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Articles

Synthesis of Permethylindenyl Complexes of the Early Transition Metals. Crystal Structures of Ti(η^5-C$_9$Me$_7$)Cl$_3$ and Zr(η^5-C$_9$Me$_7$)$_2$Cl$_2$

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Addition of 1-(trimethylsilyl)heptamethylindene (C$_9$Me$_7$SiMe$_3$) to a suspension of the anhydrous halides MCl$_4$ (M = Ti, Zr, and Hf) in THF gives the half-sandwich complexes M(η^5-C$_9$Me$_7$)Cl$_3$ (M = Ti, Zr, and Hf) in good yield. Ti(η^5-C$_9$Me$_7$)$_2$Cl$_3$ crystallizes in the centrosymmetric orthorhombic space group *Pbca* with $a = 16.875(4)$ Å, $b = 14.706(3)$ Å, $c = 13.781(3)$ Å, $V = 3420$ Å^3, $Z = 8$, $R = 0.047$, and $R_w = 0.049$. The Ti−C distances range from 2.352(4) to 2.400(4) Å with a mean value of 2.370(5) Å and are consistent with symmetrical bonding of the indenyl ligand to the metal center. The Ti−(η^5-ring centroid) distance is 2.036(4) Å. Addition of 2 equiv of lithium heptamethylindenide (Li$^+$C$_9$Me$_7^-$) to the anhydrous halides MCl$_4$ (M = Zr and Hf) in THF gives the metallocene derivatives M(η^5-C$_9$Me$_7$)$_2$Cl$_2$ (M = Zr and Hf) in good yield. Zr(η^5-C$_9$Me$_7$)$_2$Cl$_2$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with $a = 14.951(12)$ Å, $b = 13.523(6)$ Å, $c = 13.913(11)$ Å, $\beta = 96.46(3)°$, $V = 2795.5$ Å^3, $R = 0.041$, and $R_w = 0.048$. The Zr−C distances range from 2.511(4) to 2.612(4) Å, with a mean value of 2.563(4) Å, and are consistent with symmetrical η^5-bonding of both indenyl ligands to the metal center. The Zr−(η^5-ring centroid) distances are 2.259(4) and 2.255(4) Å with a centroid−Zr−centroid angle of 139.0(4)°. The indenyl ligands are oriented away from the chloride ligands which causes a significant distortion from planarity by folding at the bridgehead carbon atoms.

Introduction

In continuation of our work on the development of the chemistry of transition metal heptamethylindenyl complexes,[1] we have investigated the synthesis of some early metal derivatives. Research aimed at the synthesis of early transition metal metallocenes is still a topic of considerable interest.[2]

In particular, chiral *ansa* metallocenes containing either substituted cyclopentadienyl or indenyl ligands now form the basis of soluble Ziegler−Natta polymerization catalysts.[3,4] For example, Rac-Et[IndH$_4$]$_2$HfCl$_2$, a soluble chiral molecule prepared by Ewen *et al.* in 1987, produces high yields of high molecular weight isotactic polypropylene when combined with methylaluminoxane cocatalyst and (η^5-C$_5$H$_4$CMe$_2$-η^5-C$_{13}$H$_8$)MCl$_2$ (M = Zr, Hf), prepared by Razavi *et al.* in 1992, catalyzes the syndiospecific polymerization of propylene under similar conditions.[5]

In this paper we report the syntheses of early metal (Ti, Zr, and Hf) sandwich and half-sandwich complexes containing the heptamethylindenyl ligand (Scheme 1).

Experimental Section

General Procedures. All reactions were performed using standard Schlenk techniques or in a Vacuum Atmospheres drybox under a nitrogen atmosphere. Solvents were dried by refluxing over an appropriate drying agent in a continuous stream of nitrogen. Solvents were distilled prior to use and stored over molecular sieves (type 4 Å) in flame-dried ampules. NMR spectra were recorded using a Bruker AM 300 (^{1}H 300 MHz) spectrometer. Samples were prepared under nitrogen and placed in air-tight 5 mm screw-topped tubes. Mass spectra were recorded on an electron impact AEI MS 9802 mass spectrometer updated by a data-handling system supplied by Mass Spectrometer Services, Ltd.

Elemental microanalyses were performed by the analytical services section of the Inorganic Chemistry Laboratory, Oxford. The synthesis of heptamethylindene and lithium heptamethylindenide has been described in detail elsewhere.[1]

1-(Trimethylsilyl)heptamethylindene (C$_9$Me$_7$SiMe$_3$). Trimethylsilyl chloride (2.47 g, 0.023 mol) was dissolved in 20 mL of THF. This mixture was added dropwise to a solution of lithium heptamethylindenide (5 g, 0.023 mol) in THF. During the addition the color of the solution changed from orange/brown to lime green and became warm. When the

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(1) Westcott, S. A.; Kakkar, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, 394, 777. O'Hare, D.; Green, J. C.; Marder, T.; Collins, S.; Stringer, G.; Kakkar, A. T.; Kaltsoyannis, N.; Kuhn, A.; Lewis, R.; Mehnert, C.; Scott, P.; Kurmoo, M.; Pugh, S. *Organometallics,* **1992**, *11,* 48. O'Hare, D.; Murphy, V. J.; Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1993**, 383.

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(4) Halterman, R. L. *Chem. Rev.* **1992**, *92,* 965.

(5) Ewen, J.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109,* 6544. Razavi, A.; Atwood, J. L. *J. Am. Chem. Soc.* **1993**, *115,* 7529.

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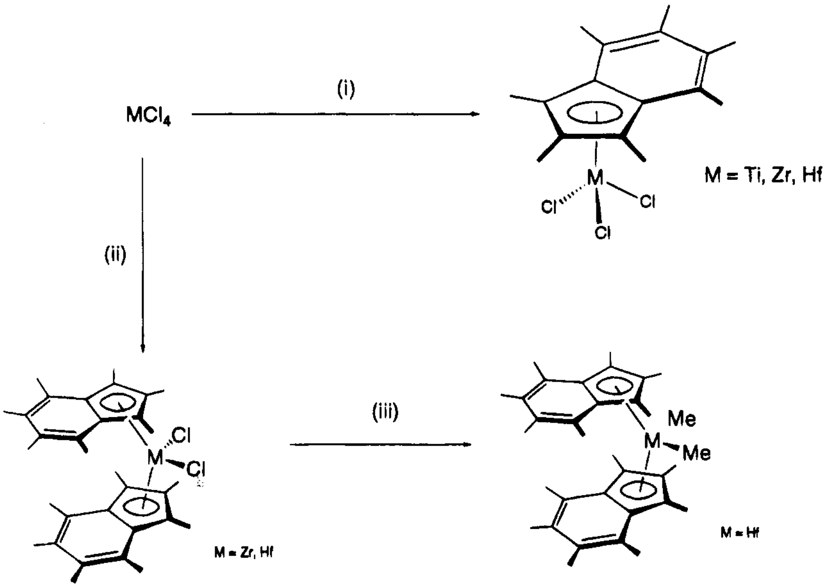
Scheme 1[a]



[a]*Key*: (i) for M = Ti, 1 equiv of $C_9Me_7SiMe_3$ in THF, rt, 24 h, 90% yield; for M = Zr, 1 equiv of $C_9Me_5SiMe_3$ in toluene, 70 °C, 3 h, 60% yield; for M = Hf, 1 equiv of $C_9Me_5SiMe_3$ in toluene, 70 °C, 3 h, 50% yield; (ii) for M = Zr, 2 equiv of $Li^+C_9Me_7^-$ in toluene, 120 °C, 3 d 50% yield; for M = Hf, 2 equiv of $Li^+C_9Me_7^-$ in toluene, 120 °C, 1 d, 40% yield; (iii) excess LiMe in diethyl ether, rt, 3 h, 70% yield

Table 1. Crystallographic Details for Ti(η^5-C_9Me_7)Cl_3 and Zr(η^5-C_9Me_7)$_2$$Cl_2$

formula	$C_{16}H_{21}TiCl_3$	$C_{32}H_{42}ZrCl_2$
formula wt	367.60	588.81
crystal size/mm	0.4 × 0.3 × 0.2	0.55 × 0.2 × 0.35
space group	*Pbca*	$P2_1/n$
a/Å	16.875(4)	14.951(12)
b/Å	14.706(3)	13.523(6)
c/Å	13.781(3)	13.913(11)
β/deg		96.46(3)
cell vol/Å^3	3418.0	2795.5
Z	8	4
D_c/g mL^{-1}	1.43	1.39
μ/cm^{-1}	9.57	5.98
F(000)	1520	1232
radian (*λ*/Å)	0.710 69	0.710 69
θ limits/deg	1−25	1−24
scan mode	*ω* − 2*θ*	*ω* − 2*θ*
total unique data	3004	4372
no. of obsvns ($I > 3\sigma(I)$)	2154	3014
no. of variables	182	317
weighting scheme	unit wts	Chebychev (8.88, −4.01, 6.78)
largest residual/e Å^{-3}	0.4 near Ti	0.9 near Zr
R^a	0.047	0.041
$R_w{}^b$	0.049	0.048

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = \{\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2\}^{1/2}$.

addition was complete a white precipitate had formed. Solvent removal under reduced pressure gave a pale green solid. Addition of toluene gave a very pale green solution which was filtered through Celite, concentrated to *ca.* 30 mL, and cooled to −80 °C to yield an off-white crystalline solid in 95% yield (6.2 g, 0.022 mol).

(Heptamethylindenyl)titanium(IV) Trichloride (Ti(η^5-C_9Me_7)Cl_3). A solution of 1-(trimethylsilyl)heptamethylindene (0.5 g, 1.75 mmol) in toluene (*ca.* 30 cm^3) was slowly added to a toluene solution of $TiCl_4$ (0.33 g, 1.75 mmol) to produce a dark green solution, which was stirred for 12 h at rt. Removal of the solvent under reduced pressure gave a dark green solid. This solid was recrystallized from toluene at −80 °C to produce dark green crystals of Ti(η^5-C_9Me_7)Cl_3 in 90% yield (0.61 g, 1.56 mmol). ^{1}H NMR ($C_6{}^2H_6$) *δ*: 2.51 (s, 2 × Me), 2.39 (s, 2 × Me), 2.00 (s, 1 × Me), 1.96 (s, 2 × Me). Mass spectrum (EI) *m/z*: (M^+) 368, (M^+ − Cl) 333. Anal. Calcd for $C_{16}H_{21}Cl_3Ti$: C, 52.28; H, 5.76. Found: C, 51.95; H, 5.80.

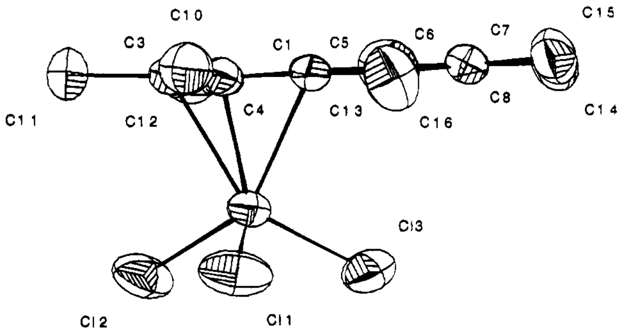


Figure 1. Molecular structure and labeling scheme for Ti(η^5-C_9Me_7)Cl_3 viewed parallel to the plane of the indenyl ligand. Atoms are represented by the 50% thermal probability ellipsoids. The hydrogen atoms have been omitted for clarity.

(Heptamethylindenyl)zirconium(IV) Trichloride (Zr(η^5-C_9Me_7)Cl_3). A solution of 1-(trimethylsilyl)heptamethylindene (0.5 g, 1.75 mmol) in toluene (*ca.* 30 cm^3) was slowly added at rt to a suspension of freshly sublimed $ZrCl_4$ (0.40 g, 1.75 mmol), vigorously stirred in toluene. The resultant deep orange/red solution was heated at 70 °C for 3 h. Solvent removal and subsequent recrystallization from a petroleum ether (bp 40/60 °C)/toluene mixture produced an orange crystalline sample of (η^5-C_9Me_7)$ZrCl_3$ in 60% yield (0.43 g, 1.05 mmol). ^{1}H NMR ($C_6{}^2H_6$) *δ*: 2.55 (s, 2 × Me), 2.48 (s, 2 × Me), 2.23 (s, 1 × Me), 2.06 (s, 2 × Me). Anal. Calcd for $C_{16}H_{21}Cl_3Zr$: C, 46.77; H, 5.57. Found: C, 46.53; H, 5.15.

(Heptamethylindenyl)hafnium(IV) Trichloride (Hf(η^5-C_9Me_7)Cl_3). A solution of 1-(trimethylsilyl)heptamethylindene (0.5 g, 1.75 mmol) in toluene (*ca.* 30 cm^3) was slowly added at rt to a suspension of freshly sublimed $HfCl_4$ (0.56 g, 1.75 mmol), vigorously stirred in toluene. The resultant deep orange solution was heated at 70 °C for 3 h. Solvent removal and subsequent recrystallization from a petroleum ether (bp 40/60 °C)/toluene mixture produced a yellow/orange crystalline sample of Hf(η^5-C_9Me_7)Cl_3 in 50% yield (0.44 g, 0.87 mmol). ^{1}H NMR (C_6D_6) *δ*: 2.68 (s, 2 × Me), 2.49 (s, 2 × Me), 2.25 (s, 1 × Me), 2.14 (s, 2 × Me). Anal. Calcd for $C_{16}H_{21}Cl_3Hf$: C, 38.57; H, 4.25. Found: C, 38.46; H, 4.65.

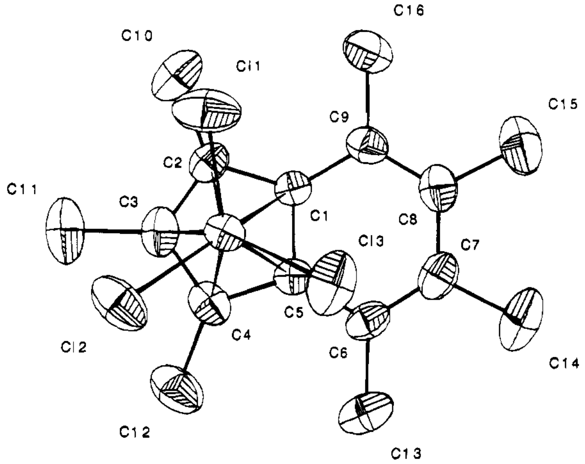


Figure 2. Molecular structure and labeling scheme for Ti(η^5-C_9Me_7)Cl_3 viewed perpendicular to the plane of the indenyl ligand. Atoms are represented by the 50% thermal probability ellipsoids. The hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ti(η^5-C_9Me_7)Cl_3 (Esd's in Parentheses)

atoms	length/Å	atoms	angle/deg
Ti(1)–Cl(1)	2.237(1)	Cl(1)–Ti(1)–Cl(2)	100.85(7)
Ti(1)–Cl(2)	2.235(2)	Cl(1)–Ti(1)–Cl(3)	102.55(7)
Ti(1)–Cl(3)	2.238(2)	Cl(2)–Ti(1)–Cl(3)	102.23(7)
Ti(1)–C(1)	2.383(4)	C(2)–C(1)–C(5)	107.2(4)
Ti(1)–C(2)	2.360(4)	C(2)–C(1)–C(9)	132.6(4)
Ti(1)–C(3)	2.356(5)	C(5)–C(1)–C(9)	120.2(4)
Ti(1)–C(4)	2.352(4)	C(1)–C(2)–C(3)	107.2(4)
Ti(1)–C(5)	2.400(4)	C(1)–C(2)–C(10)	127.9(5)
C(1)–C(2)	1.444(6)	C(3)–C(2)–C(10)	124.3(4)
C(1)–C(5)	1.444(6)	C(2)–C(3)–C(4)	111.0(4)
C(1)–C(9)	1.430(6)	C(2)–C(3)–C(11)	123.7(5)
C(2)–C(3)	1.396(7)	C(4)–C(3)–C(11)	125.3(5)
C(2)–C(10)	1.503(6)	C(3)–C(4)–C(5)	106.7(4)
C(3)–C(4)	1.410(7)	C(3)–C(4)–C(12)	124.6(5)
C(3)–C(11)	1.521(7)	C(1)–C(5)–C(4)	107.8(4)
C(4)–C(5)	1.440(6)	C(1)–C(5)–C(6)	119.9(4)
C(4)–C(12)	1.496(7)	C(4)–C(5)–C(6)	132.3(4)
C(5)–C(6)	1.437(6)	C(5)–C(6)–C(7)	117.7(4)
C(6)–C(7)	1.363(7)	C(7)–C(6)–C(13)	123.5(5)
C(6)–C(13)	1.502(7)	C(6)–C(7)–C(8)	122.4(4)
C(7)–C(8)	1.435(7)	C(7)–C(8)–C(9)	121.6(4)
C(7)–C(14)	1.527(7)	C(6)–C(7)–C(14)	120.0(5)
C(8)–C(9)	1.364(7)	C(1)–C(9)–C(8)	118.1(4)
C(8)–C(15)	1.516(7)	C(1)–C(9)–C(16)	120.2(4)
C(9)–C(16)	1.510(7)	C(8)–C(9)–C(16)	121.7(5)

Bis(heptamethylindenyl)zirconium(IV) Dichloride (Zr(η^5-C_9Me_7)$_2$$Cl_2$). A slurry of lithium heptamethylindenide (1.9 g, 8.5 mmol) in toluene was added to a suspension of freshly sublimed $ZrCl_4$ (0.99 g, 4.25 mmol) vigorously stirred in toluene, and the resultant mixture was refluxed for 3 days. Subsequent solvent removal and recrystallization from a petroleum ether (bp 40/60 °C)/toluene mixture produced orange crystals of (η^5-C_9Me_7)$_2$$ZrCl_2$ in 50% yield (1.25 g, 2.12 mmol). ^{1}H NMR ($C_6{}^2H_6$) δ: 2.35 (s, 4 × Me), 2.12 (s, 4 × Me), 2.08 (s, 2 × Me), 1.88 (s, 4 × Me). $^{13}C\{^1H\}$ NMR ($C_6{}^2H_6$) δ: 136, 133, 130, 126, 112 (s, ring carbons), 19, 16, 14, 13 (s, Me's). Anal. Calcd for $C_{32}H_{42}Cl_2Zr$: C, 65.26; H, 7.17; Cl, 12.04. Found: C, 64.01; H, 7.53; Cl, 11.62 (C could not be obtained within acceptable limits).

Bis(heptamethylindenyl)hafnium(IV) Dichloride (Hf(η^5-C_9Me_7)$_2$$Cl_2$). A slurry of lithium heptamethylindenide (1.9 g, 8.5 mmol) in toluene was added to a suspension of freshly sublimed $HfCl_4$ (1.36 g, 4.25 mmol), vigorously stirred in toluene. This mixture was refluxed for 24 hours to produce an orange/yellow solution. The desired product, Hf(η^5-C_9Me_7)$_2$$Cl_2$, was isolated as a yellow crystalline solid in 40% yield (1.15 g, 1.70 mmol) by solvent removal and subsequent recrystallization from THF. ^{1}H NMR ($C_6{}^2H_6$) δ: 2.37 (s, 4 × Me), 2.19 (s, 4 × Me), 2.10 (s, 4 × Me), 1.93 (s, 2 × Me). Mass spectrum (EI) *m/z*: (M^+) 676, (M^+ − C_9Me_7) 463, (M^+ − C_9Me_7 − Me) 448. Anal. Calcd for $C_{32}H_{42}Cl_2Hf$: C, 56.2; H, 6.3. Found: C, 56.6; H, 6.5.

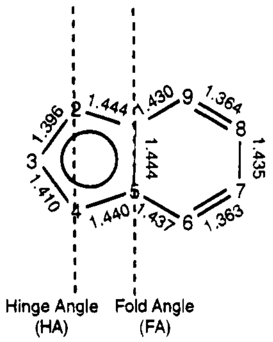


Figure 3. Schematic diagram illustrating the folding axes and bond distances of the indenyl ligand in Ti(η^5-C_9Me_7)Cl_3.

Table 3. Fractional Atomic Coordinates for Ti(η^5-C_9Me_7)Cl_3 (Esd's in Parentheses)

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ti(1)	0.66296(5)	0.82337(5)	0.08435(6)
Cl(1)	0.61371(9)	0.68225(9)	0.0795(1)
Cl(2)	0.77511(8)	0.8052(1)	0.0002(1)
Cl(3)	0.7074(1)	0.8340(1)	0.2369(1)
C(1)	0.5415(2)	0.9043(3)	0.1029(3)
C(2)	0.5443(3)	0.8665(3)	0.0062(3)
C(3)	0.6067(3)	0.9091(3)	−0.0425(3)
C(4)	0.6469(3)	0.9700(3)	0.0192(4)
C(5)	0.6046(2)	0.9703(3)	0.1099(3)
C(6)	0.6158(3)	1.0204(3)	0.1983(4)
C(7)	0.5652(3)	1.0033(3)	0.2732(4)
C(8)	0.5020(3)	0.9384(3)	0.2659(3)
C(9)	0.4910(3)	0.8875(3)	0.1843(4)
C(10)	0.4856(3)	0.8037(3)	−0.0411(4)
C(11)	0.6265(4)	0.8921(4)	−0.1487(4)
C(12)	0.7164(3)	1.0268(4)	−0.0105(5)
C(13)	0.6834(3)	1.0867(4)	0.2045(5)
C(14)	0.5768(4)	1.0510(4)	0.3706(4)
C(15)	0.4468(4)	0.9281(4)	0.3519(4)
C(16)	0.4278(3)	0.8150(4)	0.1788(5)

Bis(heptamethylindenyl)dimethylhafnium(IV) (Hf(η^5-C_9Me_7)$_2$$(CH_3)_2$). Hf($\eta^5$-$C_9Me_7$)$_2$($Cl_2$) (0.080 g, 0.17 mmol) was dissolved in diethyl ether to produce a light yellow solution. An excess of methyllithium was added dropwise at ice temperature, with continuous stirring to produce a pale green solution. This mixture was stirred for 3 h. Solvent removaland recrystallization from THF gave pale green air-sensitive crystals of (η^5-C_9Me_7)$_2$Hf$(CH_3)_2$ in 70% yield (0.054g, 0.12 mmol). ^{1}H NMR ($C_6{}^2H_6$) δ: 2.34 (s, 4 × Me), 2.17 (s, 4 × Me), 2.15 (s, 4 × Me), 1.71 (s, 2 × Me), −1.0 (s, 2 × Hf-*Me*). ^{13}C NMR ($C_6{}^2H_6$) δ: 132, 125, 105 (s, ring carbons), (other peaks obscured by solvent peak), 44 (s, Me), 17.8, 16.4, 14.3, 11.6 (s, ring Me's).

Crystal Structure Determinations for Ti(η^5-C_9Me_7)Cl_3 and Zr(η^5-C_9Me_7)$_2$$Cl_2$. Crystal data, data collection, and processing parameters are given in Table 1. The general procedure was as follows. A crystal was mounted in a Lindemann tube (0.7 mm) under dinitrogen and sealed with a small flame. This was transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were calculated from the setting angles of 25 carefully centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections. The data were corrected for Lorentz and polariza-

Table 4. Comparison of the Solid State Structures of Some Heptamethylindenyl Complexes

compd	M−C(av)/Å	Δ_{M-C}/Å	HA/deg	FA/deg	RA/deg	ref
$[Co(\eta\text{-}C_9Me_7)_2]^+$	2.077(8)	0.079(9), 0.087(9), 0.079(9), 0.049(9)	5.4, 4.7 3.9, 4.0	5.5, 5.4 4.8, 3.4	89	1
$[Cr(\eta\text{-}C_9Me_7)_2]^+$	2.208(6)	0.010(9), 0.025(8), 0.035(8), 0.020(7)	5.0, 5.3 5.4, 4.8	1.5, 4.3 3.8, 0.2	89	1
$[Cr(\eta\text{-}C_9Me_7)_2]$	2.182(8)	0.097(9)	7.2	3.6	180	1
$[Fe(\eta\text{-}C_9Me_7)_2]$	2.074(4)	0.030(14)	2.5	4.4	151	1
$[Ti(\eta\text{-}C_9Me_7)Cl_3]$	2.370(4)	0.035(4)	3.4	3.1		this work
$[Zr(\eta\text{-}C_9Me_7)_2Cl_2]$	2.562(4)	0.038(4), 0.035(4)	8.3(5), 11.3(5)	10.3(4), 10.5(5)	98	this work

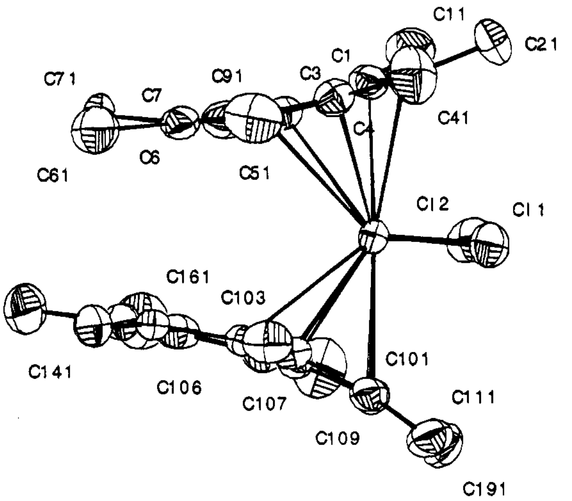


Figure 4. Molecular structure and labeling scheme for $Zr(\eta^5\text{-}C_9Me_7)_2Cl_2$ viewed parallel to the Cl−Zr−Cl plane. Atoms are represented by the 50% thermal probability ellipsoids. The hydrogen atoms have been omitted for clarity.

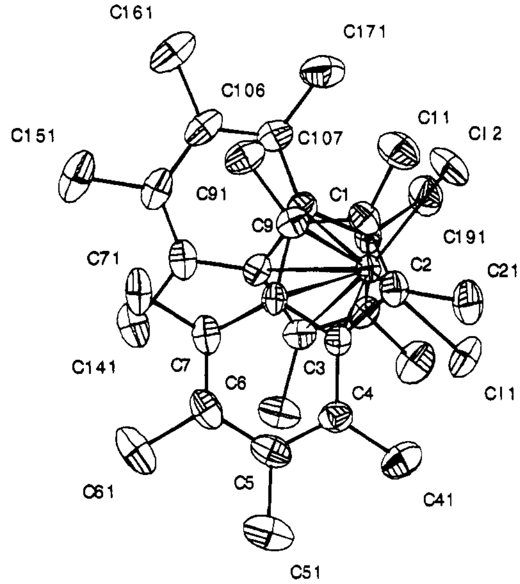


Figure 5. Molecular structure and labeling scheme for $Zr(\eta^5\text{-}C_9Me_7)_2Cl_2$ viewed perpendicular to the Cl−Zr−Cl plane. Atoms are represented by the 50% thermal probability ellipsoids. The hydrogen atoms have been omitted for clarity.

tion effects.[6] For both structures the heavy atom positions were revealed by direct methods. Subsequent Fourier difference syntheses revealed the positions of the other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures. The hydrogen atoms were fixed in geometrically idealized positions and allowed to ride on their attached carbon atoms. The hydrogen atoms were given isotropic thermal parameters according to the atom to which they were attached (these were not refined). For $Ti(\eta^5\text{-}C_9Me_7)Cl_3$ and $Zr(\eta^5\text{-}C_9Me_7)_2Cl_2$ empirical absorption corrections using DIFABS[7] were applied. A Chebyshev weighting scheme[8] was applied for $Zr(\eta^5\text{-}C_9Me_7)_2Cl_2$, and in both determinations the data were corrected for the effects of anomalous dispersion and isotropic extinction (via an overall extinction parameter)[9] in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite[10] on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Neutral atom scattering factors were taken from the usual sources.[11]

Results and Discussion

Synthesis of Heptamethylindenyl Complexes $M(\eta^5\text{-}C_9Me_7)Cl_3$ (M = Ti, Zr, and Hf). The synthesis of the half-sandwich complexes $M(Ind^*)Cl_3$ (M = Ti, Zr, and Hf; Ind* = $\eta^5\text{-}C_9Me_7$) was achieved using the silylpermethylindene derivative ($C_9Me_7SiMe_3$). Silyl- and stannylcyclopentadienyl have been used previously as mild ligand transfer reagents.[12] The dropwise addition of a toluene solution of $C_9Me_7SiMe_3$ to a toluene solution of MCl_4 (M = Ti, Zr, and Hf) gives, after workup and recrystallization from toluene, crystals of the heptamethylindenyl complexes $M(Ind^*)Cl_3$ (Ind* = $\eta^5\text{-}C_9Me_7$) in good yield.

All three compounds are air sensitive, decomposing in minutes both in the solid state and in solution. They are all readily soluble in toluene, petroleum ether, diethyl ether, and dichloromethane. The ^1H NMR spectra of these compounds in $C_6{}^2H_6$ solution exhibit four singlets of relative intensity 2:2:2:1 assignable to the methyl groups of the η^5-coordinated heptamethylindenyl ligand.

Structure of $Ti(Ind^*)Cl_3$. Crystals suitable for single crystal X-ray analysis were grown by slowly cooling a concentrated CH_2Cl_2 solution to −80 °C. Details of the crystallographic parameters are given in Table 1. The molecular structure of $Ti(\eta^5\text{-}C_9Me_7)Cl_3$ together with the atomic labeling is shown in Figures 1 and 2. Selected bond lengths and angles are presented in Table 2. The positional parameters are given in Table 3. The compound crystallizes in the centrosymmetric orthorhombic space group *Pbca*. $Ti(Ind^*)Cl_3$ in the solid state adopts a distorted tetrahedral arrangement with Cl−Ti−Cl bond angles ranging between

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for $Zr(\eta^5\text{-}C_9Me_7)_2Cl_2$ (Esd's in Parentheses)

atoms	length/Å	atoms	angle/deg
Zr(1)−Cl(1)	2.440(1)	C(2)−C(1)−C(9)	110.0(4)
Zr(1)−Cl(2)	2.419(1)	C(2)−C(1)−C(11)	125.3(4)
Zr(1)−C(1)	2.575(4)	C(9)−C(1)−C(11)	124.4(4)
Zr(1)−C(2)	2.546(4)	C(1)−C(2)−C(3)	107.5(4)
Zr(1)−C(3)	2.573(4)	C(1)−C(2)−C(21)	122.4(4)
Zr(1)−C(8)	2.602(4)	C(3)−C(2)−C(21)	129.4(4)
Zr(1)−C(9)	2.527(4)	C(2)−C(3)−C(4)	132.4(4)
Zr(1)−C(101)	2.571(4)	C(2)−C(3)−C(8)	107.1(4)
Zr(1)−C(102)	2.511(4)	C(4)−C(3)−C(8)	120.4(4)
Zr(1)−C(103)	2.612(4)	C(3)−C(4)−C(5)	118.6(4)
Zr(1)−C(108)	2.554(4)	C(3)−C(4)−C(41)	120.4(4)
Zr(1)−C(109)	2.561(4)	C(5)−C(4)−C(41)	120.9(4)
C(1)−C(2)	1.404(7)	C(4)−C(5)−C(6)	120.6(4)
C(1)−C(9)	1.419(6)	C(4)−C(5)−C(51)	119.4(5)
C(1)−C(11)	1.499(6)	C(6)−C(5)−C(51)	120.0(5)
C(2)−C(3)	1.446(6)	C(5)−C(6)−C(7)	122.3(4)
C(2)−C(21)	1.514(6)	C(5)−C(6)−C(61)	117.7(5)
C(3)−C(4)	1.428(6)	C(7)−C(6)−C(61)	119.9(5)
C(3)−C(8)	1.436(6)	C(6)−C(7)−C(8)	117.8(4)
C(4)−C(5)	1.383(7)	C(6)−C(7)−C(71)	122.3(4)
C(4)−C(41)	1.509(7)	C(8)−C(7)−C(71)	119.3(4)
C(5)−C(6)	1.433(7)	C(3)−C(8)−C(7)	119.3(4)
C(5)−C(51)	1.510(7)	C(3)−C(8)−C(9)	108.3(3)
C(6)−C(7)	1.375(7)	C(7)−C(8)−C(9)	131.5(4)
C(6)−C(61)	1.523(6)	C(1)−C(9)−C(8)	106.6(4)
C(7)−C(8)	1.445(6)	C(1)−C(9)−C(91)	122.6(4)
C(7)−C(71)	1.502(7)	C(8)−C(9)−C(91)	129.6(4)
C(8)−C(9)	1.436(6)	C(102)−C(101)−C(109)	110.0(4)
C(9)−C(91)	1.509(6)	C(102)−C(101)−C(111)	124.9(4)
C(101)−C(102)	1.414(6)	C(109)−C(101)−C(111)	124.7(4)
C(101)−C(109)	1.407(6)	C(101)−C(102)−C(103)	106.9(4)
C(101)−C(111)	1.496(6)	C(101)−C(102)−C(121)	122.5(4)
C(102)−C(103)	1.440(6)	C(103)−C(102)−C(121)	129.7(4)
C(102)−C(121)	1.508(6)	C(102)−C(103)−C(104)	131.7(4)
C(103)−C(104)	1.432(6)	C(102)−C(103)−C(108)	107.7(3)
C(103)−C(108)	1.441(6)	C(104)−C(103)−C(108)	119.8(4)
C(104)−C(105)	1.383(7)	C(103)−C(104)−C(105)	117.8(4)
C(104)−C(141)	1.516(7)	C(103)−C(104)−C(141)	119.0(4)
C(105)−C(106)	1.434(7)	C(105)−C(104)−C(141)	122.4(4)
C(105)−C(151)	1.504(7)	C(104)−C(105)−C(106)	121.6(4)
C(106)−C(107)	1.838(7)	C(104)−C(105)−C(151)	119.5(5)
C(106)−C(161)	1.516(7)	C(106)−C(105)−C(151)	118.9(5)
C(107)−C(108)	1.431(6)	C(105)−C(106)−C(107)	121.9(4)
C(107)−C(171)	1.499(7)	C(105)−C(106)−C(161)	119.0(5)
C(108)−C(109)	1.448(6)	C(107)−C(106)−C(161)	119.2(5)
C(109)−C(191)	1.506(6)	C(106)−C(107)−C(108)	117.3(4)
		C(106)−C(107)−C(171)	121.9(4)
		C(108)−C(107)−C(171)	120.8(4)
		C(103)−C(108)−C(107)	120.7(4)
		C(103)−C(108)−C(109)	107.1(4)
		C(107)−C(108)−C(109)	132.0(4)
		C(101)−C(109)−C(108)	107.4(4)
		C(101)−C(109)−C(191)	123.2(4)
		C(108)−C(109)−C(191)	128.4(4)

Table 6. Fractional Atomic Coordinates for $Zr(\eta^5\text{-}C_9Me_7)_2Cl_2$ (Esd's in Parentheses)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)	occ
Zr(1)	0.29242(2)	0.19045(3)	0.02682(3)	0.0258	1.0000
Cl(1)	0.34899(8)	0.3054(1)	0.15458(8)	0.0448	1.0000
Cl(2)	0.42035(8)	0.0811(1)	0.05869(9)	0.0468	1.0000
C(1)	0.3820(3)	0.2176(3)	−0.1185(3)	0.0354	1.0000
C(2)	0.3836(3)	0.3073(3)	−0.0676(3)	0.0341	1.0000
C(3)	0.2931(3)	0.3466(3)	−0.0788(3)	0.0290	1.0000
C(4)	0.2561(3)	0.4377(3)	−0.0496(3)	0.0360	1.0000
C(5)	0.1666(3)	0.4581(4)	−0.0796(3)	0.0405	1.0000
C(6)	0.1147(3)	0.3937(4)	−0.1460(3)	0.0380	1.0000
C(7)	0.1484(3)	0.3061(4)	−0.1770(3)	0.0333	1.0000
C(8)	0.2377(3)	0.2770(3)	−0.1363(3)	0.0274	1.0000
C(9)	0.2922(3)	0.1932(3)	−0.1548(3)	0.0328	1.0000
C(11)	0.4633(3)	0.1610(4)	−0.1409(4)	0.0518	1.0000
C(21)	0.4705(3)	0.3553(4)	−0.0244(4)	0.0482	1.0000
C(41)	0.3150(4)	0.5123(4)	0.0079(5)	0.0583	1.0000
C(51)	0.1250(4)	0.5517(4)	−0.0456(5)	0.0612	1.0000
C(61)	0.0204(3)	0.4270(5)	−0.1854(4)	0.0568	1.0000
C(71)	0.1016(3)	0.2483(4)	−0.2601(3)	0.0448	1.0000
C(91)	0.2692(4)	0.1044(4)	−0.2185(3)	0.0435	1.0000
C(101)	0.1958(3)	0.1525(3)	0.1639(3)	0.0332	1.0000
C(102)	0.1392(3)	0.1910(3)	0.0845(3)	0.0321	1.0000
C(103)	0.1305(3)	0.1154(3)	0.0111(3)	0.0281	1.0000
C(104)	0.0650(3)	0.1003(4)	−0.0709(3)	0.0340	1.0000
C(105)	0.0713(3)	0.0150(4)	−0.1246(3)	0.0396	1.0000
C(106)	0.1422(3)	−0.0554(4)	−0.1012(3)	0.0380	1.0000
C(107)	0.2028(3)	−0.0464(3)	−0.0190(3)	0.0395	1.0000
C(108)	0.1938(3)	0.0381(3)	0.0412(3)	0.0309	1.0000
C(109)	0.2327(3)	0.0617(3)	0.1386(3)	0.0309	1.0000
C(111)	0.2057(4)	0.1952(4)	0.2638(3)	0.0488	1.0000
C(121)	0.0878(3)	0.2863(4)	0.0902(4)	0.0463	1.0000
C(141)	−0.0156(3)	0.1689(4)	−0.0862(4)	0.0474	1.0000
C(151)	0.0016(4)	−0.0056(5)	−0.2088(4)	0.0595	1.0000
C(161)	0.1495(5)	−0.1432(5)	−0.1676(4)	0.0621	1.0000
C(171)	0.2737(4)	−0.1228(4)	0.0083(5)	0.0618	1.0000
C(191)	0.2882(3)	−0.0035(4)	0.2100(4)	0.0470	1.0000

100.85(7)° and 102.55(7)°. The Ti−C bond lengths range between 2.352(4) and 2.400(4) Å with an average of 2.370(5) Å. The Ti−C_5−ring centroid distance is 2.036(4) Å. These Ti−C bond lengths are very similar to those reported for $Ti(C_5Me_5)Me_3$, $Ti(C_5Me_5)Cl_3$, $Ti(C_5Me_5)_2Cl_2$, $Ti(C_5H_5)_2Cl_2$, and $Ti(C_5Me_5)(C_5H_5)Cl_2$.[13]

Recently, several parameters have been devised to quantify possible distortions in metal−indenyl complexes.[1] The slip parameter (Δ_{M-C}), is defined as the difference in the average bond lengths of the metal to the ring-junction carbons C(1), C(5) and the metal to adjacent carbon atoms of the five membered ring, C(2), C(3), and C(4). The hinge angle (HA) is defined as the angle between the planes defined by [C(2), C(3), C(4)] and [C(1), C(2), C(4), C(5)]. The fold angle (FA) is defined as the angle between the planes defined by [C(1), C(2), C(3), C(4), C(5)] and [C(1), C(5), C(6), C(7), C(8), C(9)]. Hence, HA represents bending along the vector C(2)−C(4) and FA represents bending along the vector C(1)−C(5) as schematically illustrated in Figure 3. Table 4 gives a summary of the these parameters together with data for other structurally characterized heptamethylindenyl complexes. The distortion parameters, Δ_{M-C}, HA, and FA were all found to be relatively small. These data suggest essentially symmetrical bonding of the indenyl ligand with no $\eta^5-\eta^3$ ring slip. However, significant bond alternation is observed in the internal C−C bond lengths of the 6-membered ring as shown in Figure 3.

Synthesis of Bis(heptamethylindenyl) Complexes $M(Ind^*)_2Cl_2$ (M = Zr and Hf). Refluxing a mixture of either $ZrCl_4$ or $HfCl_4$ with 2 equiv of $Li^+(C_9Me_7)^-$ in toluene for 1−3 days produces, after workup and recrystallization from toluene or THF, crystals of the bis(heptamethylindenyl) complexes $M(Ind^*)_2Cl_2$ (M = Zr, Hf) in moderate yield. Both compounds are air stable in the solid state. They are all readily soluble in toluene, petroleum ether, diethyl ether, and dichloromethane. The ^1H NMR spectra of these compounds in $C_6{}^2H_6$ solution exhibit four singlets of relative intensity 2:2:2:1 assignable to methyl substituents of two equivalent η^5-coordinated heptamethylindenyl ligands.

Structure of $Zr(Ind^*)_2Cl_2$. Crystals suitable for single-crystal X-ray analysis were grown by slowly cooling a concentrated toluene/petroleum ether (1:1) solution to −80 °C. Details of the crystallographic parameters are given in Table 1. The molecular struc-

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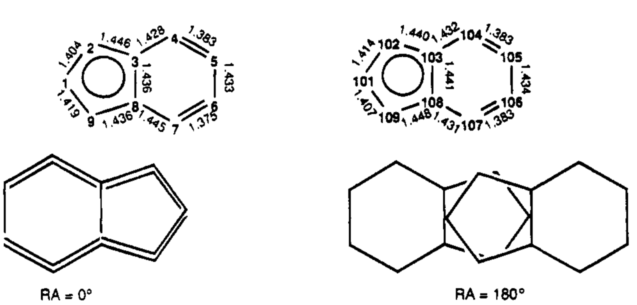

Figure 6. Schematic diagram illustrating the rotation axes and bond distances of the indenyl ligands in Zr(η^5-$C_9Me_7)_2Cl_2$.

ture of $Zr(Ind^*)_2Cl_2$ together with the atomic labeling is shown in Figures 4 and 5. Selected bond lengths and angles are presented in Table 5. The positional parameters are given in Table 6. This complex crystallizes in the monoclinic space group $P2_1/n$. In the solid state the zirconium is in a pseudotetrahedral environment, with Zr–C bond lengths ranging between 2.511(4) Å and 2.612(4) Å with an average of 2.563(4) Å. The Zr–C_5–ring centroid distances are 2.259(4) and 2.255(4) Å. The angle between the normals to the ring centroids is 139.0(4)°. These values are very similar to those reported for Zr(η^5-$C_9H_7)_2Me_2$, Zr(η^5-$C_5H_5)_2Cl_2$, Zr(η^5-$C_5H_5)_2Me_2$, and Zr(η^5-$C_5Me_5)_2Me_2$.[14]

The indenyl rotation angle (RA) has been defined as the angle formed by the projection of the two lines determined by the centroids of the 5- and 6-membered rings on to the Cl–Zr–Cl plane. Hence, an RA value of 180° would correspond to a fully staggered arrangement, while an RA value of 0° would correspond to a fully eclipsed arrangement (Figure 6). The value of RA for $Zr(Ind^*)_2Cl_2$ is 98° indicating a partially staggered arrangement of the heptamethylindenyl rings. Although the RA value for Zr(η^5-$C_9H_7)_2Me_2$ was not reported, the structure determination indicates that the indenyl rings are almost eclipsed in a similar fashion to that of Fe(η^5-$C_9H_7)_2$, i.e., an RA value of around 10°. Surprisingly, the X-ray structure of $Zr(Ind)_2Me_2$ shows that the indenyl ligands are oriented with the 6-membered rings directed over the Zr–Me ligands, while for Zr(η^5-$C_9Me_7)_2Cl_2$ the Ind* ligands have the 6-membered rings tilted back in the opposite direction.

The distortion parameters Δ_{M-C}, HA, and FA measured for Zr(η^5-$C_9Me_7)_2Cl_2$ are given in Table 2. The data suggest essentially symmetrical bonding of the indenyl ligand with no $\eta^5-\eta^3$ ring slip. However, the large values of HA and FA indicate that the indenyl ligands are significantly distorted from planarity, which is possibly due to the nonbonded methyl–methyl repulsions between the two ligands.

Preparation of $Hf(Ind^*)_2(CH_3)_2$. Addition of 2 equiv of methyllithium to a solution of $Hf(Ind^*)_2Cl_2$ in toluene at 0 °C gave a pale green solution. Solvent removal and recrystallization from THF gave pale green air-sensitive crystals of the dimethyl complex $Hf(Ind^*)_2(CH_3)_2$ in good yield. The ^1H NMR ($C_6{}^2H_6$) of this complex reveals a peak a $\delta = -1.0$ corresponding to the Hf-*Me* protons. This chemical shift (in C_6D_6) compares with $\delta = -0.62$ for $Zr(C_5Me_5)_2(Me)_2$ and $\delta = -0.70$ for $Hf(C_5Me_5)_2(Me)_2$ has been ascribed to shielding effects of the indenyl ring currents.[16]

Summary

In this paper we have demonstrated the accessibility of heptamethylindenyl group 4 chemistry. The complexes (η^5-$C_9Me_7)MCl_3$ (M = Ti, Zr, Hf) and (η^5-$C_9Me_7)_2MCl_2$ (M = Zr, Hf) and have been conveniently prepared in reasonable yields; this should facilitate future chemical and mechanistic studies into these compounds containing the powerful electron-releasing heptamethylindenyl ligand.

In addition, in view of the catalytic activity of the corresponding cyclopentadienyl and pentamethylcyclopentadienyl complexes, and the importance of ring substituents on the stereochemical outcome of polymerization reactions, it is possible that the heptamethylindenyl ligand might become important in the stereoselective polymerization of α-olefins.[16]

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Supplementary Material Available: Listings of anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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