Bis(cyclooctatetraene) Derivatives of Zirconium(IV) and Hafnium(IV): Syntheses and Lewis Base Adducts. Crystal Structures of $[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$, $[Hf\{\eta^8\text{-}C_8H_6(SiMe_3)_2\}\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}]$, $[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(NH_3)]$ and $[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(CNBu^t)]$†

Pietro Berno,[a] Carlo Floriani,*,[a] Angiola Chiesi-Villa[b] and Corrado Rizzoli[b]
[a] *Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland*
[b] *Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy*

The syntheses of $[M(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$ (M = Zr, **2** or Hf, **3**) and $[M\{\eta^8\text{-}C_8H_6(SiMe_3)_2\}\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}]$ (M = Zr, **4** or Hf, **5**) are reported. The η^8 and η^4 bonding modes for C_8H_8 were established in the solid state by X-ray analyses, while in solution a single C_8H_8 environment was observed by ^1H NMR spectroscopy even at low temperature in accord with fluxional behaviour for these compounds. Complexes **2–5** behave as Lewis acids toward tetrahydrofuran, NH_3 and Bu^tNC and the adducts $[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(NH_3)]$ **6** and $[M(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(CNBu^t)]$ (M = Zr, **7** or Hf, **8**) have been isolated and characterized by X-ray analysis. Crystallographic details: **2**, monoclinic, space group $P2_1/c$, a = 13.754(1), b = 7.798(1), c = 12.753(1) Å, β = 114.02(1)°, Z = 4 and R = 0.037 for 1267 independent observed reflections; **5**, orthorhombic, space group $Pca2_1$, a = 14.418(1), b = 11.285(1), c = 18.898(1) Å, Z = 4 and R = 0.036 for 2239 independent observed reflections; **6**, orthorhombic, space group $P2_12_12_1$, a = 9.815(1), b = 14.129(2), c = 9.561(1) Å, Z = 4 and R = 0.022 for 1556 independent observed reflections; **7**, triclinic, space group $P\bar{1}$, a = 11.172(1), b = 13.469(1), c = 14.303(1) Å, α = 62.80(1), β = 78.01(1), γ = 77.26(1)°, Z = 4 and R = 0.028 for 2994 independent observed reflections.

Cyclooctatetraene is an electronically versatile ligand which can act either as a planar aromatic anion $C_8H_8^{2-}$ (10 electrons) or as a tube-shaped tetraolefin (8 electrons).[1] As the latter η^2, η^4, η^6 or η^8 co-ordination can be adopted. Cyclooctatetraene should be particularly useful in the chemistry of electron-deficient early transition metals,[2–4] yet its use in organometallic chemistry is much more limited than that of the cyclopentadienyl ($\eta\text{-}C_5H_5$) ligand. Whereas the $M(\eta\text{-}C_5H_5)$ fragment remains intact the $M(\eta\text{-}C_8H_8)$ fragment is much less resistant to oxidation at the metal centre. This is associated with facile transition between M^{n+} to $M^{(n-2)+}$ oxidation states, through the formal transfer of an electron pair from the aromatic $C_8H_8^{2-}$ ligand which is converted into the labile tetraolefin.

Herein we report the synthesis and the structural characterization of bis(cyclooctatetraene)-zirconium(IV) and -hafnium(IV) derivatives, the only previously characterized example being the complex $[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(thf)]$ (thf = tetrahydrofuran).[5,6] Such complexes can be considered as starting materials for the synthesis of $[M(\eta^8\text{-}C_8H_8)X_2]$ derivatives[3,7] and plausible precursors of the $M^{II}(\eta^8\text{-}C_8H_8)]$ fragment by the displacement of one of the C_8H_8 ligands.

Results and Discussion

Previously bis(cyclooctatetraene)zirconium has been isolated and structurally characterized as its thf solvate, **1**.[5,6] We found, however, that by heating complex **1** in the solid state and recrystallizing it from toluene or 1,2-dimethoxyethane (dme) the unsolvated form, **2** could be obtained [equation (1)].

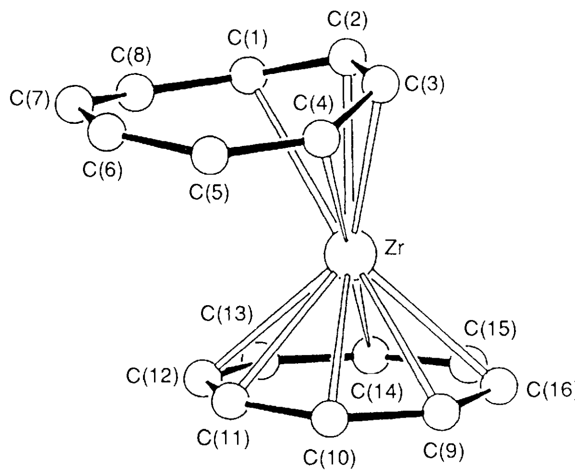


Fig. 1 A SCHAKAL drawing of complex **2**

$$\underset{\mathbf{1}}{[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(thf)]} \xrightarrow{-\text{thf}} \underset{\mathbf{2}}{[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]} \quad (1)$$

The ^1H NMR spectrum of complex **2** showed a singlet at δ 6.01, coincident with the singlet for the C_8H_8 ligand in **1**. This is in agreement with only a weakly bonded thf molecule in **1**. The

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

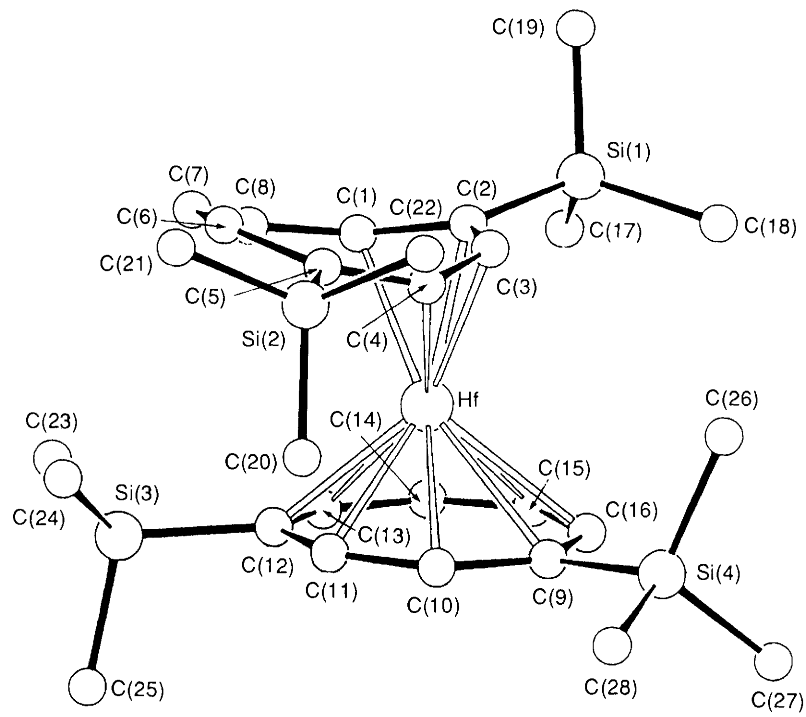


Fig. 2 A SCHAKAL drawing of complex **5**

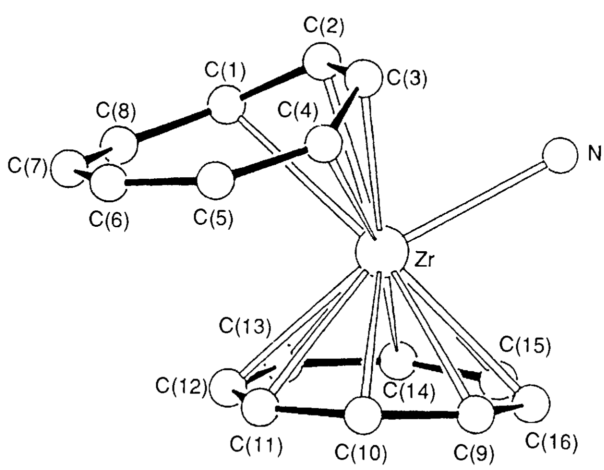


Fig. 3 A SCHAKAL drawing of complex **6**

averaged singlet was observed even at low temperature (203 K) and suggests a very high degree of fluxionality for the molecule. The molecule of thf does not greatly affect the solid state η^8 and η^4 bonding modes of the two C_8H_8 ligands, as seen by comparison of the already known structure of **1**[5,6] and that of **2** shown in Fig. 1. By contrast to Zr, the synthesis of the bis(cyclooctatetraene) derivative of hafnium in thf led directly to the isolation of the unsolvated form, $[Hf(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$ **3**,[8] possibly as a consequence of the difference in acidity between Zr and Hf. The difference in ease of formation of the unsolvated hafnium compound compared to its zirconium analogue may, however, also be due to the slightly smaller radius of Hf^{4+} The differing sizes of the two elements are suggested to be responsible for the gross difference in structure of their tetrakis(cyclopentadienyl) derivatives $[Zr(\eta^5\text{-}C_5H_5)_3(\sigma\text{-}C_5H_5)]$[9a] and $[Hf(\eta^5\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)_2]$.[9b]

The desolvation of complex **1** in toluene or dme gave two crystallographically different forms of **2**, form **A** from toluene and form **B** from dme, with similar chemical features. Form **B** is isostructural to complex **3**.*

Following a recent procedure proposed by Cloke and co-workers[10] we introduced two trimethylsilyl substituents into the C_8H_8 ligand to give $C_8H_8(SiMe_3)_2$-1,4 which was then reduced with LiBu and treated with Zr and Hf as for the unsubstituted C_8H_8 ligand [equation (2)].

$$C_8H_8(SiMe_3)_2\text{-}1,4 \xrightarrow{2LiBu} Li_2[C_8H_6(SiMe_3)_2\text{-}1,4] \quad (2)$$

$$\xrightarrow[2LiCl]{[MCl_4(thf)_2]} [M\{\eta^8\text{-}C_8H_6(SiMe_3)_2\}\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}]$$

M = Zr, **4** or Hf, **5**

The steric crowding provided by the two substituted cyclooctatetraene ligands is probably responsible for the absence of solvation in **4** and **5**, rather than the decreased acidity of the metal. The solution behaviour of **4** and **5**, as monitored by ^1H NMR spectroscopy, shows only one averaged ligand environment as for the unsubstituted derivatives indicating a fluxional structure, although the solid-state structure of **5** (Fig. 2) shows both η^8- and η^4-co-ordinated cyclooctatetraene.

Some of the most intriguing reactions of complexes **1** and **2** concern their hydrolysis, which has been observed to lead to some interesting oxo aggregates.[11] The binding of water by zirconium in **2** is expected to increase its acidity and lead to hydrolysis. A model of such a preliminary binding of water was obtained on treating **1** with gaseous NH_3 [equation (3)].

$$\mathbf{1} + NH_3 \xrightarrow{-thf} [Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(NH_3)] \quad (3)$$

6

* Complexes **3** and **2** (form **B**) are isostructural with a = 11.195(4), b = 7.874(3), c = 7.059(3) Å, β = 96.3°, U = 618.5 Å^3, Z = 2, space group $P2_1/n$ from systematic absences. The molar volume is nearly the same of **2** (form **A**). The structure of **3** has been solved in the space group P_n, by considering the hafnium atom to be distributed statistically over two positions (50% site occupancy factor), at a distance of 0.40 Å to each other. The two C_8H_8 rings η^4- and η^8-bonded both to Hf and Hf′ were clearly located from a difference map and refined isotropically to R = 0.054. In spite of disorder which prevented any further refinement we can conclude that the structure of these compounds is the same as **2** (form **A**), and the disorder does not imply an interchange of the η^4- and η^8-C_8H_8 rings between the two disordered hafnium atoms.

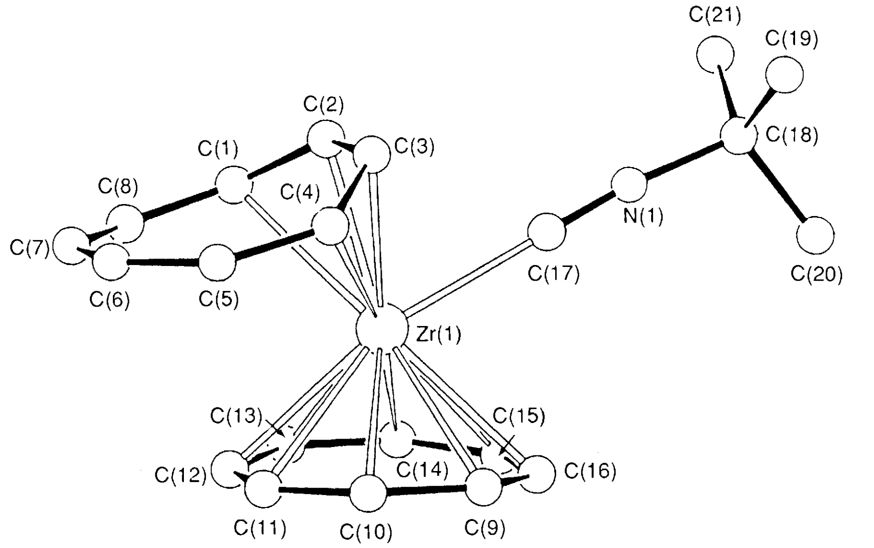


Fig. 4 A SCHAKAL drawing of complex **7** (molecule A)

Complex **6** was characterized by X-ray analysis (Fig. 3) owing to its insolubility in all common solvents. The IR spectrum (Nujol) showed two distinct strong peaks at 3328 and 3250 cm^{-1} arising from N–H stretches.

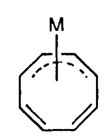
In an attempt to obtain derivatives of type $[M^{II}(\eta^8\text{-}C_8H_8)X_2]$ we performed reactions of the bis(cyclooctatetraene) complexes with isocyanides. However reaction of either **1** or **3** with Bu^tCN [equations (4) and (5)] did not proceed beyond the formation of the 1 : 1 adducts even when a large excess of the isocyanide was used.

$$\mathbf{1} + Bu^tNC \longrightarrow \underset{\mathbf{7}}{[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(CNBu^t)]} \quad (4)$$

$$\mathbf{3} + Bu^tNC \longrightarrow \underset{\mathbf{8}}{[Hf(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(CNBu^t)]} \quad (5)$$

The IR spectra (Nujol) of the products showed shifts of the C≡N stretching band from 2136 cm^{-1} in the (neat) free ligand to 2176 (**7**) and 2177 cm^{-1} (**8**), in accord with a high oxidation state and acidity at the metal. The IR spectra of **7** and **8** in solution did not show any evidence of free Bu^tNC arising from their dissociation. Additional evidence for the stability of **7** and **8** came from their NMR spectra, which showed significant shifts of the singlet for the C_8H_8 protons, and of the Bu^t group of the isocyanide. The relative stability of the adducts increases significantly from thf to NH_3 and Bu^tNC. Fluxionality of the $M(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)$ fragment is still present in **7** and **8** but is reduced relative to **1** and **3**. While the C_8H_8 protons gave one singlet in their ^1H NMR spectra at 303 K, lowering the temperature to 203 K led to the observation of two singlets, with a coalescence temperature at 263 K. The solid state structure of **7** has been determined by an X-ray analysis (Fig. 4) Removal of a C_8H_8 ligand from the Zr or Hf bis(cyclooctatetraene) species probably requires the use of very electron-rich ligands.

The structures of complexes **2**, **5**, **6** and **7** are given in Figs. 1–4, experimental details of X-ray data collections are given in Table 1, atomic coordinates in Tables 2–5 and selected structural parameters in Tables 6 and 7. All the compounds contain both an η^8- and an η^4-C_8H_8 ligand. The relative dihedral angles between the three least-squares mean planes defined by C(1)–C(4) (A), C(5)–C(8) (B) and C(9)–C(16) (C) (Table 7), and the Cn_A–M–Cn_C angles, where Cn_A and Cn_C are the centroids to the A and C planes respectively (Table 7), are diagnostic for the relative orientation of the two η^8-C_8H_8 ligands, which are essentially eclipsed in all the compounds. The dihedral angle between the two planes A and B, related to the metal-bonded and non-bonded portion of the η^4-C_8H_8 ligand respectively, is not much affected by the presence of an additional ligand (NH_3, Bu^tNC or thf) in complexes **6**, **7** and **1**. By contrast the steric hindrance caused by the $SiMe_3$ substituents in complex **5** is responsible for a significant influence on this dihedral angle. The dihedral angle between planes A and C and consequently the angle Cn_A–M–Cn_C increases significantly when an extra ligand (L = NH_3 or Bu^tNC) is added to the $M(\eta^8\text{-}C_8H_8)_2$ fragment (Tables 6 and 7). The ligand L lies closer to η^4-C_8H_8 than to η^8-C_8H_8 as can be seen from the Cn_A–M–Cn_C and Cn_C–M–X angles (Table 6). The addition of NH_3 or Bu^tCN also has a significant influence on the M–Cn_C and M–Cn_A bond distances which are significantly longer in **6** and **7** compared with **2** (Table 6). Co-ordination of NH_3 or Bu^tCN seems to weaken the M–C_8H_8 interaction, a significant observation relevant to the use of **2** or **3** as sources of the $M^{II}(C_8H_8)$ fragment. While the structural features of the $M(\eta^8\text{-}C_8H_8)$ moiety are normal, as gauged by comparison with **1**, $[Zr(\eta^8\text{-}C_8H_8)Cl_2(thf)]$,[7] $[Zr(\eta^8\text{-}C_8H_8)(C_6H_2Me_3\text{-}2,4,6)_2]$[3] and related mono(cyclooctatetraene) complexes,[4,12] the structural features of the $M(\eta^4\text{-}C_8H_8)$ moiety are more unusual.[6] The distribution of the C–C bond lengths are not consistent with those found in $[Fe(\eta^4\text{-}C_8H_8)(CO)_3]$[13] and $[Ru(\eta^4\text{-}C_8H_8)(CO)_3]$[14] for which the bonding mode shown below was proposed.



In addition, while we can exclude any bonding between the metal and C(5)–C(9) in all complexes, the distances M–C(1) and M–C(4) are much longer than M–C(2) and M–C(3) (Table 6). An alternative bonding mode which may be suggested is an η^2 bonding mode through the C(2) and C(3) atoms.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The compounds $[ZrCl_4(thf)_2]$,[15] $[HfCl_4(thf)_2]$,[15] $K_2[C_8H_8]$[3] and $[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(thf)]$ **1**[3] were prepared as reported in the literature. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer, ^1H NMR spectra using a 200-AC Bruker instrument.

Preparations.—$C_8H_8(SiMe_3)_2$-1,4.[10] Chlorotrimethylsilane

Table 1 Experimental data for the X-ray diffraction studies on crystalline complexes **2**, **5**, **6** and **7** [a]

Compound	**2**	**5**	**6**	**7**
Formula	$C_{16}H_{16}Zr$	$C_{28}H_{48}HfSi_4$	$C_{16}H_{19}NZr$	$C_{21}H_{25}NZr$
M	299.5	675.5	316.6	382.7
Crystal dimensions/mm	0.15 × 0.35 × 0.40	0.25 × 0.30 × 0.38	0.28 × 0.33 × 0.38	0.20 × 0.30 × 0.32
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$Pca2_1$	$P2_12_12_1$	$P\bar{1}$
Cell parameters at 295 K [b]				
a/Å	13.754(1)	14.418(1)	9.815(1)	11.172(1)
b/Å	7.798(1)	11.285(1)	14.129(2)	13.469(1)
c/Å	12.753(1)	18.898(1)	9.561(1)	14.303(1)
α/°	90	90	90	62.80(1)
β/°	114.02(1)	90	90	78.01(1)
γ/°	90	90	90	77.26(1)
U/Å^3	1249.4(2)	3074.8(4)	1325.9(3)	1852.9(3)
Z	4	4	4	4
D_c/g cm^{-3}	1.592	1.459	1.586	1.371
F(000)	608	1376	648	792
μ/cm^{-1}	8.38	35.30	7.96	5.82
Diffractometer	Philips PW 1100	Siemens AED	Philips PW 1100	CAD-4
Scan speed/° min^{-1}	3–12	2.5–12	2.5–12	3–12
2θ range/°	6–48	6–50	6–50	6–46
Reflections measured	$\pm h\ k\ l$	$h\ k\ l$	$h\ k\ l$	$\pm h\ \pm k\ l$
Unique total data	1955	2948	1679	5119
Criterion for observation	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$
Unique observed data (N_o)	1267	2239	1556	2994
Parameters varied (N_v)	154	297	163	415
N_o/N_v	8.2	7.5	9.5	7.2
Max. Δ/σ on last cycle	0.1	0.3	0.1	0.2
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.037	0.036	0.022	0.028
R' [c]	0.038	—	—	—
Goodness of fit [d]	0.97	—	—	—

[a] Details pertaining to all complexes: graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å); equatorial diffraction geometry; scan type ω–2θ (θ–2θ for **5**); scan width (θ − 0.60) − [θ + (0.60 + Δθ)]; $\Delta\theta = [(\lambda\alpha_2 - \lambda\alpha_1)/\lambda]\tan\theta$. [b] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 25–30 carefully centred reflections chosen from diverse regions of reciprocal space. [c] $R' = \Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$. [d] $[\Sigma w|\Delta F|^2/(N_o - N_v)]^{\frac{1}{2}}$.

Table 2 Fractional atomic coordinates (× 10^4) for complex **2**

Atom	X/a	Y/b	Z/c
Zr	2591.8(5)	438.4(7)	2051.1(5)
C(1)	1135(6)	2077(10)	2451(6)
C(2)	1982(7)	3053(8)	2451(6)
C(3)	3095(6)	2964(9)	3109(6)
C(4)	3698(5)	1831(10)	3998(7)
C(5)	3506(7)	819(10)	4779(7)
C(6)	2632(10)	383(11)	4992(6)
C(7)	1528(9)	493(11)	4333(9)
C(8)	963(6)	1051(10)	3261(9)
C(9)	4063(8)	−1038(16)	1865(16)
C(10)	3861(11)	−1920(15)	2682(11)
C(11)	2950(16)	−2409(11)	2808(7)
C(12)	1879(14)	−2330(12)	2115(14)
C(13)	1240(7)	−1710(14)	1021(14)
C(14)	1472(10)	−849(14)	234(10)
C(15)	2363(16)	−254(13)	154(8)
C(16)	3434(15)	−295(15)	822(15)

(90 cm^3, 158 mmol) was added dropwise to a thf solution of $K_2[C_8H_8]$ (230 cm^3, 0.321 mol dm^{-3}) at −30 °C. The yellow-brown solution became a white, viscous mixture which was allowed to warm up to room temperature over a period of 30 min. After filtration over a Celite pad the solution was evaporated to dryness and the residue recrystallized from hot methanol (12.02 g, 65%). ^{1}H NMR ($CDCl_3$): δ 5.83–5.75 (m, 2 H), 5.57–5.48 (m, 4 H), 2.84–2.77 (m, 2 H) and 0.01 (s, 18 H).

$Li_2[C_8H_6(SiMe_3)_2$-1,4].[10] A colourless solution of C_8H_8-$(SiMe_3)_2$-1,4 (24.04 g, 96 mmol) in thf (150 cm^3) was cooled to −30 °C and LiBu (120 cm^3, 1.6 mol dm^{-3} in hexane) added dropwise, resulting in a yellow-brown solution. The filtered solution was titrated against standard 0.1 mol dm^{-3} HCl to determine its molarity, and it was used without further purification in the following reactions.

$[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$ **2**. *Method* (*a*) Complex $[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(thf)]$ **1** (5.00 g, 13.4 mmol) was dried under vacuum for 5 h at 100 °C during which time the microcrystalline powder changed from red to violet. Suspension of this powder in toluene (300 cm^3) resulted in a blue solid which was extracted with the mother-liquor for 3 h yielding a violet-blue microcrystalline product (3.21 g, *ca.* 80%) (Found: C, 63.90; H, 5.15. $C_{16}H_{16}Zr$ requires C, 64.15; H, 5.40%); ^{1}H NMR (CD_2Cl_2): at 303 K, δ 6.01 (s); at 203 K, δ 5.59 (s).

Method (*b*). Complex $[Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(thf)]$ **1** (3.32 g, 8.92 mmol) was dried in a Schlenk tube at 100 °C for 5 h during which time it changed from red to violet. Addition of dme (100 cm^3) gave a microcrystalline violet solid suspended in a brown solution. This was filtered off using a G4 filter and extracted to give a violet solution which, on standing overnight at room temperature, gave a deep green crystalline solid suspended in a violet liquor (2.20 g, *ca.* 82%) (Found: C, 63.60; H, 4.95. $C_{16}H_{16}Zr$ requires C, 64.15; H, 5.40%); ^{1}H NMR (CD_2Cl_2 at 303 K): δ 6.01 (s).

$[Hf(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)]$ **3**. A thf solution of $K_2[C_8H_8]$ (330 cm^3, 0.52 mol dm^{-3}) prepared as above, was added dropwise at room temperature over a period of 2 h to a suspension of $[HfCl_4(thf)_2]$ (39.2 g, 86 mmol) in thf (150 cm^3). The microcrystalline dark red suspension obtained was refluxed overnight and the product was extracted for 5 d with the mother-liquor (25.85 g, *ca.* 78%) (Found: C, 49.15; H, 3.90. $C_{16}H_{16}Hf$ requires C, 49.70; H, 4.15%); ^{1}H NMR (CD_2Cl_2): δ 5.98 (s).

$[M\{\eta^8\text{-}C_8H_6(SiMe_3)_2\}\{\eta^4\text{-}C_8H_6(SiMe_3)_2\}]$ (M = Zr, **4** or Hf, **5**). A solution of $Li_2[C_8H_6(SiMe_3)_2$-1,4] (270 cm^3, 0.35 mol dm^{-3}) prepared as outlined above was added dropwise to a thf

(150 cm^3) suspension of [$ZrCl_4(thf)_2$] (17.85 g, 48 mmol). A viscous red-lilac solution was obtained containing a white solid which was filtered off, the filtrate being concentrated to dryness and the residue dissolved in pentane (150 cm^3). This solution afforded blue-violet crystals after standing overnight at −27 °C. (10.29 g, 36%) (Found: C, 57.15; H, 8.20. $C_{28}H_{48}Si_4Zr$ requires C, 56.50; H, 9.25%); ^{1}H NMR (C_6D_6): δ 6.35–6.26 (m, 8 H), 6.01–5.87 (m, 4 H) and 0.41 (s, 36 H). The Hf analogue was prepared similarly from [$HfCl_4(thf)_2$]; ^{1}H NMR (C_6D_6): δ 6.40–6.26 (m, 8 H), 6.02–5.88 (m, 4 H) and 0.41 (s, 36 H).

[Zr(η^8-C_8H_8)(η^4-C_8H_8)(NH_3)] **6**. A flask containing a red suspension of [Zr(η^8-C_8H_8)(η^4-C_8H_8)(thf)] **1** (1.80 g, 4.84 mmol) in thf (250 cm^3) was evacuated and filled with dry ammonia gas. The solid dissolved while the solution became lighter in colour and a pale red crystalline solid formed immediately in quantitative yield. Owing to the insoluble nature of the product in all common solvents, characterization by ^{1}H NMR spectroscopy was impossible (Found: C, 60.10; H, 5.70; N, 4.20. $C_{16}H_{19}NZr$ requires C, 60.70; H, 6.05; N, 4.40%).

[Zr(η^8-C_8H_8)(η^4-C_8H_8)($CNBu^t$)] **7**. A suspension of [Zr(η^8-C_8H_8)(η^4-C_8H_8)(thf)] **1** (3.50 g, 9.40 mmol) was refluxed in toluene (80 cm^3) for 30 min producing a dark red-blue crystalline solid suspended in a blue liquor. The suspension was allowed to cool, the solvent gently evaporated and Bu^{t}NC (1.05 cm^3, 1 equiv.) added by syringe. An orange crystalline product formed whilst the mixture was being stirred and this was filtered off after standing at room temperature for 24 h (2.81 g, *ca.* 80%). Red crystals suitable for X-ray analysis were obtained from the mother-liquor which had been kept in a refrigerator for several hours (Found: C, 65.15; H, 6.15; N, 3.05. $C_{21}H_{25}NZr$ requires C,

Table 3 Fractional atomic coordinates (× 10^4) for complex **5**

Atom	*X/a*	*Y/b*	*Z/c*
Hf	−4814.4(3)	−6110.1(4)	0
Si(1)	−5681(2)	−3220(3)	16(6)
Si(2)	−7176(3)	−8514(4)	1155(3)
Si(3)	−4608(3)	−8827(4)	−1329(2)
Si(4)	−3717(4)	−6429(5)	1977(3)
C(1)	−5960(16)	−5275(20)	−736(11)
C(2)	−5948(8)	−4760(9)	−13(16)
C(3)	−6099(16)	−5357(18)	605(10)
C(4)	−6326(12)	−6503(14)	779(8)
C(5)	−6865(13)	−7353(13)	509(9)
C(6)	−7225(11)	−7515(13)	−188(7)
C(7)	−7032(12)	−7056(13)	−831(9)
C(8)	−6413(13)	−6182(17)	−1046(8)
C(9)	−3728(18)	−6539(22)	989(10)
C(10)	−4098(20)	−7576(20)	712(11)
C(11)	−4328(8)	−8026(9)	61(15)
C(12)	−4273(17)	−7693(20)	−684(11)
C(13)	−3905(16)	−6690(18)	−958(12)
C(14)	−3554(16)	−5656(18)	−724(11)
C(15)	−3368(11)	−5191(12)	−95(10)
C(16)	−3403(18)	−5498(21)	608(13)
C(17)	−4837(18)	−2827(26)	−682(15)
C(18)	−5193(23)	−2841(22)	887(14)
C(19)	−6722(13)	−2393(14)	−150(15)
C(20)	−6153(16)	−9445(20)	1315(12)
C(21)	−8125(15)	−9453(16)	853(14)
C(22)	−7526(20)	−7865(19)	2016(13)
C(23)	−4881(18)	−8214(21)	−2220(10)
C(24)	−5596(15)	−9626(16)	−1012(10)
C(25)	−3584(16)	−9770(16)	−1425(10)
C(26)	−4619(18)	−5445(23)	2292(9)
C(27)	−2633(16)	−5820(30)	2262(12)
C(28)	−3776(27)	−7832(28)	2379(11)

Table 4 Fractional atomic coordinates (× 10^4) for complex **6**

Atom	*X/a*	*Y/b*	*Z/c*
Zr	−6082.3(3)	−1662.1(4)	−2917.8(3)
N	−7060(3)	−3206(2)	−3433(4)
C(1)	−5255(5)	−1032(3)	−5390(4)
C(2)	−5096(4)	−2003(3)	−5115(4)
C(3)	−4310(4)	−2495(3)	−4109(4)
C(4)	−3428(4)	−2181(3)	−3056(5)
C(5)	−2579(4)	−1376(3)	−2868(5)
C(6)	−2418(4)	−519(3)	−3523(5)
C(7)	−3211(5)	−30(3)	−4492(5)
C(8)	−4413(5)	−222(3)	−5163(6)
C(9)	−6327(6)	−1869(3)	−347(4)
C(10)	−5363(5)	−1169(4)	−563(5)
C(11)	−5302(5)	−348(3)	−1385(5)
C(12)	−6131(6)	70(3)	−2381(5)
C(13)	−7366(6)	−162(3)	−3036(6)
C(14)	−8341(5)	−882(4)	−2835(6)
C(15)	−8431(4)	−1633(4)	−1907(6)
C(16)	−7611(6)	−2039(4)	−872(6)

Table 5 Fractional atomic coordinates (× 10^4) for complex **7**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Zr(1A)	2480.9(5)	2999.1(5)	519.5(4)	Zr(1B)	7463.1(5)	455.5(5)	3192.5(4)
N(1A)	2512(5)	4676(5)	1803(4)	N(1B)	7509(5)	2055(5)	4567(5)
C(1A)	4830(6)	2453(6)	86(5)	C(1B)	7765(7)	−1457(8)	4836(6)
C(2A)	4465(5)	3562(6)	−69(5)	C(2B)	8649(8)	−775(6)	4602(6)
C(3A)	3664(6)	4442(5)	−726(5)	C(3B)	9486(7)	−314(6)	3719(7)
C(4A)	2971(6)	4463(5)	−1484(6)	C(4B)	9750(6)	−461(9)	2826(7)
C(5A)	3172(7)	3881(6)	−2147(5)	C(5B)	9745(9)	−1305(13)	2538(8)
C(6A)	3987(8)	2969(7)	−2199(6)	C(6B)	9240(15)	−2263(12)	2963(12)
C(7A)	4772(7)	2111(6)	−1500(7)	C(7B)	8333(17)	−2686(8)	3815(13)
C(8A)	5014(6)	1879(6)	−534(6)	C(8B)	7656(10)	−2300(10)	4527(9)
C(9A)	204(6)	3362(6)	538(10)	C(9B)	5778(7)	−260(5)	2919(6)
C(10A)	692(9)	2905(9)	−188(6)	C(10B)	6701(7)	−222(6)	2094(6)
C(11A)	1554(10)	1973(9)	−156(7)	C(11B)	7494(7)	515(7)	1427(6)
C(12A)	2329(9)	1164(7)	543(9)	C(12B)	7737(6)	1540(6)	1258(5)
C(13A)	2590(7)	944(6)	1520(8)	C(13B)	7201(6)	2301(5)	1647(6)
C(14A)	2128(8)	1367(7)	2248(6)	C(14B)	6191(7)	2368(5)	2375(6)
C(15A)	1202(8)	2218(7)	2292(6)	C(15B)	5367(6)	1625(7)	3119(6)
C(16A)	400(7)	3039(7)	1593(8)	C(16B)	5208(6)	495(7)	3378(6)
C(17A)	2520(6)	4145(6)	1371(5)	C(17B)	7543(6)	1501(6)	4129(6)
C(18A)	2419(5)	5334(5)	2402(5)	C(18B)	7372(6)	2780(5)	5090(5)
C(19A)	2288(6)	6565(5)	1620(5)	C(19B)	8514(7)	3377(7)	4694(7)
C(20A)	1284(6)	5049(6)	3213(5)	C(20B)	6189(7)	3613(6)	4787(6)
C(21A)	3600(6)	4969(6)	2922(6)	C(21B)	7273(7)	2031(6)	6261(5)

Table 6 Selected interatomic distances (Å) and angles (°) for complexes **2**, **5**, **6** and **7** (M = Zr or Hf)*

				7	
	2	**5**	**6**	Molecule A	Molecule B
M–C(1)	2.596(9)	2.356(22)	2.653(4)	2.589(6)	2.586(7)
M–C(2)	2.339(8)	2.235(11)	2.362(4)	2.362(6)	2.378(8)
M–C(3)	2.328(7)	2.337(22)	2.389(4)	2.385(6)	2.389(8)
M–C(4)	2.566(7)	2.667(17)	2.709(4)	2.657(6)	2.640(7)
M–C(5)	3.196(8)	3.411(18)	3.462(4)	3.405(7)	3.372(14)
M–C(6)	3.279(9)	3.837(16)	3.984(4)	3.918(9)	3.883(16)
M–C(7)	3.752(14)	3.719(17)	3.940(5)	3.881(9)	3.840(11)
M–C(8)	3.232(11)	3.038(17)	3.381(5)	3.313(7)	3.287(12)
M–C(9)	2.422(14)	2.486(22)	2.487(4)	2.479(7)	2.465(9)
M–C(10)	2.435(12)	2.369(23)	2.460(5)	2.470(12)	2.497(10)
M–C(11)	2.391(8)	2.276(10)	2.486(4)	2.487(14)	2.483(10)
M–C(12)	2.386(12)	2.339(22)	2.501(4)	2.499(12)	2.456(6)
M–C(13)	2.450(10)	2.329(23)	2.468(5)	2.455(7)	2.465(6)
M–C(14)	2.417(11)	2.332(22)	2.477(5)	2.472(7)	2.519(6)
M–C(15)	2.371(12)	2.336(16)	2.500(4)	2.509(7)	2.510(7)
M–C(16)	2.367(23)	2.437(26)	2.522(6)	2.510(8)	2.469(7)
M–Cn_A	2.047(8)	1.988(20)	2.131(4)	2.099(7)	2.122(6)
M–Cn_C	1.604(12)	1.524(18)	1.697(4)	1.702(8)	1.693(8)
M–X			2.434(3)	2.374(10)	2.370(10)
C(9)–M–C(10)	32.7(5)	33.1(8)	32.5(2)	32.8(4)	32.4(3)
C(10)–M–C(11)	33.2(4)	34.3(6)	32.9(2)	32.6(4)	31.7(3)
C(11)–M–C(12)	33.5(4)	36.8(9)	32.2(1)	32.0(4)	32.2(3)
C(12)–M–C(13)	33.6(5)	33.7(8)	32.8(2)	32.1(3)	31.9(3)
C(13)–M–C(14)	32.2(4)	33.6(8)	33.1(2)	32.2(3)	32.3(2)
C(14)–M–C(15)	32.8(4)	33.0(6)	32.3(2)	32.2(3)	32.7(3)
C(15)–M–C(16)	33.6(6)	33.4(8)	32.3(2)	32.3(3)	33.5(3)
C(9)–M–C(16)	33.6(6)	34.4(8)	31.9(2)	33.0(4)	33.5(2)
C(1)–M–C(2)	32.2(3)	37.6(6)	31.9(1)	32.0(2)	32.0(3)
C(2)–M–C(3)	35.3(3)	34.7(7)	34.7(1)	34.2(2)	33.7(3)
C(3)–M–C(4)	33.0(2)	31.0(6)	31.1(1)	32.7(2)	30.5(3)
Cn_A–M–Cn_C	170.7(5)	172.1(6)	153.4(2)	155.7(2)	154.8(2)
Cn_A–M–X			89.4(2)	87.8(3)	89.0(4)
Cn_C–M–X			117.2(2)	116.6(3)	116.0(5)

* Cn_A and Cn_C refer to the centroids defined by C(1)–C(4) and C(9)–C(16) respectively; X indicates atom N or C(17) for complex **6** or **7** respectively.

Table 7 Selected dihedral angles (°) and out-of-plane distances *D*/Å of metal atoms in complexes **2**, **5**, **6** and **7***

Complex	A ∧ B	A ∧ C	*D*
2	28.8(5)	21.9(3)	1.996
5	35.9(10)	13.4(8)	1.917
6	28.8(3)	35.7(2)	2.107
7 (Molecule A)	32.5(4)	36.6(3)	2.054
7 (Molecule B)	30.5(8)	36.8(3)	2.071

* A, B and C are the least-squares mean planes defined by C(1)–C(4), C(5)–C(8) and C(9)–C(16) respectively.

65.90; H, 6.60; N, 3.65%); ^{1}H NMR (CD_2Cl_2); at 303 K, δ 5.62 (s, 16 H) and 1.55 (s, 9 H); at 203 K, δ 5.68 (s, 8 H, C_8H_8), 5.39 (s, 8 H, C_8H_8) and 1.48 (s, 9 H, Bu^t); ν_{C-N} at 2177 cm^{-1}.

[Hf(η^8-C_8H_8)(η^4-C_8H_8)(CNBu^t)] **8**. *tert*-Butyl isocyanide (0.18 cm^3, 1.61 mmol) was added *via* a syringe to a suspension of [Hf(η^8-C_8H_8)(η^4-C_8H_8)] **3** (0.62 g, 1.60 mmol) in toluene (100 cm^3). An immediate reaction ensued and the violet suspension turned into an orange microcrystalline powder (0.40 g, *ca.* 53%) (Found: C, 53.25; H, 5.25; N, 2.85. $C_{21}H_{25}HfN$ requires C, 53.65; H, 5.35; N, 2.95%): ^{1}H NMR (CD_2Cl_2 at 303 K): δ 5.57 (s, 16 H), 1.55 (s, 9 H); ν_{C-N} at 2176 cm^{-1}.

X-Ray Crystallography.—The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[16] Crystal data and details associated with the data collection are given in Table 1. Data were collected at room temperature (295 K) on a single-crystal diffractometer. Data reduction, structure solution and refinement were carried out on a GOULD 32/77 computer using the SHELX 76 system of computer programs.[17] For intensities and background the profile measurement technique[18] was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections[17] and the absolute scale was established by the Wilson method.[19] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected for all the complexes. The function minimized during the least-squares refinement was $\Sigma w|\Delta F_o|^2$. A weighting scheme based on counting statistics[17] was applied for complex **2**. Unit weights were used for complexes **5**–**7** since these gave a satisfactory analysis of variance.[17] Anomalous scattering corrections were included in all structure-factor calculations.[20b] Scattering factors for neutral atoms were taken from ref. 20*a* for the non-hydrogen atoms and from ref. 21 for the hydrogen atoms. Among the low-angle reflections no corrections for secondary extinction were deemed necessary.

Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first isotropic, then anisotropic for non-hydrogen atoms, and by full-matrix least squares for the four complexes. All the hydrogen atoms were located from difference Fourier maps and introduced in the subsequent refinement as fixed atom contributions with U_{iso} fixed at 0.08 Å^2. The final difference maps showed no unusual features, with no significant peaks above the general background. Since the space groups of complexes **5** and **6** are polar the structures were refined to convergence once again by inverting all the coordinates ($x,y,z \longrightarrow -x,-y,-z$). The resulting *R* values [complex **5**:

$R = 0.037$, $R_G = 0.041$ and $R = 0.036$, $R_G = 0.040$ for the original choice and the 'inverted' structure respectively; **6**: $R = 0.024$, $R_G = 0.026$ and $R = 0.022$, $R_G = 0.025$ for the original choice and the 'inverted' structure respectively, $R_G = (\Sigma w|\Delta F^2|/\Sigma w F_o^2)^{\frac{1}{2}}]$ indicated that the 'inverted' structures could be considered as the correct ones. The atomic coordinates given in Tables 3 and 4 refer to the 'inverted' structures. The final atomic coordinates are listed in Tables 2–5 for the non-hydrogen atoms. Figs. 1–4 were drawn using the SCHAKAL program.[22]

Additional material available at the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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