

Synthesis and Reactions of η -Cycloheptatriene and η -Cycloheptatrienyl Derivatives of Zirconium and Hafnium†

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The new compounds $[M(\eta\text{-C}_7\text{H}_8)\text{L}_2\text{Cl}_2]$ ($M = \text{Zr}$, $\text{L} = \text{PMe}_3$ **1**; $M = \text{Hf}$, $\text{L} = \text{PMe}_3$ **2**; $M = \text{Zr}$, $\text{L} = \text{PMe}_2\text{Ph}$ **3**; $M = \text{Hf}$, $\text{L} = \text{PMe}_2\text{Ph}$ **4**; $M = \text{Zr}$, $\text{L} = \text{PMePh}_2$ **5**) have been synthesised by reduction of MCl_4 using sodium amalgam in the presence of the tertiary phosphine and cycloheptatriene. Lithium indenide reacts with the triene compounds to give $[M(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)]$ ($M = \text{Zr}$ **6** or Hf **8**) which react with trimethylphosphine or 1,2-bis(dimethylphosphino)ethane (dmpe) to form $[M(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)(\text{PMe}_3)]$ ($M = \text{Zr}$ **7** or Hf **9**) and $[\{\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)\}_2(\mu\text{-dmpe})]$ **10** respectively. Treatment of **1** or **2** with sodium cyclopentadienide gives $[M(\eta\text{-C}_5\text{H}_5)_2\{\eta^2\text{-1,2- (or -3,4-) C}_7\text{H}_8\}(\text{PMe}_3)]$ [$M = \text{Zr}$ **11** or Hf **12**]. The X-ray crystal structures of **1**, **10** and $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-3,4-C}_7\text{H}_8)(\text{PMe}_3)]$ **11a** have been determined.

The chemistry of divalent molecular compounds of zirconium and hafnium is mainly represented by compounds in the classes $[M(\eta\text{-C}_5\text{H}_5)_2\text{L}_2]$ ¹ and $[M(\eta\text{-C}_5\text{H}_5)\text{L}_4\text{X}]$.² Here we describe the synthesis and reactions of the divalent triene compounds $[M(\eta\text{-C}_7\text{H}_8)(\text{PR}_3)_2\text{Cl}_2]$ ($M = \text{Zr}$ **1** or Hf **2**).^{3,4} Part of this work has been the subject of preliminary communications.³⁻⁵

Results and Discussion

Pure zirconium tetrachloride in toluene was treated with 2 equivalents of trimethylphosphine, then an excess of cycloheptatriene was added and the mixture reduced by sodium amalgam (2 equivalents) for 20 h giving deep red, highly air-sensitive crystals of $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ **1**. Typically the reaction could be carried out on a scale giving 5–10 g of **1**. The analytical and spectroscopic data characterising **1** and all the other new compounds **2–12** described below are given in Table 1. These data will not be further discussed except where interpretation is not straightforward. The hafnium analogue of **1**, namely $[\text{Hf}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ **2**, may be prepared similarly in high yields from HfCl_4 . Replacement of trimethylphosphine by PMe_2Ph or PMePh_2 gave analogues of **1** or **2**, namely $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_2\text{Ph})_2\text{Cl}_2]$ **3**, $[\text{Hf}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_2\text{Ph})_2\text{Cl}_2]$ **4** and $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PMePh}_2)_2\text{Cl}_2]$ **5**. However, attempts to prepare the triphenylphosphine compound $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PPh}_3)_2\text{Cl}_2]$ were unsuccessful.

The crystal structure of compound **1** has been determined. It crystallises in the orthorhombic crystal system in the space group $P2_12_12_1$. The molecular structure is shown in Fig. 1 and the fractional atomic coordinates and selected interatomic distances and angles are given in Tables 2 and 3. As illustrated in Fig. 1(a), there is a positional disorder of the cycloheptatriene ring, with the two different orientations exhibiting site occupancies of $\approx 1:1$. This was shown not to be the result of an individual crystal defect, since diffraction data were collected for a number of crystals which showed the disorder was present both at room temperature and at 200 K.

Addition of tetrahydrofuran (thf) to a mixture of lithium

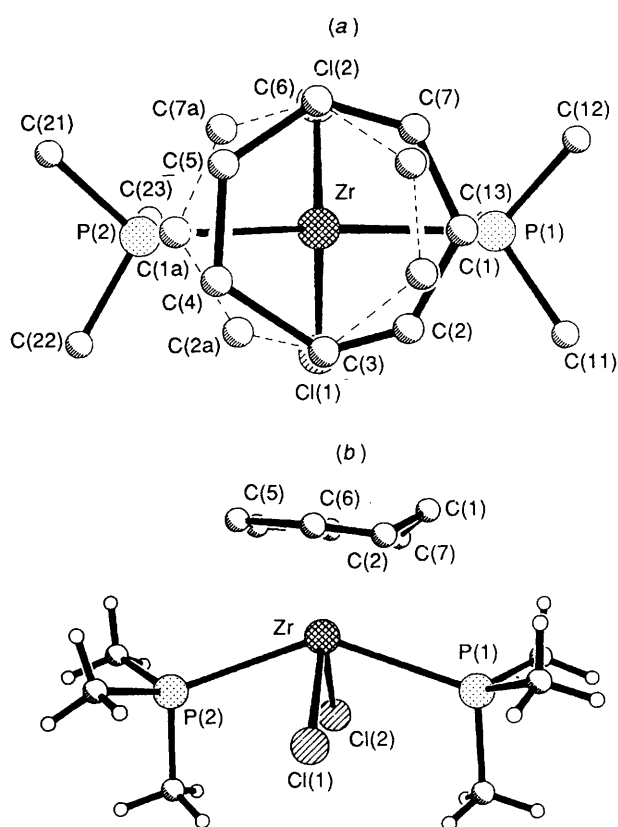


Fig. 1 Two view of the molecular structure of $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ **1**: (a) perpendicular to the $\eta\text{-C}_7\text{H}_8$ ring showing the positional disorder; (b) generalised view (only one orientation of the $\eta\text{-C}_7\text{H}_8$ ligand shown). Hydrogen atoms are omitted for clarity

indenide and the compound $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ **1** gave a dark coloured solution, from which a mixture of purple **6** and red crystals **7** could be isolated. These were initially separated by hand. Later it was found that recrystallisation of the mixture from a solution of toluene–light petroleum (1:1) in the presence of trimethylphosphine gave only large red platelets of the compound $[\text{Zr}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)(\text{PMe}_3)]$ **7**. These were

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

Non-SI unit employed: mmHg \approx 133 Pa.

Table 1 Analytical and spectroscopic data

Compound	Colour	NMR data ^a
1 C, 38.2 (38.4); H, 6.2 (6.4); Cl, 17.7 (17.5)%	Red	δ_{H}^b 5.75 (m, 2 H, H ²), 5.26 (m, 2 H, H ³), 4.10 (m, 2 H, H ¹), 1.41 [dt, 1 H, $J(\text{H}_{\text{exo}}-\text{H}_{\text{endo}})$ 11, $J(\text{H}_{\text{endo}}-\text{H}^1)$ 7, H_{endo}], 1.27 [d, 9 H, $J(\text{P}-\text{H})$ 7, 3 P-CH ₃], 0.99 (d, 9 H, $J(\text{P}-\text{H})$ 6, 3 P-CH ₃), -0.11 (m, H_{exo}) δ_{P}^b -25.9 [d, 1P, $J(\text{P}-\text{P})$ 70], -30.3 [d, 1P, $J(\text{P}-\text{P})$ 70] δ_{C}^b 123.7 [ddd, $J(\text{C}-\text{H})$ 160, $J(\text{P}-\text{C})$ 3, $J(\text{P}-\text{C})$ 2, C ²], 100.0 [dt, $J(\text{C}-\text{H})$ 163, $J(\text{P}-\text{C})$ 11, C ³], 83.7 [ddd, $J(\text{C}-\text{H})$ 166, $J(\text{P}-\text{C})$ 4, $J(\text{P}-\text{C})$ 2, C ¹], 19.6 [ddt, $J(\text{C}-\text{H})$ 138, $J(\text{P}-\text{C})$ 10, $J(\text{P}-\text{C})$ 5, CH ₂], 14.7 [dq, $J(\text{C}-\text{H})$ 130, $J(\text{P}-\text{C})$ 16, P-CH ₃], 14.0 [dq, $J(\text{C}-\text{H})$ 129, $J(\text{P}-\text{C})$ 15, P-CH ₃]
2 C, 31.55 (31.6); H, 5.1 (5.3); Cl, 14.2 (14.4)%	Orange	δ_{H}^b 5.90 (m, 2 H, H ²), 5.15 (m, 2 H, H ³), 4.03 (m, 2 H, H ¹), 1.50 [dt, 1 H, $\text{H}_{\text{exo}}-\text{H}_{\text{endo}}$ 10, $J(\text{H}_{\text{endo}}-\text{H}^1)$ 8, H_{endo}], 1.35 [d, 9 H, $J(\text{P}-\text{H})$ 6, 3P-CH ₃], 1.05 [d, 9 H, $J(\text{P}-\text{H})$ 6, 3P-CH ₃], -0.48 [br t, 1 H, $J(\text{H}_{\text{exo}}-\text{H}_{\text{endo}})$ 10, H_{exo}] δ_{P}^b -23.1 [d, 1P, $J(\text{P}-\text{P})$ 71], -32.0 [d, 1P, $J(\text{P}-\text{P})$ 71] δ_{C}^b 123.8 [d, $J(\text{C}-\text{H})$ 156, C ²], 98.0 [dt, $J(\text{C}-\text{H})$ 164, $J(\text{P}-\text{C})$ 11, C ³], 82.3 [d, $J(\text{C}-\text{H})$ 164, C ¹], 19.5 [t, $J(\text{C}-\text{H})$ 131, CH ₂], 14.8 [dq, $J(\text{C}-\text{H})$ 129, $J(\text{P}-\text{C})$ 18, P-CH ₃], 13.8 [dq, $J(\text{C}-\text{H})$ 129, $J(\text{P}-\text{C})$ 17, P-CH ₃]
3 C, 52.3 (52.1); H, 5.6 (5.7); Cl, 13.2 (13.4)%	Red	δ_{H}^b 7.9, 7.6, 7.1 (m, 10 H, Ph), 5.80 (m, 2 H, H ²), 5.1 (m, 2 H, H ³), 4.0 (m, 2 H, H ¹), 1.9 [d, 6 H, $J(\text{P}-\text{H})$ 6, 2P-CH ₃], 1.5 [d, 6 H, $J(\text{P}-\text{H})$ 6, 2P-CH ₃], 1.3 (m, 1 H, H_{endo}), -0.55 (m, 1 H, H_{exo}) δ_{P}^b -12.5 [d, 1P, $J(\text{P}-\text{P})$ 63], -14.9 [d, 1P, $J(\text{P}-\text{P})$ 63] δ_{C}^b 139.5 (br m, C _{quat}), 132-127 (m, Ph), 123.1 [d, $J(\text{C}-\text{H})$ 160, C ²], 101.9 [d, $J(\text{C}-\text{H})$ 163, C ³], 86.7 [d, $J(\text{C}-\text{H})$ 168, C ¹], 18.7 [t, $J(\text{C}-\text{H})$ 135, CH ₂], 13.6 [dq, $J(\text{C}-\text{H})$ 123, $J(\text{P}-\text{C})$ 17, P-CH ₃], 13.2 [dq, $J(\text{C}-\text{H})$ 123, $J(\text{P}-\text{C})$ 20, P-CH ₃]
4 C, 44.45 (44.7); H, 5.0 (4.9)%	Orange	δ_{H}^b 7.8, 7.6, 7.05 (m, 10 H, Ph), 5.80 (m, 2 H, H ²), 4.9 (m, 2 H, H ³), 3.8 (m, 2 H, H ¹), 1.9 [d, 6 H, $J(\text{P}-\text{H})$ 6, 3P-CH ₃], 1.5 [d, 6 H, $J(\text{P}-\text{H})$ 7, 3P-CH ₃], 1.4 (m, 1 H, H_{endo}), -1.0 (m, 1 H, H_{exo}) δ_{P}^b 21.5 [d, 1P, $J(\text{P}-\text{P})$ 65], 14.3 [d, 1P, $J(\text{P}-\text{P})$ 63] δ_{C}^b 139.5 (br s, C _{quat}), 130.6-128.3 (Ph, C _{ortho} , C _{meta} , C _{para}), 123.1 [d, $J(\text{C}-\text{H})$ 162, C ²], 99.9 [d, $J(\text{C}-\text{H})$ 164, C ³], 85.4 [d, $J(\text{C}-\text{H})$ 168, C ¹], 18.6 [t, $J(\text{C}-\text{H})$ 128, CH ₂], 13.7 [dq, $J(\text{C}-\text{H})$ 132, $J(\text{P}-\text{C})$ 17, P-CH ₃], 12.9 [dq, $J(\text{C}-\text{H})$ 132, $J(\text{P}-\text{C})$ 18, P-CH ₃]
5 C, 60.7 (60.5); H, 5.1 (5.2)%	Red	δ_{H}^b 7.8, 7.1 (br m, 20 H, Ph), 5.9 (m, 2 H, H ²), 5.2 (m, 2 H, H ³), 4.1 (m, 2 H, H ¹), 2.05 [br s, 6 H, 2P-CH ₃], 1.6 (m, 1 H, H_{endo}), -0.28 (m, 1 H, H_{exo}) δ_{P}^b -2 (br s) $\delta_{\text{C}}^{(13\text{C}-\{^1\text{H}\}^b)}$ 137.2 [d, $J(\text{P}-\text{C})$ 18, C _{quat}], 133.5-128.3 (Ph, C _{ortho} , C _{meta} , C _{para}), 124.2 (s, C ²), 102.8 (s, C ³), 88.3 (s, C ¹), 18.8 (s, CH ₂), 15.7 (br s, P-CH ₃)
6 C, 64.5 (64.6); H, 4.9 (4.7)%	Purple	δ_{H}^b 7.2 (m, 2 H, H_a or H_b), 6.7 (m, 2 H, H_a or H_b), 5.6 [d, 2 H, $J(\text{H}^1-\text{H}^2)$ 3.6, H ¹], 5.4 [t, 1 H, $J(\text{H}^1-\text{H}^2)$ 3.6, H ²], 5.0 (s, 7 H, C ₇ H ₇) δ_{C}^b 122.8 [d, $J(\text{C}-\text{H})$ 158, C _a or C _b], 122.6 [d, $J(\text{C}-\text{H})$ 159, C _a or C _b], 121.8, s, C _{quat}], 106.1 [d, $J(\text{C}-\text{H})$ 168, C ²], 92.4 [d, $J(\text{C}-\text{H})$ 173, C ¹], 83.3 [d, $J(\text{C}-\text{H})$ 167, C ₇ H ₇]
7	Red ^c	δ_{H}^d 7.17 (m, 2 H, H_a or H_b), 6.84 (m, 2 H, H_a or H_b), 5.62 [d, 2 H, $J(\text{H}^1-\text{H}^2)$ 3.4, H ¹], 5.26 [t, 1 H, $J(\text{H}^1-\text{H}^2)$ 3.4, H ²], 4.32 (s, 7 H, C ₇ H ₇), 0.69 [d, 9 H, $J(\text{P}-\text{H})$ 4.0, 3 P-CH ₃] δ_{P}^d -51.6 (s) δ_{C}^d 123.7 [d, $J(\text{C}-\text{H})$ 161, C _a and C _b], 122.0 [d, $J(\text{C}-\text{H})$ 157, C _a or C _b], 121.3 (s, C _{quat}), 103.4 [d, $J(\text{C}-\text{H})$ 167, C ²], 91.3 [d, $J(\text{C}-\text{H})$ 170, C ¹], 82.5 [d, $J(\text{C}-\text{H})$ 166, C ₇ H ₇], 17.5 [dq, $J(\text{C}-\text{H})$ 131, $J(\text{P}-\text{C})$ 8, P-CH ₃]
8 C, 49.7 (49.9); H, 3.7 (3.7)%	Red	δ_{H}^b 7.15 (m, 2 H, H_a or H_b), 6.70 (m, 2 H, H_a or H_b), 5.60 [d, 2 H, $J(\text{H}^1-\text{H}^2)$ 3.6, H ¹], 5.30 [t, 1 H, $J(\text{H}^1-\text{H}^2)$ 3.6, H ²], 4.90 (s, 7 H, C ₇ H ₇) δ_{C}^b 123.1 (C _a or C _b), 122.8 (C _a or C _b), 120.1 (C _{quat}), 104.0 (C ²), 89.7 (C ¹), 79.4 (C ₇ H ₇)
9 C, 49.5 (49.3); H, 4.9 (5.0)%	Orange	δ_{H}^b 7.17 (m, 2 H, H_a or H_b), 6.84 (m, 2 H, H_a or H_b), 5.62 [d, 2 H, $J(\text{H}^1-\text{H}^2)$ 3.2, H ¹], 5.18 [t, 1 H, $J(\text{H}^1-\text{H}^2)$ 3.2, H ²], 4.29 [d, 7 H, $J(\text{P}-\text{H})$ 1, C ₇ H ₇], 0.69 [d, 9 H, $J(\text{P}-\text{H})$ 4.3, 3 P-CH ₃] δ_{P}^b -51.4 (s) δ_{C}^b 124.1 [d, $J(\text{C}-\text{H})$ 162, C _a or C _b], 122.4 [d, $J(\text{C}-\text{H})$ 158, C _a or C _b], 119.8 (s, C _{quat}), 102.2 [d, $J(\text{C}-\text{H})$ 167, C ²], 89.3 [d, $J(\text{C}-\text{H})$ 172, C ¹], 79.2 [d, $J(\text{C}-\text{H})$ 159, C ₇ H ₇], 18.1 [dq, $J(\text{C}-\text{H})$ 125, $J(\text{P}-\text{C})$ 10, P-CH ₃]
10 C, 49.5 (49.6); H, 4.8 (4.8)%	Red	δ_{H}^b 7.16 (m, 4 H, H_a or H_b), 6.74 (m, 4 H, H_a or H_b), 5.60 [d, 4 H, $J(\text{H}^1-\text{H}^2)$ 3.5, H ¹], 5.31 [t, 2 H, $J(\text{H}^1-\text{H}^2)$ 3.5, H ²], 4.71 (s, 14 H, C ₇ H ₇), 1.30 (m, 4 H, 2P-CH ₂), 0.80 (s, 12 H, 4 P-CH ₃) δ_{P}^b -47.3 (s)
11a C, 61.5 (61.65); H, 6.9 (7.0)%	Red	δ_{H}^b 6.65 (m, 1 H, H ⁶ or H ¹), 6.15 (m, 1 H, H ⁶ or H ¹), 5.20 (m, 1 H, H ⁵ or H ²), 5.05 [d, 5 H, $J(\text{P}-\text{H})$ 1.8, C ₅ H ₅], 4.90 [d, 5 H, $J(\text{P}-\text{H})$ 1.9, C ₅ H ₅], 4.75 (m, 1 H, H ⁵ or H ²), 3.30 (m, 2 H, H ⁴ and H ³), 2.25 (m, 1 H, H ⁷ or H ⁸), 1.85 (m, 1 H, H ⁷ or H ⁸), 0.81 [d, 9 H, $J(\text{P}-\text{H})$ 5.7, 3 P-CH ₃] δ_{P}^b -1.3 (s, 1 PMe ₃) δ_{C}^b 138.2 [d, $J(\text{C}-\text{H})$ 146.5, C ¹ , C ² , C ⁵ or C ⁶], 136.6 [d, $J(\text{C}-\text{H})$ 144.0, C ¹ , C ² , C ⁵ or C ⁶], 112.4 [d, $J(\text{C}-\text{H})$ 151.0, C ¹ , C ² , C ⁵ or C ⁶], 110.9 [d, $J(\text{C}-\text{H})$ 147.7, C ¹ , C ² , C ⁵ or C ⁶], 106.2 [d, $J(\text{C}-\text{H})$ 172.1, C ₅ H ₅], 101.8 [d, $J(\text{C}-\text{H})$ 169.3, C ₅ H ₅], 43.1 [dd, $J(\text{C}-\text{H})$ 137.9, $J(\text{P}-\text{C})$ 3, C ³ or C ⁴], 41.7 [dd, $J(\text{C}-\text{H})$ 140.4, $J(\text{P}-\text{C})$ 6, C ³ or C ⁴], 34.2 [t, $J(\text{C}-\text{H})$ 119, CH ₂], 17.5 [dq, $J(\text{C}-\text{H})$ 128, $J(\text{P}-\text{C})$ 16, 3 P-CH ₃]
11b	Red	δ_{H}^b 6.40 (m, 1 H, H ⁶), 6.15 (m, 1 H, H ⁴), 5.75 (m, 1 H, H ³), 5.00 [d, 5 H, $J(\text{PH})$ 1.6, C ₅ H ₅], 5.00 (m, 1 H, H ⁵), 4.95 [d, 5 H, $J(\text{PH})$ 1.4, C ₅ H ₅], 4.35 (m, 1 H, H ¹), 3.30 (m, 1 H, H ²), 2.50 (m, 1 H, H ⁷ or H ⁸), 2.00 (m, 1 H, H ⁷ or H ⁸), 0.80 [d, $J(\text{PH})$ 5.6, 3 P-CH ₃] δ_{P}^b -2.8 (s, 1 PMe ₃) $\delta_{\text{C}}^{(13\text{C}-\{^1\text{H}\}^b)}$ 138.2 (C ³ , C ⁴ , C ⁵ or C ⁶), 123.7 (C ³ , C ⁴ , C ⁵ or C ⁶), 106.6 (C ₅ H ₅), 106.0 (C ³ , C ⁴ , C ⁵ or C ⁶), 102.3 (C ₅ H ₅), 52.5 (C ¹ or C ²), 47.8 (C ¹ or C ²), 38.2 (CH ₂), 17.3 (P-CH ₃); ^c one of C ³ , C ⁴ , C ⁵ or C ⁶ was not detected
12a C, 50.1 (50.4); H, 5.5 (5.7)%	Orange	δ_{H}^b 6.80 (m, 1 H, H ⁶ or H ¹), 6.20 (m, 1 H, H ⁶ or H ¹), 5.20 (m, 1 H, H ⁵ or H ²), 5.01 [d, 5 H, $J(\text{P}-\text{H})$ 1.7, C ₅ H ₅], 4.90 [d, 5 H, $J(\text{P}-\text{H})$ 1.7, C ₅ H ₅], 4.75 (m, 1 H, H ⁵ or H ²), 3.80 + 3.50 (m, 2 H, H ⁴ and H ³), 1.90 (m, 1 H, H ⁷ or H ⁸), 1.70 (m, 1 H, H ⁷ or H ⁸), 0.87 [d, 9 H, $J(\text{P}-\text{H})$ 6.2, 3 P-CH ₃] δ_{P}^b -13.0 (s, 1 PMe ₃) δ_{C}^b 139.6 [d, $J(\text{C}-\text{H})$ 139.6, C ¹ , C ² , C ⁵ or C ⁶], 137.9 [d, $J(\text{C}-\text{H})$ 134.3, C ¹ , C ² , C ⁵ or C ⁶], 112.8 [d, $J(\text{C}-\text{H})$ 137.9, C ¹ , C ² , C ⁵ or C ⁶], 111.1 [d, $J(\text{C}-\text{H})$ 140.4, C ¹ , C ² , C ⁵ or C ⁶], 104.9 [d, $J(\text{C}-\text{H})$ 173.3, C ₅ H ₅], 101.0 [d, $J(\text{C}-\text{H})$ 172.1, C ₅ H ₅], 40.9 [d, $J(\text{C}-\text{H})$ 142.8, C ³ or C ⁴], 38.7 [d, $J(\text{C}-\text{H})$ 148.8, C ³ or C ⁴], 33.5 [t, $J(\text{C}-\text{H})$ 121, CH ₂], 17.6 [dq, $J(\text{C}-\text{H})$ 128, $J(\text{P}-\text{C})$ 18, 3 P-CH ₃]
12b	Orange	δ_{H}^b 6.50 (m, 1 H, H ⁶), 6.20 (m, 1 H, H ⁴), 5.75 (m, 1 H, H ³), 4.93 [d, 5 H, $J(\text{P}-\text{H})$ 2, C ₅ H ₅], 5.05 (m, 1 H, H ¹), 4.91 [d, 5 H, $J(\text{P}-\text{H})$ 2, C ₅ H ₅], 2.35 (m, 1 H, H ⁷ or H ⁸), 1.7 (m, 1 H, H ⁷ or H ⁸), 0.87 (d, 3 P-CH ₃) δ_{P}^b -13.4 (s, 1 PMe ₃) $\delta_{\text{C}}^{(13\text{C}-\{^1\text{H}\}^b)}$ 142.3, 134.0, 124.5, 106.8 (all C ³ , C ⁴ , C ⁵ or C ⁶), 101.6 (C ₅ H ₅), 52.7 (C ¹ or C ²), 44.3 (C ¹ or C ²), 38.1 (CH ₂), 17.3 (P-CH ₃); ^c a band due to a second C ₅ H ₅ group was not identified

^a ¹H NMR at 300, ³¹P at 120, ¹³C at 75 MHz, coupling constants *J* in Hz, all δ_{P} are proton decoupled. Analytical data given as Found (Calc.). ^b In [²H₆]benzene. ^c Thermally unstable. ^d In [²H₈]toluene. ^e Partially obscured.

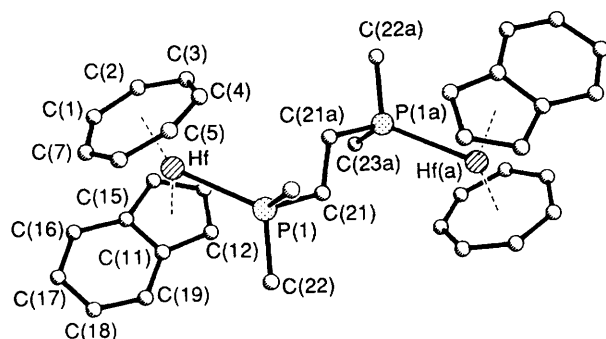
Table 2 Fractional atomic coordinates ($\times 10^4$) for all non-hydrogen atoms of $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ **1**

Atom	x	y	z
Zr	1 805.8(4)	5 252.5(4)	8 876.1(4)
P(1)	3 844(1)	3 882(1)	8 822(1)
P(2)	−820(1)	5 217(1)	9 027(1)
Cl(1)	1 368(2)	3 997(1)	10 271(1)
Cl(2)	1 216(2)	4 093(1)	7 451(1)
C(1)	4 124(15)	6 397(13)	8 869(13)
C(2)	3 385(14)	6 163(11)	9 814(11)
C(3)	2 481(12)	6 628(6)	10 061(5)
C(4)	1 327(17)	7 065(12)	9 400(16)
C(5)	1 323(19)	7 021(16)	8 328(15)
C(6)	2 310(7)	6 659(5)	7 668(5)
C(7)	3 480(35)	6 159(23)	7 949(28)
C(1A)	856(14)	7 349(10)	8 993(15)
C(2A)	1 369(18)	6 731(12)	9 878(12)
C(3A)	2 481(12)	6 628(6)	10 061(5)
C(4A)	3 607(17)	6 379(11)	9 282(19)
C(5A)	3 363(35)	6 431(21)	8 196(31)
C(6A)	2 310(7)	6 659(5)	7 668(5)
C(7A)	1 106(22)	6 815(16)	7 988(14)
C(11)	4 861(7)	3 847(5)	9 903(5)
C(12)	4 941(7)	3 977(7)	7 806(5)
C(13)	3 344(6)	2 513(5)	8 723(6)
C(21)	1 801(7)	5 984(6)	8 196(6)
C(22)	−1 490(7)	5 546(6)	10 225(6)
C(23)	−1 451(5)	3 903(4)	8 825(5)

C(nA) indicates the alternative ring C atom positions.

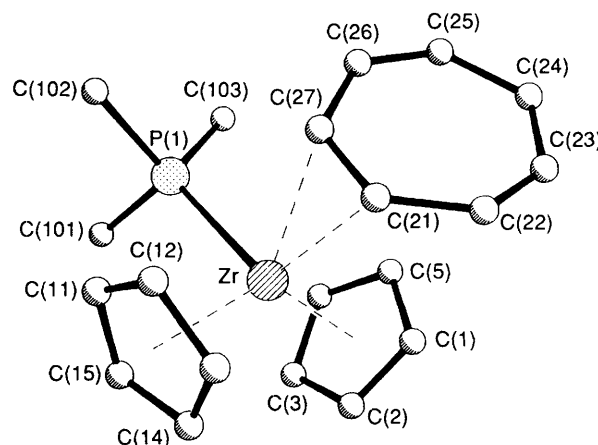
Table 3 Selected bond lengths and angles for $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ **1**

Zr–Cl(1)	2.525(3)	Zr–C(7)	2.455(36)
Zr–Cl(2)	2.516(3)	Zr–C(1A)	2.846(14)
Zr–P(1)	2.763(3)	Zr–C(2A)	2.366(16)
Zr–P(2)	2.770(3)	Zr–C(3A)	2.482(9)
Zr–C(1)	2.839(16)	Zr–C(4A)	2.438(18)
Zr–C(2)	2.395(15)	Zr–C(5A)	2.405(34)
Zr–C(3)	2.482(9)	Zr–C(6A)	2.487(7)
Zr–C(4)	2.461(16)	Zr–C(7A)	2.438(21)
Zr–C(5)	2.419(21)	Zr–C(mean triene)	2.444(41)
Zr–C(6)	2.487(7)		
P(1)–Zr–Cl(1)	76.4(1)	P(2)–Zr–Cl(1)	75.6(1)
P(1)–Zr–Cl(2)	78.6(1)	P(2)–Zr–Cl(2)	78.6(1)
P(1)–Zr–P(2)	140.0(1)		

**Fig. 2** Molecular structure of $[\{\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)\}_2(\mu\text{-dmpe})]$ **10**. Hydrogen atoms are omitted for clarity

found to be thermally unstable and on heating under vacuum evolved trimethylphosphine to give the purple compound $[\text{Zr}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)]$ **6**.

Treatment of the compound $[\text{Hf}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ **2** with lithium indenide gave a mixture of the compounds $[\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)]$ **8** and $[\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)(\text{PMe}_3)]$ **9**.

**Fig. 3** Molecular structure of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-3,4-C}_7\text{H}_8)(\text{PMe}_3)]$ **11a**. Hydrogen atoms are omitted for clarity

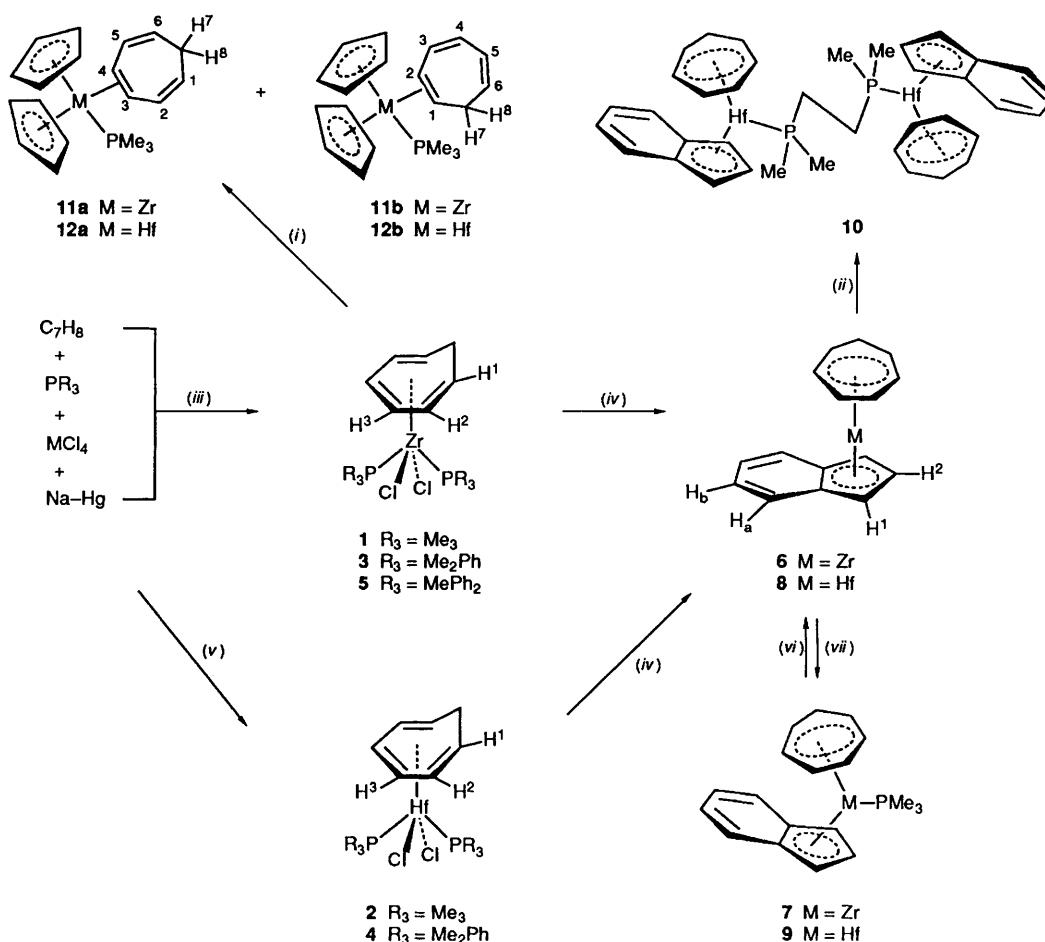
Pure **8** was obtained by vacuum pyrolysis of **9**. It is interesting that the hafnium phosphine adduct **9** is thermally more robust than its zirconium counterpart **7** and does not lose trimethylphosphine under vacuum at ambient temperature. Pure **9** was obtained by crystallisation of the mixture of **8** and **9** in the presence of an excess of trimethylphosphine. The NMR spectrum of the initial reaction mixture of **8** and **9** showed the presence of traces (2%) of the zirconium analogues **6** and **7**. These were removed by fractional crystallisation.

The addition of $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (dmpe) to a toluene solution of compound $[\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)]$ **8** gave red crystals of $[\{\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)\}_2(\mu\text{-dmpe})]$ **10**. Unfortunately **10** was not sufficiently soluble for detailed NMR studies. However, the ^1H NMR spectrum of a dilute solution in hot toluene and the microanalytical data suggested a binuclear bridged structure such as was found for $[\{\text{Zr}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_7\text{H}_9)\}_2(\text{dmpe})]$.⁵

In order further to characterise compound **10** the single-crystal X-ray structure has been determined.⁴ The molecular structure is shown in Fig. 2 and details of the structure determination, bond lengths and angles, fractional atomic coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. The solid-state structure of **10** is consistent with the solution NMR data and consists of two $\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta^5\text{-C}_9\text{H}_7)$ units bridged by a $\mu\text{-dmpe}$ ligand. There is no apparent tendency for the indenyl ligand to adopt a η^3 co-ordination. The only other previous crystal structure of a $\text{Hf-}\eta\text{-C}_7\text{H}_7$ moiety is for the 16-electron $[\text{Hf}(\eta\text{-C}_7\text{H}_7)(\eta\text{-C}_5\text{Me}_5)]$.⁶

Treatment of $[\text{Zr}(\eta\text{-C}_7\text{H}_8)(\text{PMe}_3)_2\text{Cl}_2]$ **1** in thf with sodium cyclopentadienide at room temperature gave orange crystals of stoichiometry $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_7\text{H}_8)(\text{PMe}_3)]$ **11**. Correlation spectroscopy COSY 45 and ^{31}P NMR spectra of **11** show the presence of a mixture of isomers **11a** and **11b** in the ratio 4:1, respectively. Attempts to separate the two isomers by fractional crystallisation were unsuccessful.

The complexity of these NMR data warranted determination of the crystal structure of one of the isomers. A crystal suitable for X-ray diffraction was selected from a mixture of isomers. The molecular structure of this isomer is shown in Fig. 3; further details are available from the Cambridge Crystallographic Data Centre. The data show the C_7H_8 ligand in this species to be η^2 -bonded to the Hf by the C(21) and C(27) carbons and the molecular structure corresponds to the 3,4 isomer **11a**. The η^2 -3,4- C_7H_8 ligand in **11a** is rare⁷ but otherwise the compound is closely related to the recently described $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{PMe}_3)\text{L}]$, where $\text{L} = \eta^2\text{-C}_2\text{H}_4$ or $\eta^2\text{-cis-PhHC=CHPh}$.⁸ The solution NMR spectrum of **11a**, **11b** identifies the isomer with the η^2 -3,4- C_7H_8 ligand to be the major isomer **11a**. For example, there is no coupling between the hydrogens bound to C(21) and C(27). The minor isomer **11b** is then tentatively assigned as



Scheme 1 Reagents and conditions: (i) NaC_5H_5 in thf at r.t. for 12 h; (ii) dmpe in toluene for 10 min at r.t.; (iii) M = Zr, 2 Na-Hg at $-80^\circ C$, gradual warm up then stirred at r.t. for 20 h; (iv) lithium indenide in thf for 20 h at r.t.; (v) M = Hf, 2 Na-Hg at $-80^\circ C$, gradual warm up then stirred at r.t. for 20 h; (vi) PMe_3 in toluene for 10 min at r.t.; (vii) warmed to $80^\circ C$ at 10^{-5} mmHg for 10 min then sublimed *in vacuo*

having a η^2 -1,2- C_7H_8 ligand (see Scheme 1). The ^{13}C NMR spectrum is in agreement with this assignment.

Treatment of compound 2 with sodium cyclopentadienide at room temperature gave red crystals 12 the NMR of which closely resembled that of the isomeric mixture 11. On this basis we propose the structures of the major isomer 12a and that of the minor isomer 12b to be analogous to those of 11a and 11b respectively (see Scheme 1).

Iodotrimethylsilane reacts instantaneously with compounds 12 accompanied by a lightening of colour, to produce $[Hf(\eta-C_5H_5)_2I_2]$. A similar reaction has been reported for divalent bis(η -cyclopentadienyl) compounds of titanium.⁹

Treatment of compound 1 with sodium cyclopentadienide in thf at $60^\circ C$ for 3 d gave low yields of small dark red crystals. Comparison of the 1H and ^{31}P NMR spectra of the red crystals with those of the previously described $[Zr(\eta-C_5H_5)(\mu-\sigma-\eta^5-C_5H_4)(PMe_3)_2]^{10}$ clearly identified them to be the same compound. This dimer was originally prepared by the reduction of $[Zr(\eta-C_5H_5)_2Cl_2]$ with magnesium in the presence of PMe_3 ,⁸ and gives a higher yield and therefore is the preferred method of synthesis.

In conclusion, the reactions and structures proposed for the new compounds 1–12 are given in Scheme 1. The divalent η -cycloheptatriene compounds 1–5 are clearly likely to be used as precursors for the further development of the chemistry of zirconium and hafnium.

Experimental

All manipulations were performed using standard vacuum-line and Schlenk vessel techniques either 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 overpressure 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 predried by heating at $240^\circ C$ in an oven before use. Solvents were pre-dried by standing over molecular sieves followed by distillation from sodium (toluene), potassium–benzophenone (tetrahydrofuran) or sodium–potassium alloy [light petroleum (b.p. 40 – $60^\circ C$), diethyl ether, pentane]. Deuteriated solvents for NMR spectroscopy were stored over sodium–potassium alloy (benzene, toluene). NMR samples were sealed under vacuum (10^{-5} mmHg). Celite 545 filtration aid (Koch-Light) was predried at $240^\circ C$ before use.

The NMR spectra were referenced internally using the residual protio-solvent (1H) or solvent (^{13}C) resonances relative to tetramethylsilane (δ 0), or externally using trimethyl phosphate $[PO(OMe)_3]$ in D_2O (^{31}P).

Microanalyses were performed by Analytische Laboratorien, Elbach, Germany.

Dichloro(η-cycloheptatriene)bis(trimethylphosphine)zirconium 1.—Pure $ZrCl_4$ (8 g, 34 mmol) in toluene (100 cm^3) was treated with 2 equivalents of trimethylphosphine (6.6 cm^3 , 70 mmol) and the mixture was added to sodium amalgam (2 equivalents) at $-78^\circ C$. An excess of cycloheptatriene (15 cm^3 , 96 mmol) was added to the mixture which was warmed slowly to

room temperature and then stirred for 16 h. It was filtered and the filtrate concentrated under reduced pressure to ca. 40 cm³. Light petroleum (5 cm³) was added and the mixture was cooled to -20 °C giving red crystals of compound **1**. Yield 6.1 g, 44%.

Dichloro(η-cycloheptatriene)bis(trimethylphosphine)hafnium 2.—Pure HfCl₄ (8 g, 25 mmol) in toluene (100 cm³) was treated with 2 equivalents of trimethylphosphine (4.8 cm³, 51 mmol) and the mixture was added to sodium amalgam (2 equivalents) at -78 °C. Then an excess of cycloheptatriene (20 cm³, 128 mmol) was added. The mixture was allowed to warm to room temperature (r.t.) and then stirred for 16 h. It was filtered and concentrated under reduced pressure (to ca. 40 cm³). Addition of light petroleum (5 cm³) and cooling to -20 °C gave orange crystals of compound **2**. Yield 5.7 g, 46%.

Dichloro(η-cycloheptatriene)bis(dimethylphenylphosphine)-zirconium 3.—Pure ZrCl₄ (4 g, 17 mmol) in toluene (100 cm³) was treated with 2 equivalents of dimethylphenylphosphine (4.8 cm³, 34 mmol) and the mixture was added to sodium amalgam (2 equivalents) at -78 °C. An excess of cycloheptatriene (20 cm³, 128 mmol) was added and the mixture was allowed to warm slowly to r.t. and was stirred for ≈ 16 h. Filtration followed by concentration of the filtrate (to ca. 20 cm³) and cooling to -20 °C gave red crystals of compound **3**. Yield 4.3 g, 47%.

Dichloro(η-cycloheptatriene)bis(dimethylphenylphosphine)-hafnium 4.—Pure HfCl₄ (4 g, 12.5 mmol) in toluene (100 cm³) was treated with 2 equivalents of dimethylphenylphosphine (3.3 cm³, 25 mmol) and the mixture was added to sodium amalgam (2 equivalents) at -78 °C. An excess of cycloheptatriene (20 cm³, 128 mmol) was added. The mixture was allowed to warm slowly to r.t. and was stirred for ≈ 16 h. Filtration followed by concentration of the filtrate (to ca. 20 cm³) and cooling to -20 °C gave orange crystals of compound **4**. Yield 3.0 g, 38%.

Dichloro(η-cycloheptatriene)bis(methyldiphenylphosphine)-zirconium 5.—Pure ZrCl₄ (4 g, 17 mmol) in toluene (100 cm³) was treated with 2 equivalents of methyldiphenylphosphine (6.4 cm³, 34 mmol) and the mixture was added to sodium amalgam (2 equivalents) at -78 °C. An excess of cycloheptatriene (20 cm³, 128 mmol) was added and the mixture was allowed to warm slowly to r.t. and was stirred for ≈ 16 h. Filtration and concentration of the filtrate (to ca. 20 cm³) then addition of light petroleum (5 cm³) and cooling to -20 °C gave red crystals of compound **5**. Yield 4.7 g, 43%.

*Reaction of Lithium Indenide with [Zr(η-C₇H₈)(PMe₃)₂Cl₂]: Synthesis of (η-Cycloheptatrienyl)(η⁵-indenyl)zirconium **6** and (η-Cycloheptatrienyl)(η⁵-indenyl)(trimethylphosphine)zirconium **7**.—Lithium indenide (ca. 500 mg) was added to [Zr(η-C₇H₈)(PMe₃)₂Cl₂] (300 mg, 0.74 mmol) and the mixture was dissolved in thf (20 cm³). The volatiles were removed under reduced pressure and the residue was extracted into light petroleum–toluene (1:1, 30 cm³). The extract was filtered and cooled to -20 °C giving a mixture of large orange platelets and small dark crystals. A few of these were separated by hand and both were clearly identified from their ¹H NMR spectra as [Zr(η-C₇H₇)(η⁵-C₉H₇)(PMe₃)] **7** (orange platelets) and [Zr(η-C₇H₇)(η⁵-C₉H₇)] **6** (purple crystals) (170 mg, yield based on total zirconium 46%). This mixture was heated to 100 °C *in vacuo* (ca. 10⁻⁵ mmHg) for 10 min and then sublimed at 130 °C. The purple sublimate was extracted into toluene and crystallised at -20 °C giving purple crystals of [Zr(η-C₇H₇)(η⁵-C₉H₇)]. Yield 120 mg, 18%. Alternatively, trimethylphosphine (≈ 0.2 cm³) was added to a toluene solution (10 cm³) of the mixture of compounds **6** and **7** (155 mg) obtained as described above and the mixture was stirred for 10 min and then*

filtered. Light petroleum (10 cm³) was added to the filtrate and large orange platelets of [Zr(η-C₇H₇)(η⁵-C₉H₇)(PMe₃)] were deposited in 30 min at -20 °C. Yield 140 mg, > 90%.

(η-Cycloheptatrienyl)(η⁵-indenyl)hafnium 8.—The compound [Hf(η-C₇H₇)(η⁵-C₉H₇)(PMe₃)] (700 mg, 1.5 mmol) (see above) was heated to 90 °C at 10⁻⁵ mmHg for 20 min. The orange solid gradually became dark red. This was extracted with hot toluene (ca. 80 °C, 2 × 10 cm³), filtered and cooled to -20 °C giving red crystals of [Hf(η-C₇H₇)(η⁵-C₉H₇)]. Yield 495 mg, 83%.

(η-Cycloheptatrienyl)(η⁵-indenyl)(trimethylphosphine)-hafnium 9.—The compound [Hf(η-C₇H₈)(PMe₃)₂Cl₂] (1.5 g, 3 mmol) and lithium indenide (2 g, 16 mmol) were dissolved in thf (30 cm³) and the solution was stirred for 2 h. The volatiles were removed under reduced pressure and the residue was extracted into toluene (4 × 20 cm³). The extract was concentrated to 20 cm³ and trimethylphosphine added (ca. 0.5 cm³). The resulting mixture was cooled to -20 °C giving large orange platelets of [Hf(η-C₇H₇)(η⁵-C₉H₇)(PMe₃)]. Yield 950 mg, 67%.

[{Hf(η-C₇H₇)(η⁵-C₉H₇)}₂(μ-dmpe)] **10**.—The ligand dmpe (ca. 0.1 cm³) was added to a toluene solution of [Hf(η-C₇H₇)(η⁵-C₉H₇)] (110 mg, 0.29 mmol) and the mixture was allowed to stand at ambient temperature for 10 min. The solution became orange and orange crystals quickly appeared. The toluene solution was heated to ca. 80 °C and the crystals dissolved. After filtration the hot solution was cooled to -20 °C giving red crystals of [{Hf(η-C₇H₇)(η⁵-C₉H₇)}₂(μ-dmpe)]. Yield 140 mg, > 90%.

Isomers of (η²-Cycloheptatriene)bis(η-cyclopentadienyl)(trimethylphosphine)zirconium, 11a and 11b.—The compound [Zr(η-C₇H₈)(PMe₃)₂Cl₂] (300 mg, 0.74 mmol) and sodium cyclopentadienide (120 mg, 1.4 mmol) were dissolved in thf (20 cm³), and the solution immediately became orange. Removal of solvent under reduced pressure gave orange crystals. These were extracted into toluene–light petroleum (1:9, 30 cm³) and the solution was cooled to -80 °C giving red crystals of [Zr(η⁵-C₅H₅)₂(η²-C₇H₈)(PMe₃)]. Yield 190 mg, 64%.

Isomers of (η²-Cycloheptatriene)bis(η-cyclopentadienyl)(trimethylphosphine)hafnium, 12a and 12b.—The compound [Hf(η-C₇H₈)(PMe₃)₂Cl₂] (1.1 g, 2.2 mmol) and sodium cyclopentadienide (1 g, 12 mmol) were dissolved in thf (40 cm³). The mixture was stirred for 1 h. The solvent was removed under reduced pressure giving orange crystals. These were extracted into toluene (4 × 20 cm³) and the solution was concentrated to 30 cm³ and cooled to -20 °C giving orange crystals of a mixture of isomers of [Hf(η-C₅H₅)₂(η²-C₇H₈)(PMe₃)]. Yield 815 mg, 84%. The component isomers were not separated by recrystallisation from toluene.

[{Zr(η-C₅H₅)(μ-σ:η⁵-C₅H₄)(PMe₃)₂}]₂.—The compound [Zr(η-C₇H₈)(PMe₃)₂Cl₂] (300 mg, 0.74 mmol) and sodium cyclopentadienide powder (120 mg, 1.4 mmol) were mixed, dissolved in thf (20 cm³) and heated at 60 °C for 3 d. Filtration followed by removal of solvent under reduced pressure gave a red crystalline solid. This was extracted into toluene (20 cm³) giving a deep red solution which produced red needles of [{Zr(η⁵-C₅H₅)(μ-σ:η⁵-C₅H₄)(PMe₃)₂}]₂ (30 mg, 14%).

Reaction between Iodotrimethylsilane and [Hf(η-C₅H₅)₂(η²-C₇H₈)(PMe₃)].—Iodotrimethylsilane (~ 0.5 cm³) was added to a toluene solution (30 cm³) of [Hf(η-C₅H₅)₂(η²-C₇H₈)(PMe₃)] (100 mg, 0.25 mmol) and the mixture was stirred for 12 h. The solution was filtered and reduced in volume to ≈ 10 cm³ and cooled to -20 °C giving pale yellow crystals of [Hf(η-C₅H₅)₂I₂] (60 mg, 45%).

Table 4 Data for the crystal structure analysis of compound **1**

Formula	C ₁₃ H ₂₇ Cl ₂ P ₂ Zr
Crystal size/mm	0.2 × 0.1 × 0.3
<i>M</i>	407.4
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	10.521(7)
<i>b</i> /Å	12.689(5)
<i>c</i> /Å	13.645(14)
<i>U</i> /Å ³	1822
<i>Z</i>	4
<i>D</i> _c /g cm ⁻³	1.486
<i>F</i> (000)	836
<i>T</i> /K	190
Scan mode	ω-2θ
Radiation	Mo-Kα (λ = 0.710 69 Å)
Minimum, maximum 2 θ	3–50
μ(Mo-Kα)/cm ⁻¹	10.48
No. of unique data	2043
No. of observations [<i>F</i> > 4σ(<i>F</i>)]	1888
Mean, maximum shift: e.s.d.	0.02, 0.22
Final difference electron density/e Å ⁻³	+0.9, -0.5
<i>R</i>	0.028
<i>R</i> '	0.034

Crystal Structure Determination.—The crystal data and other experimental data are summarised in Table 4. Red crystals of compound **1** were obtained from toluene at -20 °C. A crystal suitable for X-ray diffraction was chosen from a number of similar crystals available. This was mounted in a 0.7 mm Lindemann tube under dry dinitrogen and sealed with a small flame.

Lorentz and polarisation corrections were applied and the data were corrected for the effects of X-ray absorption by an empirical method using Ψ-scan data. The structure was solved using the SHELXTL system of programs¹¹ and all non-

hydrogen atoms located by conventional heavy-atom and Fourier difference methods, with refinement by full-matrix least squares. Except for hydrogen atoms all atoms were refined with anisotropic displacement thermal parameters. Hydrogen atoms were generated in calculated positions (C-H 0.96 Å) with fixed isotropic parameters (1.2 times the *U*_{equiv} of their ligated carbon atom). Weights were calculated according to the expression $w^{-1} = \sigma^2(F_o) + g(F_o^2)$, where *g* = 0.0002.

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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