Diene and Arene Compounds of Zirconium and Hafnium†

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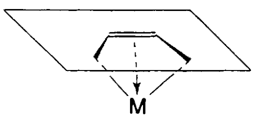
The diene compounds $[Hf(\eta^4\text{-}CH_2{=}CMeCMe{=}CH_2)(PMe_3)_2Cl_2]$ **1**, $[M(\eta^4\text{-}C_6H_8)(PMe_3)_2Cl_2]$ (M = Zr **2** or Hf **3**) and the divalent $[Zr(\eta^6\text{-}C_6H_5Me)(PMe_3)_2Cl_2]$ **5** have been prepared. The structure of compound **1** has been determined by low-temperature neutron diffraction (15 K) and the σ^2, π nature of the bonding mode of the 2,3-dimethylbutadiene ligand demonstrated from the methylene hydrogen positions. Treatment of **1** with lithium indenide gave $[Hf(\eta^5\text{-}C_9H_7)_2(\eta^4\text{-}CH_2{=}CMeCMe{=}CH_2)]$ **4**. The crystal structure of **5** has been determined by X-ray diffraction.

Most of the chemistry of divalent molecular compounds of zirconium and hafnium is represented by compounds in the classes $[M(\eta\text{-}C_5H_5)_2L_2]$[1] (L = CO or PPh_3, L_2 = butadiene) and $[M(\eta\text{-}C_5H_5)L_4Cl]$ [L_4 = 2 dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$) or dmpe + 2 CO].[2] Early examples of (η-arene)zirconium compounds are $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)]Cl$[3] and the related compound $[Zr_3Cl_6(\eta^6\text{-}C_6Me_6)][Al_2Cl_7]_2$ for which the X-ray crystal structure has been determined.[4] Other known η-arene Group 4 compounds include the sandwich compounds $[Zr(\eta\text{-arene})_2(PMe_3)]$[5] and $[Zr(\eta^6\text{-}1,3,5\text{-}Bu^t{}_3C_6H_3)_2]$[6] and the zerovalent η^6-naphthalene compound $[Ti(\eta^6\text{-}C_{10}H_8)\{SiBu^t(CH_2PMe_2)_3\}]$.[7] Over the last two years the divalent Group 4 compounds $[Zr(\eta\text{-arene})(AlCl_4)_2]$[8] and $[\{Hf(PMe_2Ph)_2I_2\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-arene})]$ (arene $= C_6H_6$ or C_6H_5Me)[9] have been reported, as has the tetravalent zwitterionic compound $[Zr(CH_2Ph)_3(\eta^6\text{-}C_6H_5BPh_3)]$.[10] Recently, we have described formally divalent η-cycloheptatriene compounds $[M(\eta\text{-}C_7H_8)(PMe_3)_2Cl_2]$.[11] Here we describe new diene and arene compounds of zirconium and hafnium. Part of this work has been the subject of preliminary communications.[12,13]

Results and Discussion

Reduction of $HfCl_4$ using sodium amalgam in the presence of PMe_3 and 2,3-dimethylbutadiene yields air-sensitive, orange crystals of the compound $[Hf(\eta^4\text{-}CH_2{=}CMeCMe{=}CH_2)(PMe_3)_2Cl_2]$ **1**. In a typical experiment 4 g of $HfCl_4$ gave 3.1 g of compound **1**. The analytical and spectroscopic data for **1**, and all the other new compounds described are given in Table 1 and only selected data will be discussed in the text.

The low-temperature neutron diffraction structure (15 K) of compound **1** has been determined. Compound **1** crystallises in the monoclinic space group $P2_1/c$. The atomic coordinates are given in Table 2. Two views of the molecular structure are shown in Fig. 1 and selected bond distances and angles are given in Table 3. It is well established that the bonding of *s-cis*-η^4-2,3-disubstituted butadienes to early transition metals is normally more accurately described as the σ^2,π-metallacyclopentene structure **I** rather than the π^2 mode **II**.[14] The neutron diffraction data for **1** show the internal carbon–carbon distance [C(2)–C(3) 1.401(3) Å] is more than 0.05 Å shorter than each of the terminal carbon–carbon bonds [C(1)–C(2) 1.452(3), C(3)–C(4) 1.475(4) Å]. This inversion of the carbon–carbon bond length sequence from that in the free diene is consistent with a σ^2,π-metallacyclopentene structure. Further support for a σ^2,π character is provided by the observation that the diene methylene carbons are closer to the hafnium than are the internal diene carbons. The differences in the Hf–C bond lengths [Δ = average(M–C_{int}) − average (M–C_{ter}) = 2.478 − 2.303 = 0.175 Å] are larger than those in predominantly π-bonded diene complexes for which Δ is often negative. For example, Δ = −0.06 Å for $[Mo(\eta^4\text{-}C_4H_6)_2(PMe_3)_2]$.[15] We note that the formally zerovalent $[Hf(\eta^4\text{-}C_4H_6)_2(dmpe)]$ also has a reversal of the carbon–carbon bond sequence [internal C–C 1.376(7), external C–C 1.428(7) Å] and a value of Δ = 0.054 Å.[16]



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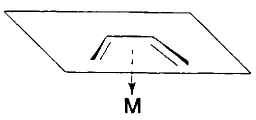

II

The hydrogen atoms of the terminal CH_2 groups of compound **1** are bent away from the hafnium atom such that there is no agostic bonding. The distances from the hafnium to the diene methylene carbon atoms [2.303(3) Å] are slightly longer than those found in $[Hf(\eta\text{-}C_5H_5)_2(\eta^4\text{-}CH_2{=}CMeCMe{=}CH_2)]$ [2.267(5) Å][17] and in the closely related $[Hf(\eta\text{-}C_5Me_5)(\eta^4\text{-}CH_2{=}CMeCMe{=}CH_2)(C_5H_5N)Cl]$ [2.276(10) Å].[18] We conclude that **1** can be considered formally to be a 14-valence-electron molecule.

An interesting feature of the molecular structure of compound **1** is the lack of mirror symmetry. This asymmetry is also observed in the solid-state ^{13}C and ^{31}P cross polarisation magic angle spinning (CP MAS) NMR spectra. Thus the ^{31}P spectrum shows two doublet resonances at δ −2.2 and −19.4. Similarly, the ^{13}C spectrum shows two resonances for the diene quaternary carbons (at δ 128.3 and 120.9) and two resonances for the methyl substituents on the diene (at δ 24.1 and 22.6). However, the solution ^{31}P NMR spectrum at room temperature showed only a sharp singlet which was slightly broadened at 183 K, the lowest temperature obtainable before the onset of viscosity broadening. It is likely that the apparent equivalence of the ^{31}P nuclei reflects a fluxional in-plane rotation (or oscillation rock) of the η-diene ligand.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical and spectroscopic data[a]

Compound	Colour	NMR data
1	Orange C, 29.5 (29.8); H, 5.6 (5.8); Cl, 14.9 (14.7)	$\delta_H{}^b$ 2.3 (s, 6 H, CH_3), 2.0 [d, 2 H, $J(H_{anti}-H_{syn})$ 6, H_{syn}], 1.1 (s, 18 H, 6PCH_3), 0.9 [d, 2 H, $J(H_{anti}-H_{syn})$ 6, H_{anti}] $\delta_P{}^c$ (at 292 K) −15.9 (s) δ_P(CP MAS, 80.6 MHz) −2.2 [d, 1 P, $J(P_A-P_B)$ 22, P_A or P_B], −19.4 [d, 1 P, $J(P_A-P_B)$ 22, P_A or P_B] $\delta_C{}^b$ 124.1 (s, C_{quat}), 66.8 [t, J(C–H) 142, CH_2], 23.2 [d, J(C–H) 126, CH_3], 12.8 [dq, J(C–H) 126, J(P–C) 15, 6PCH_3] δ_C (CP MAS, 50.32 MHz) 128.3 (s, C_{quat}), 120.9 (s, C_{quat}), 66.0 (m, both CH_2), 24.1 (s, CH_3), 22.6 (s, CH_3), 13.1 (m, PCH_3)
2	Purple C, 36.5 (36.5); H, 6.8 (6.6); Cl, 18.0 (18.2)	$\delta_H{}^c$ 5.75 (m, 2 H, H_b), 3.25 (m, 2 H, H_a), 2.29 (m, 2 H, H_u or H_d), 1.70 (m, 2 H, H_u or H_d), 1.06 [t, 18 H, J(P–H) 6, 6PCH_3] $\delta_P{}^c$ (296 K) −24.5 (s) $\delta_P{}^c$ (180 K) −22.2 [d, 1 P, J(P–P) 76], −24.3 [d, 1 P, J(P–P) 76] $\delta_C{}^b$ 114.0 [d, J(C–H) 161, C_b], 76.4 [d, J(C–H) 152, C_a], 26.0 [t, J(C–H) 127, CH_2], 12.8 [q, J(C–H) 138, PCH_3]
3	Red C, 29.8 (29.9); H, 5.4 (5.4); Cl, 14.6 (14.7)	$\delta_H{}^b$ 6.15 (m, 2 H, H_b), 2.97 (m, 2 H, H_a), 2.80 (m, 2 H, H_{exo} or H_{endo}), 2.18 (m, 2 H, H_{exo} or H_{endo}), 1.06 [t, 18 H, J(P–H) 3.4, 6PCH_3], $\delta_P{}^b$ −16.1 (s) $\delta_C{}^b$ 116.5 [d, J(C–H) 160, C_b], 75.4 [d, J(C–H) 146, C_a], 29.1 [t, J(C–H) 127, CH_2], 12.5 [tq, J(C–H) 130, J(P–C) 9, PCH_3]
4	Pale yellow C, 58.5 (58.7); 1 H, 4.9 (4.9)	$\delta_H{}^c$ (291 K) 7.20 (m, 4 H, H_a or H_b), 6.90 (m, 4 H, H_a or H_b), 5.43 [d, 4 H, $J(H^1-H^2)$ 3.3, H^1], 4.39 [t, 2 H, $J(H^1-H^2)$ 3.3, H^2], 1.77 (s, 6 H, CH_3), −0.07 (s, 4 H, H_{int} and H_{ext}) $\delta_H{}^c$ (183 K) 7.10 (m, 8 H, H_a and H_b), 5.87 [br s, 2 H, H^1 (up or down)], 5.35 [br s, 1 H, H^2 (up or down)], 5.02 [br s, 2 H, H^1 (up or down)], 3.32 [br s, 1 H, H^2 (up or down)], 2.19 [br d, 2 H, $J(H_{int}-H_{ext})$ 10, H_{ext}], 1.76 (s, 6 H, 2CH_3), −2.15 [br d, 2 H, $J(H_{int}-H_{ext})$ 10, H_{int}] $\delta_C{}^b$ 129.3 [s, C_{quat} (diene or indene)], 123.6 [dd, J(C–H) 160, 7, C_a or C_b], 123.0 [d, J(C–H) 153, C_a or C_b], 121.2 [s, C_{quat} (diene or indene)], 114.4 [d, J(C–H) 174, C^2], 87.5 [d, J(C–H) 175, C^1), 54.2 [t, J(C–H) 138.3, CH_2(diene)], 23.1 [q, J(C–H) 124, CH_3(diene)]
5	Green	$\delta_H{}^b$ 4.67 [1 H, tt, $J(H_{meta}-H_{para})$ 7.8, $J(H_{ortho}-H_{para})$ 1.7, H_{para}], 3.50 (2 H, m, H_{meta}), 3.26 (2 H, m, H_{ortho}), 1.12 [18 H, d, J(P–H) 7, 6P-Me], 1.10 (3 H, s, Me) $\delta_P(C_6D_6)$ −19.2 $\delta_C({}^{13}C\text{-}\{{}^1H\}^b)$ 117.9 (s, C_{para}), 95.4 (s, C_{ortho} or C_{para}), 94.6 (s, C_{ortho} or C_{para}), 21.8 (s, CH_3), 13.9 [t, J(P–C) 7, PCH_3]

[a] Unless otherwise stated ^1H NMR at 300 MHz, ^{31}P at 121.5 MHz, ^{13}C at 75 MHz; J in Hz. Analytical data given as: found (calculated) %. [b] In [$^2H_6$]benzene. [c] In [$^2H_8$]toluene.

Table 2 Atomic coordinates (× 10^4) obtained from neutron results for all atoms of compound **1** excluding methyl hydrogen atoms

Atom	X/a	Y/b	Z/c
Hf	3243(1)	45(2)	2385(1)
Cl(1)	4920(1)	−790(2)	3030(1)
Cl(2)	2453(1)	1757(2)	3304(1)
P(1)	2879(2)	−1499(3)	3934(2)
P(2)	4281(2)	2276(3)	1996(2)
C(1)	3480(2)	−276(3)	804(2)
C(2)	3256(2)	−1634(2)	1090(2)
C(02)	4012(2)	−2747(3)	1043(3)
C(3)	2350(2)	−1833(2)	1456(2)
C(03)	2005(2)	−3202(3)	1731(2)
C(4)	1725(2)	−635(3)	1563(2)
C(11)	3305(2)	−3249(3)	4077(3)
C(12)	3575(2)	−728(3)	5009(2)
C(13)	1591(2)	−1546(3)	4212(2)
C(21)	3549(2)	3355(3)	1118(2)
C(22)	4664(2)	3411(3)	3002(2)
C(23)	5452(2)	2002(3)	1502(3)
H(1a)	4227(4)	−156(5)	580(4)
H(1b)	2892(4)	269(6)	337(4)
H(4a)	1515(4)	−41(6)	917(5)
H(4b)	1075(4)	−836(5)	1923(4)

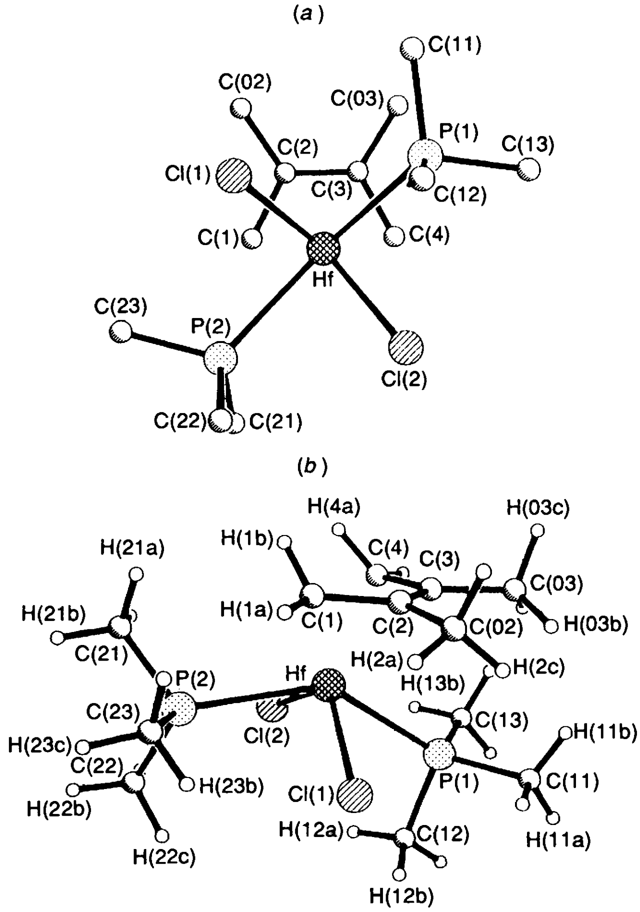


Fig. 1 Two views of the molecular structure of compound **1**: (*a*) showing the disposition of the $CH_2{=}CMeCMe{=}CH_2$ unit relative to the $Hf(PMe_3)_2Cl_2$ fragment, hydrogen atoms omitted for clarity; (*b*) a general view

Reduction of $ZrCl_4$ using sodium amalgam in the presence of cyclohexa-1,3-diene and trimethylphosphine gave purple crystals of $[Zr(\eta^4\text{-}C_6H_8)(PMe_3)_2Cl_2]$ **2** in good yield. In a typical experiment 1.2 g of **2** could be obtained from 4 g of $ZrCl_4$. The ^{31}P NMR spectrum of **2** shows a singlet at room temperature which broadens on cooling and resolves to an AB quartet at 183 K. This low-temperature spectrum is consistent with a structure similar to that observed in the solid state for compound **1**. Thus, the diene ligand is not bonded symmetrically with respect to the four-legged piano-stool defined by the two chloro and two PMe_3 ligands. Also, the ^{31}P NMR spectrum gave J(P–P) = 76 Hz which is similar to the value of 70 Hz found for $[Zr(\eta^6\text{-}C_7H_8)(PMe_3)_2Cl_2]$[11] and this

Table 3 Selected bond lengths (Å) and angles (°) for compound **1** obtained from neutron diffraction data

Hf–Cl(1)	2.450(2)	C(2)–C(3)	1.401(3)
Hf–Cl(2)	2.464(2)	C(3)–C(4)	1.475(4)
Hf–P(1)	2.760(4)	C(2)–C(02)	1.509(5)
Hf–P(2)	2.715(3)	C(3)–C(03)	1.505(4)
Hf–C(1)	2.308(3)	C(4)–H(4a)	1.086(7)
Hf–C(2)	2.470(3)	C(4)–H(4b)	1.088(6)
Hf–C(3)	2.486(3)	C(1)–H(1a)	1.099(6)
Hf–C(4)	2.298(3)	C(1)–H(1b)	1.096(6)
C(1)–C(2)	1.452(3)		
Cl(2)–Hf–Cl(1)	118.1(1)	C(2)–C(3)–C(03)	122.4(2)
P(1)–Hf–Cl(1)	77.1(1)	H(4a)–C(4)–H(4b)	110.9(4)
P(2)–Hf–P(1)	139.9(1)	H(1a)–C(1)–H(1b)	112.7(6)
Hf–C(1)–C(2)	78.5(2)	Hf–C(4)–H(4a)	111.6(3)
C(1)–C(2)–C(3)	117.2(2)	Hf–C(4)–H(4b)	122.2(3)
C(1)–C(2)–C(02)	120.2(2)	Hf–C(1)–H(1a)	121.0(3)
C(2)–C(3)–C(4)	117.3(2)	Hf–C(1)–H(1b)	108.7(3)
C(03)–C(3)–C(4)	120.3(2)		

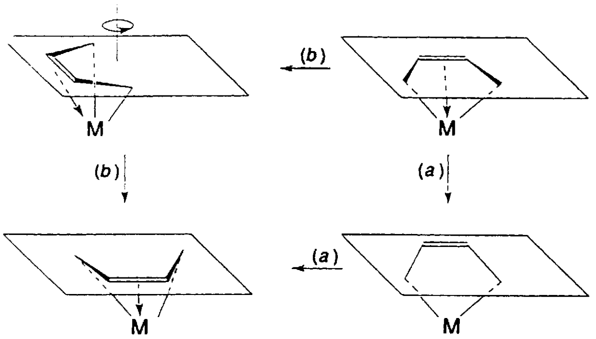


Fig. 2 Exchange mechanisms in M(dienes): (*a*) flip, (*b*) rotational

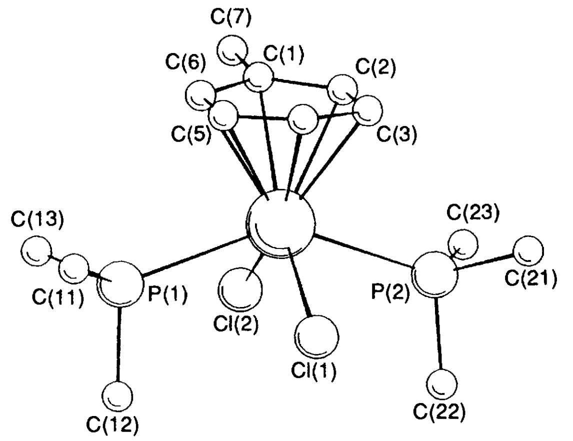


Fig. 3 Molecular structure of complex **5**; only one molecule in the asymmetric unit is shown. Hydrogen atoms omitted for clarity

is consistent with a *trans* arrangement of the phosphine ligands in **2**. The fluxional process which causes the ^{31}P NMR resonances to become equivalent at room temperature is presumed to be an in-plane rotation of the dienyl ligand, and consistent with this mechanism the *exo*- and *endo*-methylene hydrogens of the diene ligand remain inequivalent at the higher temperature.

Sodium amalgam reduction of $HfCl_4$ in the presence of cyclohexa-1,3-diene and trimethylphosphine proceeded smoothly, yielding substantial quantities of $[Hf(\eta^4\text{-}C_6H_8)(PMe_3)_2Cl_2]$ **3** as large orange crystals. The ^1H, ^{13}C and ^{31}P NMR spectra of **3** are similar to those of compound **2** and suggest they have the same basic structure.

Addition of tetrahydrofuran (thf) to a mixture of solid lithium indenide and compound **1** gave a dark red solution from which pale yellow crystals of the compound $[Hf(\eta^5\text{-}C_9H_7)_2(\eta^4\text{-}CH_2{=}CMeCMe{=}CH_2)]$ **4** were isolated. The variable-temperature ^1H NMR spectrum shows **4** to be fluxional. Thus, the spectrum at 183 K shows resonances assignable to two non-equivalent $\eta\text{-}C_9H_7$ ligands. There are also resonances assignable to the CH_3 group of the diene ligand and two assignable to the internal and external methylene hydrogens of the diene ligand. As the temperature is raised the resonances due to the $\eta\text{-}C_9H_7$ ligands coalesce (at 213 K for the 2-proton resonances and 219 K for the 1-proton resonances) to give resonances which may be assigned to two equivalent $\eta\text{-}C_9H_7$ ligands: the internal and external hydrogen resonances also coalesce (at 235 K). From these coalescence temperatures and frequency separation in the slow-exchange limit the activation barrier for this fluxional process was calculated to be $\Delta G^{\ddagger}_{av}$ = 42 ± 3 kJ mol^{-1}. The process responsible for this fluxionality is believed to be a diene flip, as shown in Fig. 2. The activation barrier obtained for the fluxional process for **4** is higher than the corresponding fluxional equilibrium for $[Hf(\eta\text{-}C_5H_5)_2(\eta^4\text{-}CH_2{=}CMeCMe{=}CH_2)]$ (35 kJ mol^{-1}).[14] This may simply reflect the greater steric bulk for the indenyl ligand in **4**.

Reduction of $ZrCl_4$ and trimethylphosphine in toluene with an excess of Na/K alloy at ambient temperature gave low yields (< 10%) of highly air-sensitive green crystals. The solution NMR spectra suggested this to be the compound $[Zr(\eta^6\text{-}C_6H_5Me)(PMe_3)_2Cl_2]$ **5**. The ^1H NMR spectrum showed no coupling of the ^{31}P nuclei to the *p*-hydrogen of the η-toluene ligand.

The X-ray crystal structure of compound **5** has been determined and the molecular structure is shown in Fig. 3. Selected bond distances and angles are given in Table 4 and fractional atomic coordinates are listed in Table 5. Compound **5** crystallises in the space group $P2_1$. The two independent molecules in the asymmetric unit differ by a slight rotation of the toluene ring. The crystal structure shows marked similarities to that reported for the triene compound $[Zr(exo\text{-}\eta^6\text{-}C_7H_7SiMe_3)(PMe_3)_2I_2]$[19] and both compounds have a similar square-pyramidal arrangement of the zirconium atom and the trimethylphosphine and halo ligands with the two PMe_3 groups being *trans*.

The synthesis of the new compounds and the structures proposed are shown in Scheme 1. Compounds **1**–**4** are readily prepared on a laboratory scale and are likely, therefore, to be useful synthons for the further exploration of the relatively underdeveloped area of the low-valent chemistry of zirconium and hafnium.

Experimental

All manipulations were performed using standard Schlenk-line techniques under an atmosphere of dinitrogen, which had been purified by passage over MnO catalyst and 4 Å molecular sieves, or in an inert-atmosphere dry-box.

Solvents and solutions were generally transferred through stainless-steel cannulae using an over-pressure of dinitrogen, and filtered using cannulae modified to be fitted with glass-fibre disks. All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of dinitrogen, or by bubbling dinitrogen through them for 20 min. All glassware was dried by heating at 240 °C in an oven before use. Solvents were dried by standing over molecular sieves followed by distillation from sodium (toluene), potassium-benzophenone (tetrahydrofuran) or sodium–potassium alloy [light petroleum (b.p. 40–60 °C), diethyl ether, pentane]. Deuteriated solvents for NMR spectroscopy were stored in Young's ampoules over sodium–potassium alloy ([$^2H_6$]benzene, [$^2H_8$]toluene). Celite 545 filtration aid (Koch-Light) was dried at 240 °C before use.

The NMR spectra were referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances

Table 4 Selected bond lengths (Å) and angles (°) for $[Zr(\eta^6\text{-}C_6H_5Me)(PMe_3)_2Cl_2]$ **5***

First molecule		Second molecule	
Zr(1)–Cl(1)	2.526(3)	Zr(101)–Cl(101)	2.508(3)
Zr(1)–Cl(2)	2.496(3)	Zr(101)–Cl(102)	2.514(3)
Zr(1)–P(1)	2.760(4)	Zr(101)–P(101)	2.750(3)
Zr(1)–P(2)	2.756(4)	Zr(101)–P(102)	2.742(3)
Zr(1)–C(1)	2.523(8)	Zr(101)–C(101)	2.522(9)
Zr(1)–C(2)	2.417(9)	Zr(101)–C(102)	2.473(9)
Zr(1)–C(3)	2.41(1)	Zr(101)–C(103)	2.349(9)
Zr(1)–C(4)	2.40(1)	Zr(101)–C(104)	2.45(1)
Zr(1)–C(5)	2.40(1)	Zr(101)–C(105)	2.47(1)
Zr(1)–C(6)	2.41(1)	Zr(101)–C(106)	2.41(1)
C(1)–C(2)	1.39(1)	C(101)–C(102)	1.36(2)
C(1)–C(6)	1.37(2)	C(101)–C(106)	1.42(2)
C(1)–C(7)	1.51(1)	C(101)–C(107)	1.53(1)
C(2)–C(3)	1.42(2)	C(102)–C(103)	1.43(1)
C(3)–C(4)	1.37(3)	C(103)–C(104)	1.44(2)
C(4)–C(5)	1.30(3)	C(104)–C(105)	1.32(2)
C(5)–C(6)	1.39(2)	C(105)–C(106)	1.42(2)
Cl(2)–Zr(1)–Cl(1)	109.40(9)	Cl(102)–Zr(101)–Cl(101)	110.2(1)
P(1)–Zr(1)–Cl(1)	80.71(8)	P(101)–Zr(101)–Cl(101)	82.2(1)
P(1)–Zr(1)–Cl(2)	77.1(1)	P(101)–Zr(101)–Cl(102)	77.2(1)
P(2)–Zr(1)–Cl(1)	80.04(9)	P(102)–Zr(101)–Cl(101)	78.3(1)
P(2)–Zr(1)–Cl(2)	78.0(1)	P(102)–Zr(101)–Cl(102)	80.8(1)
P(2)–Zr(1)–P(1)	141.14(8)	P(102)–Zr(101)–P(101)	143.4(1)

* The crystals contain two molecules of compound 5 in the asymmetric unit. The atoms of the first molecule have serial numbers *n*, and the corresponding atoms of the second molecule have the serial numbers 10*n* (or 1*n* where $n > 10$).

Table 5 Fractional atomic coordinates for the non-hydrogen atoms of $[Zr(\eta^6\text{-}C_6H_5Me)(PMe_3)_2Cl_2]$ **5**

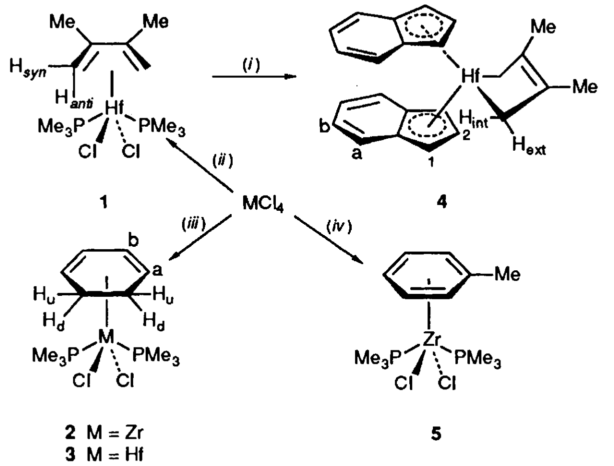
Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Zr(1)	0.772 86(7)	−0.548 7(3)	0.965 14(7)	Zr(101)	0.714 47(6)	0.052 5(3)	1.461 20(7)
Cl(1)	0.667 7(2)	−0.606 4(4)	0.805 2(2)	Cl(101)	0.844 7(2)	−0.048 9(5)	1.575 1(2)
Cl(2)	0.689 3(3)	−0.386 7(4)	1.057 4(3)	Cl(102)	0.777 4(3)	0.089 7(4)	1.284 9(2)
P(1)	0.622 3(3)	−0.664 7(4)	1.058 2(3)	P(101)	0.701 1(2)	−0.166 3(4)	1.369 7(2)
P(2)	0.805 6(2)	−0.357 3(5)	0.840 3(3)	P(102)	0.842 5(3)	0.234 3(5)	1.510 2(3)
C(1)	0.917 9(7)	−0.553(1)	1.097 0(9)	C(101)	0.607 5(6)	0.078(1)	1.613 1(8)
C(2)	0.948 8(7)	−0.521(1)	1.000(1)	C(102)	0.620 9(6)	0.186(1)	1.570 9(8)
C(3)	0.936(1)	−0.596(2)	0.912(1)	C(103)	0.598 3(6)	0.206(1)	1.462 8(9)
C(4)	0.890(1)	−0.701(2)	0.929(2)	C(104)	0.546 4(7)	0.114(2)	1.405(1)
C(5)	0.851 8(9)	−0.732(1)	1.015(2)	C(105)	0.535 7(7)	0.008(1)	1.445(1)
C(6)	0.864 9(7)	−0.656(1)	1.100(1)	C(106)	0.572 7(7)	−0.016(1)	1.548(1)
C(7)	0.936 5(8)	−0.476(1)	1.191 9(9)	C(107)	0.634 9(7)	0.053(1)	1.727 4(8)
C(11)	0.609(1)	−0.821(1)	1.041(1)	C(111)	0.618(1)	−0.178(2)	1.256(1)
C(12)	0.502(1)	−0.609(2)	1.010(1)	C(112)	0.819(1)	−0.211(1)	1.321(1)
C(13)	0.616(1)	−0.648(1)	1.197 2(9)	C(113)	0.671(1)	−0.293(1)	1.448(1)
C(21)	0.878(1)	−0.373(2)	0.731(2)	C(121)	0.881 7(9)	0.257(1)	1.645 3(9)
C(22)	0.694(1)	−0.298(1)	0.783(1)	C(122)	0.809(1)	0.381(1)	1.466(1)
C(23)	0.858(1)	−0.228(2)	0.898(2)	C(123)	0.958(1)	0.212(2)	1.454(1)

relative to tetramethylsilane (δ 0), or externally using trimethyl phosphate $[PO(OMe)_3]$ in D_2O (^{31}P). Solid-state CP MAS ^{13}C and ^{31}P NMR spectra were recorded using a Brüker CXP 200 instrument, equipped with an Andrews-type MAS probe and high-power proton decoupler. All chemical shifts are quoted in δ and coupling constants are in Hz. Microanalyses were performed by Analytische Laboratorien, Elbach, Germany.

Dichloro[(η^4)-2,3-*dimethylbutadiene*]*bis*(*trimethylphosphine*)*hafnium* 1.—The compound $HfCl_4$ (4 g, 12.5 mmol) in toluene (50 cm^3) was treated with trimethylphosphine (3.0 cm^3, 32 mmol) and the mixture added to sodium amalgam (0.6 g Na in 30 cm^3 Hg) at −78 °C. An excess of 2,3-dimethylbutadiene (*ca.* 5 g) was added and the mixture was warmed slowly to room temperature and then stirred for 14 h. The reaction mixture was filtered and the filtrate concentrated to 10 cm^3 and then cooled to −20 °C giving orange crystals of $[Hf(\eta^4\text{-}CH_2{=}CMe\text{-}CMe{=}CH_2)(PMe_3)_2Cl_2]$. Yield 3.1 g, 52%.

Dichloro[(1,2,3,4-η)-*cyclohexa*-1,3-*diene*]*bis*(*trimethylphosphine*)*zirconium* 2.—The compound $ZrCl_4$ (4 g, 17 mmol) in toluene (50 cm^3) was treated with trimethylphosphine (3.3 cm^3, 35 mmol) and the mixture was added to sodium amalgam (0.8 g Na in 30 cm^3 Hg) at −78 °C. Then an excess of cyclohexa-1,3-diene (5 g, 63 mmol) was added. The mixture was allowed to warm slowly to room temperature and was stirred for 14 h. Filtration, removal of volatile components and extraction into light petroleum (2 × 20 cm^3) gave a purple solution. This was concentrated to 20 cm^3 and cooled to −20 °C, giving purple crystals of $[Zr(\eta^4\text{-}C_6H_8)(PMe_3)_2Cl_2]$. Yield 1.21 g, 18%.

Dichloro[(1,2,3,4-η)-*cyclohexa*-1,3-*diene*]*bis*(*trimethylphosphine*)*hafnium* 3.—The compound $HfCl_4$ (4 g, 12.5 mmol) in toluene (60 cm^3) was treated with *ca.* 2 equivalents of trimethylphosphine (3.1 cm^3, 32 mmol) and the mixture was added to sodium amalgam (0.6 g Na in 30 cm^3 Hg) at −78 °C. Then an excess of cyclohexa-1,3-diene (5 g, 63 mmol) was



Scheme 1 Reagents and conditions: (*i*) lithium indenide in thf for 2 h, yield 75%; (*ii*) $HfCl_4$, 2 equivalents PMe_3, Na/Hg (2 equivalents) in toluene at −78 °C, excess of 2,3-dimethylbutadiene, stirring at room temperature (r.t.) for 14 h, 52%; (*iii*) M = Zr or Hf, 2 equivalents PMe_3, Na/Hg (2 equivalents) in toluene at −78 °C, cyclohexa-1,3-diene, stirring at r.t. for 14 h, 18% (Zr), or 12 h, 34% (Hf); (*iv*) $ZrCl_4$, PMe_3 (2 equivalents), Na/K (excess) in toluene at r.t. for 12 h, 5%

Table 6 Data for the crystal structure analyses

Compound	**1**	**5**
Experiment	Neutron[a]	X-Ray[b]
Formula	$C_{12}H_{28}Cl_2HfP_2$	$C_{13}H_{26}Cl_2P_2Zr$
M	473.6	406.4
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
a/Å	13.4297(7)[c]	13.527(5)
b/Å	9.9371(5)	11.338(5)
c/Å	14.0381(8)	12.922(6)
β/°	98.120(3)	93.37(3)
U/Å^3	1854	1978.5
Z	4	4
D_c/g cm^{-3}	1.70	1.37
F(000)	48.8[d]	832
μ/cm^{-1}	3.21	9.65
T/K	15	295
Radiation	Neutrons	Mo-Kα
λ/Å	1.3162	0.710 69
θ range/°	0–50	3–46 (2θ)
Crystal size/mm	4 × 4 × 1.5	0.05 × 0.4 × 0.6
Total data recorded	3385	4127
No. of unique data	1985	3433
No. of data used	1985	2994
n in $I > n\sigma(I)$	0	3
R[e]	0.052	0.034
R'[f]	0.040	0.043

[a] Grenoble D19 neutron diffractometer, germanium-monochromated thermal neutrons. [b] Enraf-Nonius CAD4 diffractometer. [c] Estimated standard deviation based on refinement which uses all 1985 data in the final stages to calculate the cell parameters. [d] Fermi units (10^{-15} m). [e] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [f] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{\frac{1}{2}}$.

added. The mixture was allowed to warm slowly to room temperature and stirred for 12 h. Filtration, followed by removal of volatile components and extraction into light petroleum (2 × 30 cm^3) gave a dark red solution. The extract was reduced in volume to 10 cm^3 and cooled to −20 °C, giving red crystals of [Hf(η^4-C_6H_8)(PMe_3)$_2$$Cl_2$]. Yield 1.72 g, 34%.

[(η^4)-2,3-*Dimethylbutadiene*]*bis*[(1,2,3,3a,7a-η)-*indenyl*]-*hafnium* **4**.—Lithium indenide (*ca.* 1 g) and [Hf(η^4-CH_2=CMe-CMe=CH_2)(PMe_3)$_2$$Cl_2$] (0.7 g, 5 mmol) were dissolved in thf (20 cm^3). The solution was stirred for 2 h and the volatiles removed under reduced pressure. The solid was extracted into toluene–light petroleum (1 : 1, 40 cm^3) and the solution reduced in volume to 10 cm^3. Cooling to −20 °C yielded two crops of pale yellow crystals of [Hf(η^5-C_9H_7)$_2$(η^4-CH_2=CMeCMe=CH_2)]. Yield 380 mg, 75%.

Dichloro[(η^6)-*toluene*]*bis*(*trimethylphosphine*)*zirconium* **5**.—The compound $ZrCl_4$ (4 g, 17 mmol) in toluene (100 cm^3) was treated with 2 equivalents of trimethylphosphine (3.3 cm^3, 34 mmol) and the mixture was added to excess of Na/K alloy (6 g) at ambient temperature under nitrogen and stirred for 12 h. The solvent was removed *in vacuo* and the residue extracted into light petroleum. The extract was concentrated and cooled to −78 °C to give air-sensitive, green crystals of [Zr(η^6-C_6H_5Me)-(PMe_3)$_2$$Cl_2$]. Yield *ca.* 300 mg, 5%.

Neutron Diffraction Experiment for Compound **1**.—Diffracted neutron intensities were recorded at the Institut Laue Langevin, Grenoble, France, on the neutron diffractometer D19 equipped with a position-sensitive detector. The data crystal, selected after investigating six other potential samples, was cooled carefully over a period of 3 h, to 15 K in a Displex[20] cryorefrigerator, constantly monitoring the intensity of one reflection. A total of 3385 intensities were recorded at 15 K in the range $0 < \theta < 50°$, of which 1985 were unique. A numerical absorption correction was applied to the measured intensities and corrections were also made for the absorption effects of the Displex vanadium heat shields. Extinction effects were minimal and a correction was not applied. The initial model was based on parameters taken from a low-temperature (190 K) X-ray study of this complex, the results of which have been deposited, together with all other supplementary data, at the Cambridge Crystallographic Data Centre. Full matrix least-squares refinement,[21] using anisotropic displacement parameters for all atoms and neutron scattering lengths from ref. 22, showed convergence at $R(R')$ of 0.052 (0.040). A weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + g|F_o|^2]$ with $g = 0.000\,175$ gave a satisfactory analysis of the variance in terms of θ and $|F_o|$. The data for the structure analysis are given in Table 6.

Crystal Structure Determination of Compound **5**.—Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation. Unit-cell parameters were calculated from the setting angles of 25 reflections. Three reflections were chosen as intensity and orientation controls and were measured at regular intervals. The data were corrected for Lorentz and polarisation effects and an empirical absorption correction based on an azimuthal scan was applied. Equivalent reflections were merged and systematically absent reflections (0*k*0, *k* = odd) rejected. The structure was solved by Patterson and Fourier methods. It consists of two independent molecules in the asymmetric unit. Non-hydrogen atoms were refined with anisotropic displacement parameters by least-squares procedures. The organic hydrogen atoms were placed in calculated positions (C–H 0.96 Å). A Chebychev weighting scheme[23] (parameters: 5.37, −1.17, 3.98) gave a satisfactory analysis of the variance in terms of θ and $|F_o|$ and the data were corrected for anomalous scattering in the final stages of refinement. Crystallographic calculations were carried out using the Oxford CRYSTALS package.[24] The data for the structure analysis are given in Table 6.

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

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