-PrNH}_2$. The reaction with $n\text{-PrNH}_2$, leading to the formation of complexes $(\mu\text{-H})(\mu\text{-C}{\equiv}\text{C—R})\text{-}\text{Re}_2(\text{CO})_7(n\text{-PrNH}_2)$, may be contrasted with the behavior of related Fe, Ru, and Os alkyne complexes in which amines react as a nucleophile at the C_α and C_β acetylide carbons.

Introduction

Since the first report appeared in 1974 describing the use of amine oxides to remove coordinated carbon monoxide,[1] these reagents have proven to be very convenient for ligand substitution reactions on metal carbonyl complexes. For example, the substitution of carbon monoxide by the ligand acetonitrile, phosphine, or pyridine is achievable by using this method. Moreover, the reaction of aldehydes, ketones, amides, alkenes, or alkynes with metal carbonyls is improved by using acetonitrile com-

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