

Homo- and hetero-binuclear *ansa*-metallocenes of the group 4 transition metals as homogeneous co-catalysts for the polymerisation of ethene and propene

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Abstract

The compounds $[M\{(CH_2)_4C(\eta-C_5H_4)_2\}(\eta-C_5H_5)Cl]$ ($M = Zr^*, Hf$), $[M\{(CH_2)_4C(\eta-C_5H_4)_2\}(\eta-C_5H_5)Me]$ ($M = Zr, Hf$), $[(\eta-C_5H_5)MCl_2\{(CH_2)_4C(\eta-C_5H_4)_2\}MCl_2(\eta-C_5H_5)]$ ($M = Zr, Hf$), $[(\eta-C_5H_5)ZrCl_2\{(\eta-C_5H_5)\}(\eta-C_9H_6)ZrCl_2(\eta-C_5H_5)]$, $[(\eta-C_5H_5)MMe_2\{(CH_2)_4C(\eta-C_5H_4)_2\}MMe_2(\eta-C_5H_5)]$ ($M = Zr, Hf$), $[(\eta-C_5H_5)ZrCl_2\{(CH_2)_4C(\eta-C_5H_4)_2\}HfCl_2(\eta-C_5H_5)]$, $[(\eta-C_5H_5)MCl_2\{(CH_2)_4C(\eta-C_5H_4)_2\}Rh(\eta-C_8H_{12})]$ ($M = Zr^*, Hf$), $[(\eta-C_5H_5)ZrCl_2\{(CH_2)_4C(\eta-C_5H_4)_2\}TiCl_3]$, $[(\eta-C_5H_5)ZrMe_2\{(CH_2)_4C(\eta-C_5H_4)_2\}HfMe_2(\eta-C_5H_5)]$, $[(\eta-C_5H_5)MMe_2\{(CH_2)_4C(\eta-C_5H_4)_2\}Rh(\eta-C_8H_{12})]$ ($M = Zr^*, Hf$) have been prepared and characterised. ^{*} indicates the crystal structure has been determined. Their catalytic properties for ethene and propene polymerisation have been explored. © 1998 Elsevier Science B.V.

1. Introduction

In 1989, Petersen [1] reported the synthesis of homo-binuclear compounds $[(\eta-C_5H_5)ZrCl_2\{X(\eta-C_5H_4)_2\}ZrCl_2(\eta-C_5H_5)]$ ($X = CH_2, SiMe_2$) via the metathesis of $[Li_2\{X(C_5H_4)_2\}]$ with two equivalents of $[Zr(\eta-C_5H_5)Cl_3 \cdot 2THF]$. Since then there have been further reports of *ansa*-bridged homo-binuclear group IV metallocenes e.g. $[TiCl_3\{SiMe_2(\eta-C_5H_4)_2\}TiCl_3]$ [2,3], $[(\eta-C_5H_5)TiCl_2\{SiMe_2(\eta-C_5H_4)_2\}TiCl_2(\eta-C_5H_5)]$ [4], $[(\eta-C_5H_5)MCl_2\{(\eta-C_5H_4)CMe_2(\eta-C_9H_6)\}MCl_2(\eta-C_5H_5)]$ ($M = Zr, Hf$) [5], $[(\eta-C_5R_5)ZrCl_2\{(1,4-C_6H_4)(\eta-$

$Cp)_2\}ZrCl_2(\eta-C_5R_5)]$ ($R = H$ or Me , $Cp' = 3,4$ -dimethylcyclopenta-1,3-diene-1-yl) [6] and $[\{(SiMe_2)(\eta-C_5H_4)_2\}TiCl_2(\eta-C_5H_5)]_2$ [7]. It was decided to prepare new *ansa*-bridged homo-binuclear compounds which incorporated a more rigid backbone. The two ligand precursors $[Li_2\{(CH_2)_4C(C_5H_4)_2\}]$ and $[Li_2\{(CH_2)_4C(C_5H_4)(C_9H_6)\}]$ were used for this purpose, as described below. We hoped the resulting bimetallic metallocenes would act as catalyst systems in which there would be the possibility that two closely located transition metal centres of the metallocenes would show novel co-operative behaviour. For example, there was the possibility that the polymer chain growing at one metal centre would form a γ -agostic (C–H–M) bond at the second metal

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centre. Such an agostic interaction could inhibit β -H elimination at the first centre and thereby restrict termination of the growing polymer chain.

2. Results and discussion

The neutral molecule $[(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_5)_2]$ was prepared as a pale yellow oil from 6,6-tetramethylenefulvene and cyclopentadiene in the presence of sodium hydroxide [8].

Treatment of the dicyclopentadiene compound $[(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_5)_2]$ with $^n\text{BuLi}$ gave a white precipitate of the corresponding dilithium dicyclopentadienide salt $\text{Li}_2[(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)_2]$: the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in THF- d_8 fully supported the expected structure.

The neutral cyclopentadiene-indene molecule $[(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_5)(\text{C}_9\text{H}_7)]$ was prepared as an orange oil by treatment of 6,6-tetramethylenefulvene with lithium indenide in THF in 86% yield. Addition of $^n\text{BuLi}$ gave the dilithium salt $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)\}]$.

Synthesis of yellow microcrystals of $[(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2]\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}$ **1**, in 67% yield, was achieved by mixing equimolar amounts of $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)_2\}]$ and $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ in toluene at room temperature for one day. The hafnium derivative $[(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2]\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}$ **2** was prepared as a pale yellow fine powder in 45% yield in an analogous manner.

The compound **1** and all the other new compounds described in this work were characterised by elemental analysis, ^1H and ^{13}C NMR and mass spectrometry. The data are given in Table 1 and are not further discussed unless the interpretation is not straightforward. Slow diffusion of petroleum ether (b.p. 40–60°C) into a saturated toluene solution of **1** at room temperature over a period of one week yielded yellow crystals, which were twinned. A single crystal suitable for X-ray structure analysis was obtained by breaking the twinned crystals in a sonicator for several minutes. The X-ray crystal

structure of **1** has been determined. The molecular structure is shown in Fig. 1 and selected interatomic distances (Å) and angles (°) are given in Table 2. The compound **1** crystallises in a triclinic lattice with the space group $P 2_1$. The most significant feature of the structure is that all three $(\eta\text{-C}_5\text{H}_5)$ rings are bound in an η^5 fashion. The Zr–C distances vary from 2.507 Å to 2.665 Å. Such a large spread of metal–C distances is often seen in complexes crowded by multiple cyclopentadienyl ligands. The Zr–C and C–C bond distances for compound **1** are shown in Fig. 2, from which it can be seen that the average Zr–C bond lengths of the three rings are similar: the overall mean Zr–C bond length is 2.59 Å, which is longer than that observed in $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (2.49 Å) [9], but is similar to the values reported for $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_3(\eta^1\text{-C}_5\text{H}_5)]$ (2.58 Å) [10], $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_3\text{Cl}]$ (2.58 Å) [11], $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_3]$ (2.58 Å) [12], and the Me_2C -bridged analogue of **1**, namely $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ (2.58 Å) [13]. The Zr–Cl distance is 2.53 Å and is very similar to those in $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_3\text{Cl}]$ (2.53 Å) [11] and $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ (2.54 Å) [13]. The Cp centroid–Zr–Cp centroid angles average 116.4° (Cp = $\eta\text{-C}_5\text{H}_5$) and the Cp centroid–Zr–Cl angles average 101.1°. These angles are similar to those observed for $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_3\text{Cl}]$ (117.3° and 99.4° respectively) [11]. The tetrahedral co-ordination environment of C(1) atom is distorted and the C(4)–C(1)–C(9) angle is 100.2°, which is 9.3° smaller than the value expected for the tetrahedral arrangement (109.5°). The C(1)–C(4)–Cp(1) centroid angle is 165.53°. The structure suggests that the Cp(1) and Cp(2) rings are forced to be canted in order to accommodate the three cyclopentadienyl rings.

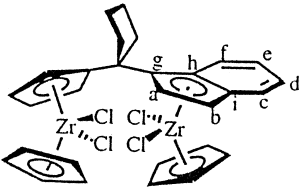
The electronic structure of compound **1** may be considered to be essentially the same as for $[\text{M}(\eta\text{-C}_5\text{H}_5)_3\text{X}]$, in which two electrons are located in the non-bonding orbital of symmetry a_2 [14].

Treatment of **1** in THF with an excess of MeMgCl gave white crystals of $[\text{Zr}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_5)_2\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$.

Table 1
Characterising data for compounds 1–16

| Compound ^a | NMR data ^b |
|---|--|
| 1 yellow, C 61.2 (61.9), H 5.45 (5.45), Cl 10.0 (9.1) | ¹ H ^c : 5.97 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.83 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.72 (5H, s, C ₅ H ₅), 5.36 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.20 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 1.95 (2H, <i>t</i> , $J_{\text{HH}} = 7$, CH ₂), 1.88 (2H, <i>t</i> , $J_{\text{HH}} = 7$, CH ₂), 1.54 (2H, m, CH ₂), 1.44 (2H, m, CH ₂). ¹³ C ^c : 146.21 (s, bridgehead C), 122.67 (s, C ₅ H ₄), 115.33 (s, C ₅ H ₅), 112.30 (s, C ₅ H ₄), 111.17 (s, C ₅ H ₄), 93.37 (s, C ₅ H ₄), 48.03 (s, C), 35.24 (s, CH ₂), 34.95 (s, CH ₂), 23.82 (s, CH ₂). |
| 2 pale yellow, C 50.4 (50.5), H 4.3 (4.45), Cl 7.55 (7.5) | ¹ H ^c : 5.90 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.78 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.63 (s, 5H, C ₅ H ₅), 5.49 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.13 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 1.97 (2H, <i>t</i> , $J_{\text{HH}} = 7$, CH ₂), 1.89 (2H, <i>t</i> , $J_{\text{HH}} = 7$, CH ₂), 1.56 (2H, m, CH ₂), 1.47 (2H, m, CH ₂). ¹³ C ^d : 139.35 (s, bridgehead C), 124.38 (s, C ₅ H ₄), 122.75 (s, C ₅ H ₄), 117.75 (s, C ₅ H ₄), 116.36 (s, C ₅ H ₅), 112.18 (s, C ₅ H ₄), 51.56 (s, C), 39.07 (s, CH ₂), 24.97 (s, CH ₂). |
| 3 white, C 68.1 (68.6), H 6.9 (6.6) | ¹ H ^c : 5.54 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.42 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.39 (5H, s, C ₅ H ₅), 5.22 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.02 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 2.00 (2H, <i>t</i> , $J_{\text{HH}} = 7$, CH ₂), 1.83 (2H, <i>t</i> , $J_{\text{HH}} = 7$, CH ₂), 1.58 (2H, m, CH ₂), 1.50 (2H, m, CH ₂), 0.58 (3H, s, CH ₃). ¹³ C ^c : 139.51 (s, bridgehead C), 117.19 (s, C ₅ H ₄), 111.26 (s, C ₅ H ₅), 107.45 (s, C ₅ H ₄), 107.25 (s, C ₅ H ₄), 91.48 (s, C ₅ H ₄), 47.52 (s, bridgehead C), 35.12 (s, CH ₂), 34.89 (s, CH ₂), 23.76 (s, CH ₂), 11.60 (s, Zr–CH ₃). |
| 4 white, C 54.9 (55.45), H 5.4 (5.3) | ¹ H ^c : 5.53 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.37 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.36 (5H, s, C ₅ H ₅), 5.23 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.01 (2H, pseudo <i>q</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 2.02 (2H, <i>t</i> , $J_{\text{HH}} = 7$, CH ₂), 1.82 (2H, <i>t</i> , $J_{\text{HH}} = 7$, CH ₂), 1.59 (2H, m, CH ₂), 1.50 (2H, m, CH ₂), 0.56 (3H, s, CH ₃). ¹³ C ^c : 138.97 (s, bridgehead C), 117.33 (s, C ₅ H ₄), 110.54 (s, C ₅ H ₅), 106.94 (s, C ₅ H ₄), 106.33 (s, C ₅ H ₄), 89.68 (s, C ₅ H ₄), 47.35 (s, bridgehead C), 35.34 (s, CH ₂), 35.12 (s, CH ₂), 23.75 (s, CH ₂), 13.04 (s, Hf–CH ₃). |
| 5 white, C 45.8 (46.1), H 4.0 (4.0), Cl 22.3 (21.8) | ¹ H ^c : 6.05 (4H, pseudo <i>t</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.88 (10H, s, C ₅ H ₅), 5.70 (4H, pseudo <i>t</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 2.61 (4H, m, CH ₂), 1.67 (4H, m, CH ₂). ¹³ C ^d : 142.68 (s, bridgehead C), 116.42 (s, C ₅ H ₅), 115.77 (s, C ₅ H ₄), 114.01 (s, C ₅ H ₄), 50.94 (s, bridgehead C), 39.09 (s, CH ₂), 25.02 (s, CH ₂). |
| 6 white, C 37.0 (36.4), H 3.2 (3.2), Cl 17.5 (17.2) | ¹ H ^c : 5.96 (4H, pseudo <i>t</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 5.60 (10H, s, C ₅ H ₅), 5.63 (4H, pseudo <i>t</i> , $J_{\text{HH}} = 3$, C ₅ H ₄), 2.58 (4H, m, CH ₂), 1.66 (4H, m, CH ₂). ¹³ C ^d : 140.68 (s, bridgehead C), 115.01 (s, C ₅ H ₅), 114.35 (s, C ₅ H ₄), 112.74 (s, C ₅ H ₄), 50.69 (s, bridgehead C), 39.05 (s, CH ₂), 25.04 (s, CH ₂). |

Table 1 (continued)

| Compound ^a | NMR data ^b |
|---|--|
| 7 yellow, C 49.35 (49.7), H 4.1 (4.0), Cl 20.2 (20.2)  | ¹ H ^d : 7.92(1H, d, <i>J</i> _{HH} = 8, H _f), 7.61(1H, d, <i>J</i> _{HH} = 8, H _c), 7.35 (1H, m, H _e), 7.29 (1H, m, H _d), 6.85 (1H, d, <i>J</i> _{HH} = 3, H _a), 6.68 (1H, d, <i>J</i> _{HH} = 3, H _b), 6.56 (1H, pseudo <i>q</i> , <i>J</i> _{HH} = 3, C ₅ H ₄), 6.34 (1H, pseudo <i>q</i> , <i>J</i> _{HH} = 3, C ₅ H ₄), 6.30 (2H, m, C ₅ H ₄), 6.14 [5H, s, Cp'Zr(C ₅ H ₅)], 6.07 [5H, s, Ind'Zr(C ₅ H ₅)], 3.15 (1H, m, CH ₂), 2.79 (1H, m, CH ₂), 2.63 (1H, m, CH ₂), 2.44 (1H, m, CH ₂), 1.86 (1H, m, CH ₂), 1.76 (2H, m, CH ₂), 1.63 (1H, m, CH ₂). ¹³ C ^d : 143.04 [s, C _{ipso} (C ₅ H ₄)], 126.28 (s, C _c), 126.16 (s, C _e), 125.86 (s, C _f), 125.41 (s, C _d), 124.05 (s, C _a), 116.82 [s, Ind'Zr(C ₅ H ₅)], 116.26 [s, Cp'Zr(C ₅ H ₅)], 116.00 (s, C ₅ H ₄), 115.35 (s, C ₅ H ₄), 115.02 (s, C ₅ H ₄), 114.27 (s, C ₅ H ₄), 99.37 (s, C _b), 51.63 [s, C(CH ₂) ₄], 39.27 (s, CH ₂), 39.14 (s, CH ₂), 25.42 (s, CH ₂), 24.56 (s, CH ₂). |
| 8 white, C 60.8 (61.2), H 6.7 (6.7) | ¹ H ^c : 5.77 (10H, s, C ₅ H ₅), 5.67 (8H, m, C ₅ H ₄), 1.98 (4H, m, CH ₂), 1.64 (4H, m, CH ₂), -0.01 (12H, s, CH ₃). ¹³ C ^c : 110.95 (s, C ₅ H ₅), 110.16 (s, C ₅ H ₄), 108.55 (s, C ₅ H ₄), 40.08 (s, CH ₂), 24.67 (s, CH ₂), 31.46 (s, Zr-CH ₃). |
| 9 white, C 47.0 (46.8), H 5.23 (5.15) | ¹ H ^c : 5.69 (10H, s, C ₅ H ₅), 5.60 (8H, m, C ₅ H ₄), 2.00 (4H, m, CH ₂), 1.64 (4H, m, CH ₂), -0.20 (12H, s, CH ₃). ¹³ C ^c : 136.72 (s, bridgehead C), 110.41 (s, C ₅ H ₅), 109.41 (s, C ₅ H ₄), 108.36 (s, C ₅ H ₄), 49.57 (s, bridgehead C), 39.94 (s, CH ₂), 24.89 (s, CH ₂), 37.55 (s, Hf-CH ₃). |
| 10 white, C 40.8 (40.7), H 3.7 (3.55), Cl 19.4 (19.2) | ¹ H ^c : 6.05 (2H, pseudo <i>t</i> , <i>J</i> _{HH} = 3, C ₅ H ₄), 5.96 (2H, pseudo <i>t</i> , <i>J</i> _{HH} = 3, C ₅ H ₄), 5.88 (5H, s, C ₅ H ₅), 5.60 (5H, s, C ₅ H ₅), 5.70 (2H, pseudo <i>t</i> , <i>J</i> _{HH} = 3, C ₅ H ₄), 5.63 (2H, pseudo <i>t</i> , <i>J</i> _{HH} = 3, C ₅ H ₄), 2.60 (4H, m, CH ₂), 1.67 (4H, m, CH ₂). ¹³ C ^d : 143.06 (s, bridgehead C), 140.68 (s, bridgehead C), 116.45 (s, C ₅ H ₅), 115.00 (s, C ₅ H ₅), 115.70 (s, C ₅ H ₄), 114.38 (s, C ₅ H ₄), 114.09 (s, C ₅ H ₄), 112.73 (s, C ₅ H ₄), 50.61 (s, C), 39.07 (s, CH ₂), 25.03 (s, CH ₂). |
| 11 white, C 53.0 (53.1), H 5.5 (5.8) | ¹ H ^c : 5.77 (5H, s, C ₅ H ₅), 5.68 (5H, s, C ₅ H ₅), 5.66 (4H, m, C ₅ H ₄), 5.60 (4H, m, C ₅ H ₄), 1.98 (4H, m, CH ₂), 1.64 (4H, m, CH ₂), -0.01 (6H, s, CH ₃), -0.20 (6H, s, CH ₃). ¹³ C ^c : 138.05 (s, bridgehead C), 136.77 (s, bridgehead C), 110.95 (s, C ₅ H ₅), 110.39 (s, C ₅ H ₅), 110.10 (s, C ₅ H ₄), 109.42 (s, C ₅ H ₄), 108.63 (s, C ₅ H ₄), 108.33 (s, C ₅ H ₄), 49.63 (s, bridgehead C), 40.04 (s, CH ₂), 24.68 |

- 12** yellow, C 53.4 (53.0), H 5.2 (5.3), Cl 12.3 (11.2) $^1\text{H}^c$: 6.03 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.94 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.91 (5H, s, C_5H_5), 4.90 (2H, pseudo *t*, $J_{\text{HH}} = 2$, C_5H_4), 4.72 (2H, pseudo *t*, $J_{\text{HH}} = 2$, C_5H_4), 3.94 (4H, b, CH = CH in COD), 2.46 (2H, m, CH_2 in bridge), 2.19 (4H, m, CH_2 in COD), 2.15 (2H, m, CH_2 in bridge), 1.94 (4H, m, CH_2 in COD), 1.77 (2H, m, CH_2 in bridge), 1.62 (2H, m, CH_2 in bridge). $^{13}\text{C}^c$: 142.77 (s, bridgehead C), 120.16 (s, bridgehead C), 116.18 (s, C_5H_5), 115.72 (s, C_5H_4), 113.49 (s, C_5H_4), 86.96 (s, C_5H_4), 85.67 (s, C_5H_4), 63.98 (d, $J_{\text{CRh}} = 14$, CH in COD), 48.84 (s, bridgehead C), 41.68 (s, CH_2 in bridge), 32.70 (s, CH_2 in COD), 25.32 (s, CH_2 in bridge).
- 13** yellow, C 46.7 (46.6), H 4.5 (4.6), Cl 9.6 (9.8) $^1\text{H}^c$: 6.01 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.96 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.86 (5H, s, C_5H_5), 4.91 (2H, pseudo *t*, $J_{\text{HH}} = 2$, C_5H_4), 4.73 (2H, pseudo *t*, $J_{\text{HH}} = 2$, C_5H_4), 3.95 (4H, b, CH = CH in COD), 2.45 (2H, m, CH_2 in bridge), 2.21 (4H, m, CH_2 in COD), 2.11 (2H, m, CH_2 in bridge), 1.94 (4H, m, CH_2 in COD), 1.78 (2H, m, CH_2 in bridge), 1.61 (2H, m, CH_2 in bridge). $^{13}\text{C}^c$: 142.12 (s, bridgehead C), 120.18 (s, bridgehead C), 114.82 (s, C_5H_5), 114.19 (s, C_5H_4), 112.47 (s, C_5H_4), 86.96 (s, C_5H_4), 85.67 (s, C_5H_4), 63.97 (d, $J_{\text{CRh}} = 14$, CH in COD), 48.71 (s, bridgehead C), 41.76 (s, CH_2 in bridge), 32.72 (s, CH_2 in COD), 25.33 (s, CH_2 in bridge).
- 14** yellow–brown, C 41.9 (41.6), H 3.65 (3.7), Cl 29.9 (30.7) $^1\text{H}^c$: 6.33 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 6.04 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.83 (5H, s, C_5H_5), 5.99 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.57 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 2.70 (2H, m, CH_2), 2.36 (2H, m, CH_2), 1.63 (2H, m, CH_2), 1.48 (2H, m, CH_2). $^{13}\text{C}^d$: 153.62 (s, bridgehead C), 139.35 (s, bridgehead C), 124.38 (s, C_5H_4), 122.76 (s, C_5H_4), 116.36 (s, C_5H_5), 117.75 (s, C_5H_4), 112.18 (s, C_5H_4), 51.56 (s, bridgehead C), 39.07 (s, CH_2), 24.96 (s, CH_2).
- 15** yellow, C 60.4 (60.7), H 6.5 (6.6) $^1\text{H}^c$: 5.78 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.73 (2H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.75 (5H, s, C_5H_5), 4.90 (2H, pseudo *t*, $J_{\text{HH}} = 2$, C_5H_4), 4.53 (2H, pseudo *t*, $J_{\text{HH}} = 2$, C_5H_4), 3.93 (4H, b, CH = CH in COD), 2.22 (6H, m, CH_2 in bridge and COD), 2.15 (2H, m, CH_2 in bridge), 1.95 (4H, m, CH_2 in COD), 1.82, (2H, m, CH_2 in bridge), 1.80 (2H, m, CH_2 in bridge), 0.00 (6H, s, CH_3). $^{13}\text{C}^c$: 138.48 (s, bridgehead C), 120.93 (s, bridgehead C), 110.98 (s, C_5H_5), 110.39 (s, C_5H_4), 107.97 (s, C_5H_4), 86.31 (s, C_5H_4), 85.45 (s, C_5H_4), 63.69 (d, $J_{\text{CRh}} = 14$, CH in COD), 48.35 (s, bridgehead C), 42.02 (s, CH_2 in bridge), 32.76 (s, CH_2 in COD), 30.85 (s, Zr– CH_3), 25.41 (s, CH_2 in bridge).
- 16** yellow, C 52.5 (52.9), H 5.8 (5.78) $^1\text{H}^c$: 5.68 (4H, pseudo *t*, $J_{\text{HH}} = 3$, C_5H_4), 5.66 (5H, s, C_5H_5), 4.90 (2H, pseudo *t*, $J_{\text{HH}} = 2$, C_5H_4), 4.54 (2H, pseudo *t*, $J_{\text{HH}} = 2$, C_5H_4), 3.93 (4H, b, CH = CH in COD), 2.22 (6H, m, CH_2 in bridge and COD), 2.13 (2H, m, CH_2 in bridge), 1.94 (4H, m, CH_2 in COD), 1.82 (2H, m, CH_2 in bridge), 1.77 (2H, m, CH_2 in bridge), –0.20 (6H, s, CH_3). $^{13}\text{C}^c$: 136.99 (s, bridgehead C), 120.87 (s, bridgehead C), 110.47 (s, C_5H_5), 109.68 (s, C_5H_4), 107.85 (s, C_5H_4), 86.42 (s, C_5H_4), 85.51 (s, C_5H_4), 63.75 (d, $J_{\text{CRh}} = 14$, CH in COD), 48.30 (s, bridgehead C), 42.08 (s, CH_2 in bridge), 37.04 (s, Hf– CH_3), 32.80 (s, CH_2 in COD), 25.45 (s, CH_2 in bridge).

^aAnalytical data given as: found (calculated) %.^bAll NMR chemical shifts are quoted in δ (ppm) and coupling constants are given in Hz. ^1H NMR at 300 MHz, ^{13}C at 75.5 MHz.^cIn C_6D_6 .^dIn CD_2Cl_2 .

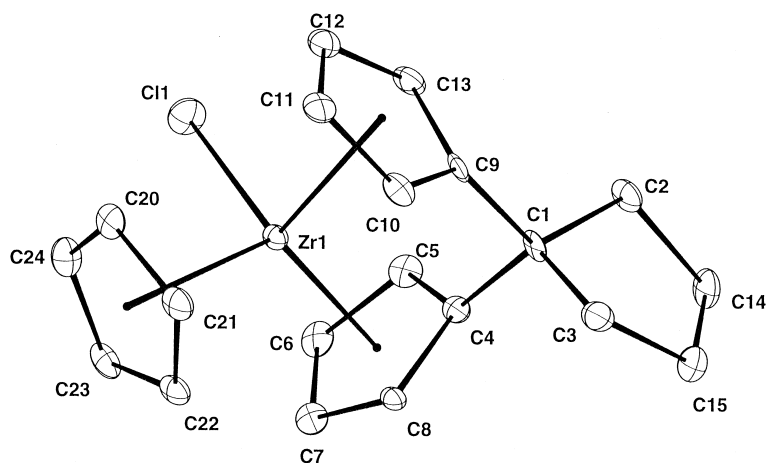


Fig. 1. The molecular structure of $[\text{Zr}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ **1**.

$\text{C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Me}]$ **3** in 65% yield. The hafnium analogue $[\text{Hf}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Me}]$ **4** was prepared similarly, in 53% yield. The compounds **3** and **4** are air- and moisture-sensitive white crystalline solids.

A mixture of $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)_2\}]$ and two equivalents of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ were refluxed in toluene to give white $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ **5** in 65% yield. The hafnium analogue $[(\eta\text{-C}_5\text{H}_5)\text{HfCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ **6** was prepared similarly in 41% yield. Treatment of $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ **5** in THF (-78°C) with an excess of MeMgCl gave the air-sensitive white microcrystalline tetramethyl derivative $[(\eta\text{-C}_5\text{H}_5)\text{ZrMe}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{ZrMe}_2$

$(\eta\text{-C}_5\text{H}_5)]$ **8** in 57% yield. White needle-like microcrystals of $[(\eta\text{-C}_5\text{H}_5)\text{HfMe}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfMe}_2(\eta\text{-C}_5\text{H}_5)]$ **9** were obtained similarly, in 56% yield.

It was decided to make a chiral binuclear complex bridged using the ligand $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)\}]$. One equivalent of $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)\}]$ and two equivalents of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ were refluxed in toluene to give the yellow crystalline compound $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)(\eta\text{-C}_9\text{H}_6)\}\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ **7** in 36% yield. Compound **7** was characterised by ^1H and ^{13}C NMR spectroscopies including a $^{13}\text{C}-^1\text{H}$ correlation experiment.

An equimolar mixture of $[\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ **1** and $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ in toluene was refluxed for two days to afford an air-sensitive white powder of $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ **10**.

In the low field region of the ^1H NMR spectrum of **10** the C_5H_4 and C_5H_5 resonances occur at identical chemical shifts to those corresponding signals for the compounds $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ **5** and $[(\eta\text{-C}_5\text{H}_5)\text{HfCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ **6**, but with only half the intensities of the latter. This indicates that the chemical environments around the zirconium and

Table 2

Selected interatomic distances (Å) and angles ($^\circ$) for compound **1**

| Bond | Length (Å) | Bond | Angle ($^\circ$) |
|--------------------|------------|-------------------|--------------------|
| Zr(1)–Cl(1) | 2.533(2) | Cp(1)–Zr(1)–Cp(2) | 110.79 |
| Zr(1)–Cp(1) | 2.2933 | Cp(1)–Zr(1)–Cp(3) | 118.94 |
| Zr(1)–Cp(2) | 2.2889 | Cp(2)–Zr(1)–Cp(3) | 119.33 |
| Zr(1)–Cp(3) | 2.2936 | Cl(1)–Zr(1)–Cp(1) | 101.70 |
| Zr(1)–C(4–8)mean | 2.5918 | Cl(1)–Zr(1)–Cp(2) | 100.99 |
| Zr(1)–C(9–13)mean | 2.5846 | Cl(1)–Zr(1)–Cp(3) | 100.73 |
| Zr(1)–C(20–24)mean | 2.5906 | C(1)–C(4)–Cp(1) | 165.65 |
| | | C(4)–C(1)–C(9) | 101.1(5) |

Cp(1), Cp(2) and Cp(3) denote the centroids of the C(4–8), C(9–13) and C(20–24) rings.

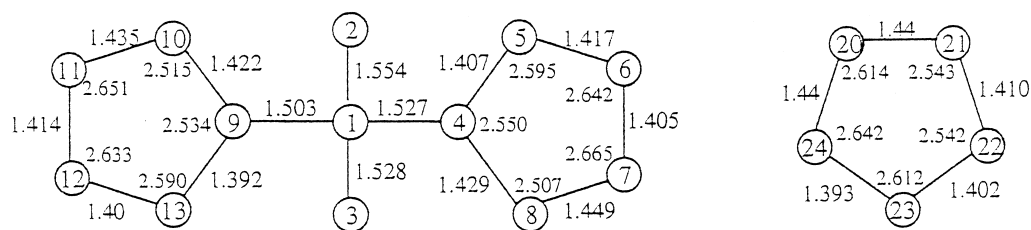


Fig. 2. Selected bond lengths for compound **1**. Numerals beside carbon atoms (inside rings) give Zr–C distances, figures beside the bond lines give C–C distances.

hafnium centres in compound **10** closely resemble those in **5** and **6**, respectively. Similar behaviour was found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10**.

A solution of hetero-binuclear compound $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ **10** in THF (-78°C) was treated with an excess of MeMgCl at 0°C , to form fine white, air sensitive needle crystals of $[(\eta\text{-C}_5\text{H}_5)\text{ZrMe}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfMe}_2(\eta\text{-C}_5\text{H}_5)]$ **11** in 39% yield.

The ^1H NMR spectrum of **11** shows only two resonances at 5.66 and 5.60 ppm for all 8 protons of the C_5H_4 rings, rather than four signals observed in compound **10**, and this is presumed to arise from overlap of resonances. The C_5H_4 and C_5H_5 resonances of **11** occur at

almost identical chemical shifts to the corresponding bands for compounds **8** and **9**, but with only half the intensities of the latter signals. This implies that the chemical environment around the zirconium and hafnium centres is the same in compound **11** as in compound **8** and **9**. Similarly the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **11** in C_6D_6 is closely related to those of compounds **8** and **9**.

Previously, Nifant'ev [4] reported the synthesis of $[(\eta\text{-C}_5\text{H}_5)\text{MCl}_2\{\text{Me}_2\text{Si}(\eta\text{-C}_5\text{H}_4)_2\}\text{Rh}(\eta^4\text{-C}_8\text{H}_{12})]$ ($\text{M} = \text{Zr}, \text{Ti}$) from the reaction between the complex $[(\eta\text{-C}_5\text{H}_5)\text{MCl}_2\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta^1\text{-C}_5\text{H}_4)\text{SnClIME}_2\}]$ and the cycloocta-1,5-diene (COD) derivative $[\text{RhCl}(\eta\text{-C}_8\text{H}_{12})]_2$. We have carried out the reaction between $[\text{RhCl}(\eta\text{-C}_8\text{H}_{12})]_2$ and $[(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ to form compound **12**.

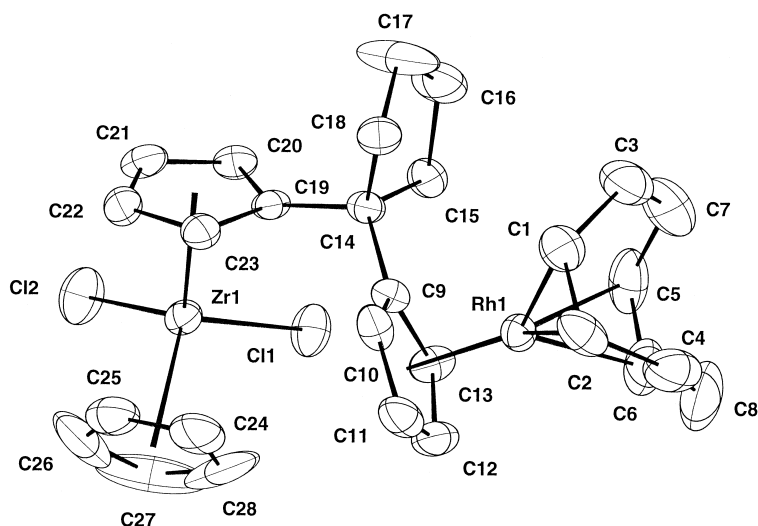


Fig. 3. The molecular structure of $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Rh}(\eta\text{-C}_8\text{H}_{12})]$ **12**.

Table 3
Selected interatomic distance (Å) and angles (°) for compound **12**

| Bond | Length (Å) | Bond | Angle (°) |
|-------------|------------|-------------------|-----------|
| Rh(1)–C(1) | 2.121(5) | C(1)–Rh(1)–C(2) | 38.5(2) |
| Rh(1)–C(9) | 2.294(5) | C(1)–Rh(1)–C(6) | 94.6(3) |
| Rh(1)–Cp(3) | 1.9105 | C(2)–Rh(1)–C(6) | 80.8(3) |
| Zr(1)–Cl(1) | 2.438(1) | C(2)–Rh(1)–C(5) | 91.7(2) |
| Zr(1)–C(19) | 2.575(4) | Cl(1)–Zr(1)–Cl(2) | 95.12(5) |
| Zr(1)–C(24) | 2.473(5) | Cp(1)–Zr(1)–Cp(2) | 129.29 |
| Zr(1)–Cp(1) | 2.2038 | C(9)–C(14)–C(19) | 110.8(4) |
| Zr(1)–Cp(2) | 2.2179 | C(1)–C(2)–C(4) | 124.1(6) |
| C(1)–C(2) | 1.399(8) | C(2)–C(4)–C(8) | 114.3(6) |
| C(9)–C(14) | 1.526(6) | C(4)–C(8)–C(6) | 115.1(7) |
| C(14)–C(19) | 1.527(7) | C(5)–C(6)–C(8) | 124.2(7) |

Cp(1), Cp(2), Cp(3) denote the centroids of the C(24–28), C(19–23) and (9–13) rings.

$C_5H_4)_2Zr(\eta-C_5H_5)Cl$ **1** and this gave yellow crystalline $[(\eta-C_5H_5)ZrCl_2\{(CH_2)_4C(\eta-C_5H_4)_2\}Rh(\eta-C_8H_{12})]$ **12** in 77% yield. Similarly, $[\{(CH_2)_4C(\eta-C_5H_4)_2\}Hf(\eta-C_5H_5)Cl]$ **2** was reacted with $[RhCl(\eta-C_8H_{12})_2]$ to give $[(\eta-C_5H_5)HfCl_2\{(CH_2)_4C(\eta-C_5H_4)_2\}Rh(\eta-C_8H_{12})]$ **13** in 72% yield.

Yellow crystals of **12** suitable for structure determination by X-ray diffraction were grown by slow diffusion of petroleum ether (b.p. 40–

60°C) into a saturated toluene solution of $[(\eta-C_5H_5)ZrCl_2\{(CH_2)_4C(\eta-C_5H_4)_2\}Rh(\eta-C_8H_{12})]$ **12** at room temperature over a period of two weeks. The molecular structure is shown in Fig. 3 and selected interatomic distance (Å) and angles (°) are given in Table 3. The compound **12** crystallises in a monoclinic crystal system with the space group $P 2_1/n$. The ring centroid–Zr–centroid and Cl–Zr–Cl angles are 129.29° and 95.12°, respectively, which are in good agreement to 126.6° and 97.1°, found for $[Zr(\eta-C_5H_5)_2Cl_2]$ [9]. The mean C–C bond length is 1.44 Å which is identical to that of $[Zr(\eta-C_5H_5)_2Cl_2]$ [9]. The coordination environment about the Rh centre is analogous to that of compound $[Rh(\eta-C_5H_5)(\eta-C_8H_{12})]$ [15]. The rhodium atom lies 1.91 Å from the mean plane of the cyclopentadienyl ring, which is same length found for $[Rh(\eta-C_5H_5)(\eta-C_8H_{12})]$ [15]. The cyclopentadienyl ring of the bridging $[(CH_2)_4C(\eta-C_5H_4)_2]^{2-}$ ligand has rotated slightly about the C–C (bridgehead) bond. This reflects the steric hindrance of the bulky $\eta-C_8H_{12}$ ligand. The $[(\eta-C_5H_5)ZrCl_2]$ and $[Rh(\eta-C_8H_{12})]$ fragments are located approximately on the opposite C_5H_4 faces of the bridging ligand,

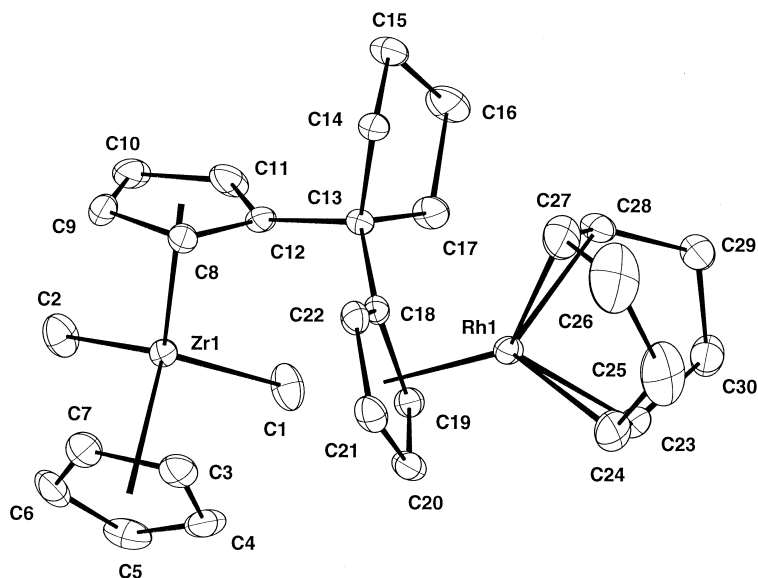


Fig. 4. The molecular structure of $[(\eta-C_5H_5)ZrMe_2\{(CH_2)_4C(\eta-C_5H_4)_2\}Rh(\eta-C_8H_{12})]$ **15**.

Table 4
Selected interatomic distances (Å) and angles (°) for compound **15**

| Bond | Length (Å) | Bond ^a | Angle (°) |
|-------------|------------|-------------------|-----------|
| Rh(1)–C(18) | 2.320(2) | C(23)–Rh(1)–C(24) | 38.8(1) |
| Rh(1)–C(20) | 2.203(2) | C(23)–Rh(1)–C(27) | 97.5(1) |
| Rh(1)–C(23) | 2.119(2) | C(24)–Rh(1)–C(27) | 82.1(1) |
| Rh(1)–Cp(3) | 1.918 | C(24)–Rh(1)–C(28) | 89.9(1) |
| Zr(1)–C(1) | 2.274(2) | C(23)–Rh(1)–Cp(3) | 131.02 |
| Zr(1)–C(2) | 2.280(2) | C(28)–Rh(1)–Cp(3) | 137.93 |
| Zr(1)–C(3) | 2.493(2) | C(1)–Zr(1)–C(2) | 96.37(9) |
| Zr(1)–C(4) | 2.533(2) | C(1)–Zr(1)–Cp(1) | 104.65 |
| Zr(1)–C(8) | 2.517(2) | C(1)–Zr(1)–Cp(2) | 108.09 |
| Zr(1)–C(12) | 2.592(2) | Cp(1)–Zr(1)–Cp(2) | 131.53 |
| Zr(1)–Cp(1) | 2.220 | C(12)–C(13)–C(18) | 110.6(2) |
| Zr(1)–Cp(2) | 2.231 | C(23)–C(24)–C(25) | 122.8(2) |
| C(12)–C(13) | 1.529(3) | C(24)–C(25)–C(26) | 111.8(2) |
| C(13)–C(18) | 1.510(3) | C(25)–C(26)–C(27) | 112.9(2) |
| C(23)–C(24) | 1.407(4) | C(26)–C(27)–C(28) | 124.4(3) |
| C(24)–C(25) | 1.528(4) | dihedral angle | |
| C(25)–C(26) | 1.527(6) | C(3–7)/C(8–12) | 128.52 |

^aCp(1), Cp(2) and Cp(3) denote the centroids of the C(3–7), C(8–12) and C(18–22) rings.

and in consequence there is a large Zr...Rh separation.

The ¹H NMR spectrum of **12** was assigned with the aid of a ¹³C–¹H heteronuclear shift correlation spectrum. The ¹H NMR spectrum of compound **13** shows a striking resemblance to that of compound **12** and so the peaks occurring at 6.01 and 5.96 ppm are assigned to the C₅H₄ ligand bound to Hf, and the peaks at 4.91 and 4.73 ppm to the C₅H₄ ligand bound to Rh. The ¹³C{¹H} NMR spectrum is also very similar to

that of compound **12** and the NMR data strongly imply that these zirconium and hafnium derivatives possess very similar configurations.

A suspension of [(CH₂)₄C(η-C₅H₄)₂]Zr(η-C₅H₅)Cl] **1** in toluene was treated dropwise with TiCl₄ to yield yellow [(η-C₅H₅)ZrCl₂{(CH₂)₄C(η-C₅H₄)₂}TiCl₃] **14** in 70% yield.

The dimethyl derivatives of **12** and **13**, namely [(η-C₅H₅)MMe₂{(CH₂)₄C(η-C₅H₄)₂}Rh(η-C₈H₁₂)] (M = Zr, **15**; M = Hf, **16**) were prepared by treatment of these compounds with MeMgCl. Yellow crystals of **15** suitable for structure determination by X-ray diffraction were grown by slowly cooling a pentane solution of [(η-C₅H₅)ZrMe₂{(CH₂)₄C(η-C₅H₄)₂}Rh(η-C₈H₁₂)] **15** to –20°C. The molecular structure is shown in Fig. 4; selected inter atomic distances (Å) and angles (°) are given in Table 4. The compound **15** crystallises in a monoclinic crystal system with P 2₁/c space group. Comparison with the structure of its dichloride derivative, [(η-C₅H₅)ZrCl₂{(CH₂)₄C(η-C₅H₄)₂}Rh(η-C₈H₁₂)] **12**, reveals that both compounds have very similar configurations. The geometry of compound **15** also has a long Zr...Rh separation with the (C₅H₅)ZrMe₂ and Rh(η-C₈H₁₂) units oriented in distorted *trans* positions. The mean Zr–C (Me) bond length is 2.28 Å which is the same as that observed in [Zr(η-C₅H₅)₂Me₂] [16]. Selected bond lengths and angles for compounds **12** and **15** are given in Table 5, and are com-

Table 5
Selected bond lengths (Å) and angles (°) for the compounds [(η-C₅H₅)ZrL₂{(CH₂)₄C(η-C₅H₄)₂}Rh(η-C₈H₁₂)], L = Cl, **12**, and L = Me, **15**

| Compounds ^a L | [(η-Cp)ZrL ₂ {(CH ₂) ₄ C(η-C ₅ H ₄) ₂ }Rh(η-C ₈ H ₁₂)] | | [(η-Cp) ₂ ZrL ₂] | |
|-----------------------------|---|--------|---|---------|
| | Cl | Me | Cl [9] | Me [16] |
| Zr–L | 2.44 | 2.28 | 2.44 | 2.28 |
| Zr–C _{mean} | 2.50 | 2.53 | 2.49 | 2.52 |
| Zr–Cp _{mean} | 2.21 | 2.23 | 2.19 | 2.23 |
| Rh–Cp ^b | 1.91 | 1.92 | | |
| L–Zr–L | 95.12 | 96.37 | 97.1 | 95.6 |
| Cp–Zr–Cp | 129.29 | 131.53 | 126.6 | 132.5 |
| δ ^c | 110.8 | 110.6 | | |

^aη-Cp refers to η-C₅H₅.

^bFor [Rh(η-Cp)(η-C₈H₁₂)], Rh–Cp is 1.91 Å [15].

^cδ denotes the angle of bridgehead C–bridge C–bridgehead C.

pared with those of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$, $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Me}_2]$ and $[(\eta\text{-C}_5\text{H}_5)\text{Rh}(\eta\text{-C}_8\text{H}_{12})]$.

We have explored a selection of the mononuclear and binuclear group IV metallocenes **1**, **2**, **5–7**, **10**, **12**, **13** and **14** as catalysts for the polymerisation of ethene and propene, in the presence of MAO as a cocatalyst. Kaminsky [17] reported the polymerisation of ethene and propene by eleven different zirconocene and hafnocene catalysts with MAO cocatalyst, under a standard set of polymerisation conditions (2 bar monomer pressure, 30°C, toluene solvent). It was, therefore, decided to follow Kaminsky's procedure [17] as closely as possible in this study.

A preliminary test showed that some of the metallocenes described above have very low activities under the conditions used by Kaminsky [17]. In order to produce sufficient quantities of polymer for characterisation it was decided to keep the same temperature, pressure, solvent volume and amount of catalyst, but to use three times more MAO in the ethene polymerisation studies, (6.25×10^{-6} mol of overall metal and 0.9 g of MAO) since the catalytic activity increases with increasing Al/M ratio [6,18–20].

The results of ethene polymerisation are given in Table 6. When comparing the activities of

binuclear compounds with the mononuclear compounds, one should bear in mind that the activities are quoted as per mole of metal. This means that in the experiments with the binuclear compounds, half the number of moles of compound and same amount of MAO were used, so that the aluminium/metal molar ratio is the same for each experiment (2500/1). All of the catalyst systems in Table 6 remained active throughout the duration of the experiment. It is apparent from Table 6 that all the compounds studied (including mononuclear and binuclear compounds) show somewhat lower activities than the related $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (M = Zr, Hf) under the same conditions. For the mononuclear compounds **1** and **2**, the lower activities may arise in part from a greater steric crowding than for the compounds $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (M = Zr, Hf). The binuclear compounds **5**, **6** and **10**, also show lower activities than the compounds $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (M = Zr, Hf) under similar conditions. The lower activities of the binuclear compounds may reflect the steric factors such as an interactions between the metal sites. For example, atoms or groups may undergo exchange between metal centres, or bridging systems may form. Several binuclear zirconocene compounds with bridging methyl or hydride groups have been reported [1,21–24].

Table 6
Results of ethylene polymerisation^a

| Compound | M | M [*] | Time (min) | Yield (g) | Activity ^b (g PE/mol M h) | T _m (°C) | M _n (×10 ⁻⁵) | M _w /M _n |
|--|----|----------------|------------|-----------|--------------------------------------|---------------------|-------------------------------------|--------------------------------|
| 1 | Zr | | 60 | 3.51 | 5.62×10^5 | 137.0 | 2.61 | 3.93 |
| 2 | Hf | | 180 | 1.59 | 8.49×10^4 | 136.9 | 2.96 | 7.30 |
| 5 | Zr | Zr | 30 | 1.43 | 4.58×10^5 | 137.2 | 3.22 | 5.40 |
| 6 | Hf | Hf | 240 | 0.46 | 1.84×10^4 | 138.9 | 2.14 | 9.87 |
| 7 | Zr | Zr | 20 | 1.94 | 9.29×10^5 | 136.0 | 2.25 | 6.22 |
| 10 | Zr | Hf | 90 | 0.59 | 6.34×10^4 | 138.0 | 2.09 | 6.48 |
| 12 | Zr | Rh | 126 | 1.04 | 7.85×10^4 | 136.3 | 0.42 | 17.24 |
| 13 | Hf | Rh | 240 | 0.53 | 2.14×10^4 | 136.4 | 2.10 | 7.18 |
| 14 | Zr | Ti | 15 | 1.36 | 8.72×10^5 | 137.8 | 2.72 | 4.06 |
| $[\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ | Zr | | 5 | 1.86 | 3.57×10^6 | 138.3 | 0.99 | 2.54 |
| $[\text{Hf}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ | Hf | | 30 | 2.80 | 8.95×10^5 | 138.7 | 1.64 | 2.54 |
| $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ | Ti | | 62 | 1.63 | 2.52×10^5 | | | |

^aAt 2 bar absolute monomer pressure, 30°C, 210 cm³ toluene, 0.9 g MAO, Al/M = 2500.

^bmol M: total amount of metal used (6.25×10^{-6} mol for each run).

The mononuclear zirconium compound **1** and binuclear zirconium compounds **5** and **12** are all considerably more active than their hafnium analogues **2**, **6** and **13**. The lower activity of hafnocenes compared with zirconocenes has been reported previously [17,25–29] and is thought to be caused by a greater strength of hafnium–carbon σ bonds. For the compounds $[\text{M}(\eta\text{-C}_5\text{Me}_5)_2\text{Me}_2]$, the metal–methyl bond enthalpies are around 306 kJ mol^{-1} for hafnium compared with 284 kJ mol^{-1} for zirconium [30,31]. This effect is also apparent in the order of activities of compounds **5**, **6** and **10**, i.e. **5** > **10** > **6**.

As can be seen in Table 6, the activity of compound **14** is relatively high among the binuclear catalysts presented here. Its activity is intermediate between that of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ and $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$, which are the two constituent parts of compound **14**. This may be due to the conformation of compound **14** being similar to that of compound **12**, whose two metal centres are held apart, so both active sites behave independently. Thus the combined effects is to average the activity of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ and $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$. Compounds **12** and **13**, would be expected to show the same effect. The extremely low activities of compound **12** and **13** may reflect inactivity of the rhodium centre. However the activity of compound **13** is higher than that of compound **6** which has two hafnium centres.

The melting point of polyethenes which were produced by all the compounds are given in Table 6, and were measured by differential scanning calorimetry (DSC). The melting points are between 136°C – 139°C , indicating that they are highly linear and highly crystalline [32]. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by gel permeation chromatography (GPC) at the Chisso Petrochemical Corporation. The molecular weight distribution curves of the polyethene are shown in Fig. 5. Except for compound **12**, the molecular weights, M_n , of the polymers produced by the new compounds are considerably

higher than those produced by $[\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ ($\text{M} = \text{Zr, Hf}$). Of the series of compounds **5**, **6** and **10**, the compound **5** which has two zirconium centres produces polyethene of the highest molecular weight (M_n). Normally hafnium centres produce polymers of higher molecular weight than zirconium analogues [17,26,28].

The mononuclear compounds **1** and **2** ($M_w/M_n = 3.93$ and 7.30 respectively) and homo-binuclear compounds **5** and **6** ($M_w/M_n > 5.4$) give polyethene with unexpectedly broader molecular weight distribution (MWD) when compared with those obtained by some mononuclear analogues, e.g. $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ ($M_w/M_n = 2.54$) and $[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ ($M_w/M_n = 2.54$). This uncharacteristic broadness for homogeneous catalysts [30,33] could imply that more than one kind of active species, each of which contributes to a narrow distribution [28]. In fact, Kaminsky and co-workers have observed this trend for polypropene by using *S*-(η -1,1'-ethylenedi-4,5,6,7-tetrahydroindenyl)zirconium dichloride as catalyst. The MWD curves are displayed in Fig. 6. Although the MWD of the total polymer is broad ($M_w/M_n = 5.8$), that of the fractionated polymer is low ($M_w/M_n = 2.8$ and 2.6 respectively) [34].

As it was anticipated, polyethene produced by homo-binuclear compound **7** ($M_w/M_n = 6.22$) and hetero-binuclear compounds **10**–**14** ($M_w/M_n = 4.06$ – 17.24) have rather broad molecular weight distributions, since they have two different active centres. This suggests that both metal centres in these compounds are active in the course of polymerisation. For example, the two peaks of compound **14** (Fig. 5) are firm diagnostics of the existence of such two different active centres, whose activities are reflected by the intensity of the peaks. It is clear in this case that the Ti centre is less active than the Zr centre. Similar situations can also be observed for other binuclear compounds. However the separation between the two peaks, which is an important factor to the overall MWD, is different in each individual system.

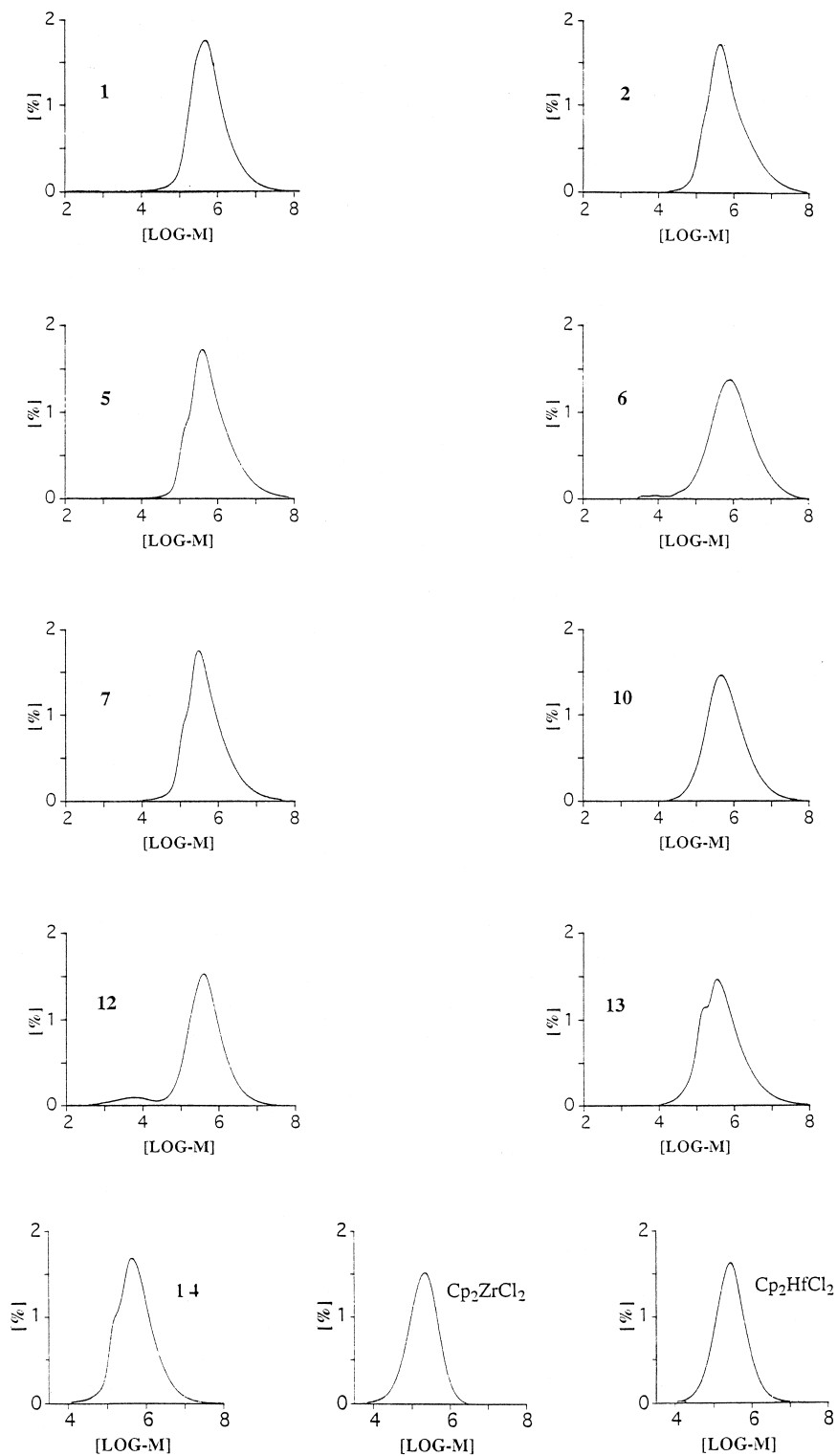


Fig. 5. The GPC curves for polyethenes produced by new metallocenes.

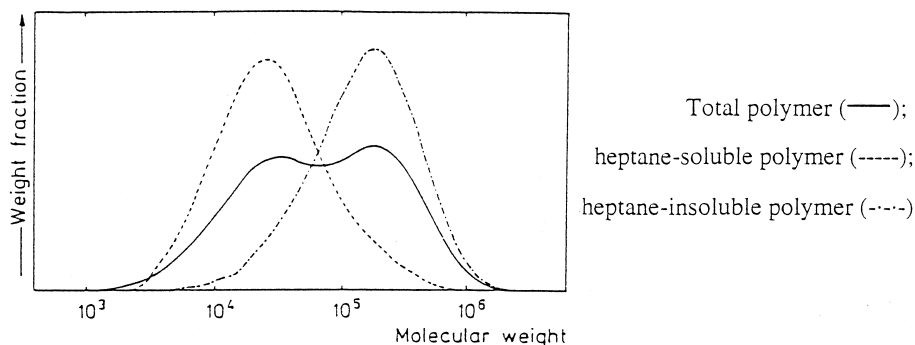


Fig. 6. The MWD curves of fractionated and of total polymer (taken from Kaminsky et al. [34]).

Compounds **5**, **6**, **10**, **7**, **12** and **14** were tested for the polymerisation of propene. For comparison, the catalysts $[M(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$, $M = \text{Zr, Hf}$, and $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$ were also tested under the same conditions. These experiments were carried out with the same temperature, monomer pressure and solvent volume, but 5 times more catalyst and MAO, (5.13×10^{-5} mol of overall metal and 4.5 g of MAO) than used for the ethene polymerisation in order to obtain sufficient polymer for characterisation. The activities of compounds **5**, **6**, **7**, **10**, **12** and **14** are shown in Table 7.

All the catalyst systems listed in Table 7 remained active throughout the experiments. However, the activities are generally lower than for ethene polymerisation. All systems that lacked a high degree of stereospecificity also

showed poor activity. All the polypropenes produced in this study were highly viscous liquids, implying that they have poor stereospecificities. The order of activity for propene polymerisations of compounds **5**, **6** and **10** is similar to that of ethene polymerisation (**5** > **10** > **6**) probably due to the greater strength of hafnium–carbon σ bond. The poor performance of compound **7** for propene polymerisation, compared with compound **5** may be due to steric effects. As in the case of ethene polymerisation, the activity of compound **14** for propene polymerisation is still intermediate between that of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ and $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$. It is also interesting to note that the activity of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$ is two orders of magnitude lower than that of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$, while it shows one order of magnitude lower activity for ethene polymerisation.

Table 7
Activity of catalysts in polymerisation of propene^a

| Compound | M | M ⁺ | Time (h) | Yield (g) | Activity ^b (g PP/mol M h) |
|---|----|----------------|----------|-----------|--------------------------------------|
| 5 | Zr | Zr | 5.0 | 11.6 | 7.44×10^4 |
| 6 | Hf | Hf | 33.0 | 5.9 | 5.71×10^3 |
| 10 | Zr | Hf | 10.0 | 8.0 | 2.56×10^4 |
| 7 | Zr | Zr | 18.5 | 18.2 | 3.16×10^4 |
| 12 | Zr | Rh | 10 | 5.1 | 1.64×10^4 |
| 14 | Zr | Ti | 4.5 | 3.0 | 2.1×10^4 |
| $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ | Zr | | 6 | 49.8 | 2.7×10^5 |
| $[\text{Hf}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ | Hf | | 6 | 22.8 | 1.2×10^5 |
| $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$ | Ti | | 18.8 | 1.1 | 1.8×10^3 |

^aAt 2 bar absolute monomer pressure, 30°C, 210 cm³ toluene, 4.5 g MAO. Al/M = 2500.

^bmol M: total amount of metal used (3.13×10^{-5} mol for each run).

Table 8
Characterising data of polypropenes

| Compound (metals) | Triad fractions | | | Dyad fractions | | Tactic block lengths | | Chain length (monomer units) | M_n^a |
|---|-------------------|-------------------|-------------------|------------------|------------------|----------------------|-------------|---------------------------------|---------|
| | [mm] ^b | [mr] ^b | [rr] ^b | [m] ^c | [r] ^c | n_{iso}^d | n_{syn}^d | | |
| 5 (Zr, Zr) | 0.32 | 0.47 | 0.22 | 0.55 | 0.45 | 2.36 | 1.94 | 24 | 1008 |
| 6 (Hf, Hf) | 0.41 | 0.44 | 0.15 | 0.63 | 0.37 | 2.86 | 1.68 | 243 | 10206 |
| 10 (Zr, Hf) | 0.34 | 0.47 | 0.19 | 0.57 | 0.43 | 2.45 | 1.80 | 37 | 1554 |
| 7 (Zr, Zr) | 0.30 | 0.48 | 0.22 | 0.54 | 0.46 | 2.25 | 1.92 | 27 | 1134 |
| 12 (Zr, Rh) | 0.19 | 0.45 | 0.36 | 0.42 | 0.58 | 1.84 | 2.60 | 19 | 798 |
| [Zr(η -C ₅ H ₅) ₂ Cl ₂] | 0.19 | 0.47 | 0.34 | 0.43 | 0.57 | 1.80 | 2.45 | 20 | 840 |
| [Hf(η -C ₅ H ₅) ₂ Cl ₂] | | | | | | | | 78 | 3272 |

^a Determined by end-group analysis using ¹H NMR.

^b From triad analysis by ¹³C{¹H} NMR.

^c [m] = [mm] + [mr]/2, [r] = [rr] + [mr]/2.

^d $n_{iso} = 2[mm]/[mr] + 1$, $n_{syn} = 2[rr]/[mr] + 1$.

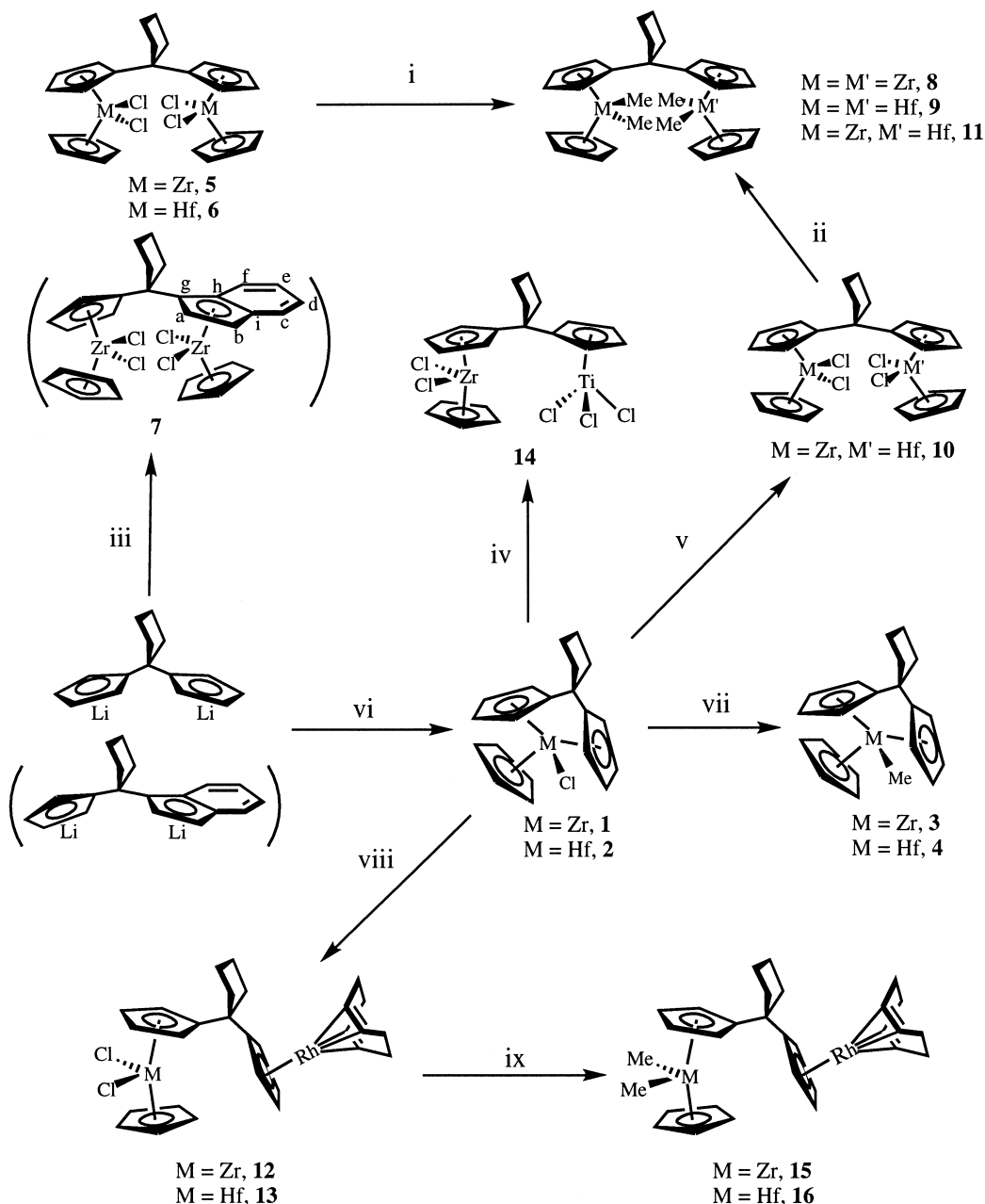
These results have been attributed to the relative ease of reduction of Ti(IV) to Ti(III) and even to Ti(II) [35]. The activity of compound **5** is more than two times higher than that of compound **12** indicating that the rhodium centre is inactive and plays no part in the reaction.

We have carried out detailed NMR studies of the polymers and these can be found in reference [36]. Table 8 shows the triad fractions, dyad fractions and tactic block lengths n_{iso} and n_{syn} for each set of polypropene, which are derived from the ¹³C{¹H} NMR data. The data in Table 8 show all of the polymers are atactic and there must be very few long segments.

The molecular weight and molecular weight distribution of the polypropenes were measured by GPC analysis. However, it was not possible to calculate the accurate molecular weight, M_n and M_w , because the polypropenes produced in this study were of very low molecular weights for which the instrument was not calibrated. However, it is qualitatively clear that all of the polypropenes produced by binuclear metallocenes show wide molecular weight distributions ($M_w/M_n > 2$). Since they all have low molecular weight, the NMR signals of the chain-end (vinylidene) group of the polymers, which has two singlets in the region of 4–5 ppm [37], can be observed and comparison of the integrated intensity of the vinylidene protons with that of the sum of the remaining group of

the polymer chain (0–2 ppm), allows estimation of the number-average molecular weight (M_n) of the polymer. The data for the compounds **5**, **6**, **7**, **10** and **12** are given in Table 8.

Data in Table 8 confirm that the polypropenes produced in this study are of fairly low molecular weight, which is also evident by their appearance as highly viscous liquids. It has been noted that propene polymers obtained with MAO-activated or cation-type Zr(η -C₅H₅)₂-based catalysts, at room temperature, have rather low degrees of polymerisation, with molecular weights in the range of 200–1000 [33]. Such relatively low molecular weights of the polymer products must be due either to an increased rate of chain termination or to a decreased rate of olefin insertion (or a combination of both), since the average degree of polymerisation P_N is determined by the ratio of chain propagation and chain termination $P_N \approx v_p/v_T$ [33,38]. Nevertheless, the new homo-binuclear compounds, in particular dihafnocene compound **6**, result in higher molecular weight polymer than the related mononuclear compounds [Cp₂ZrCl₂] and [Cp₂HfCl₂]. This suggests that for the binuclear compounds chain termination is suppressed (the effect is not due to chain propagation as they have low activities). The molecular weight of the polypropenes in Table 8 decreases in the order (Hf, Hf) > (Zr, Hf) > (Zr, Zr). This trend is consistent with the M_n -enhancing (and



Scheme 1. (i) For **8** and **9**, MeMgCl in THF at 0°C, then r.t. for 12 h., 56% (**8**), 57% (**9**). (ii) For **11**, MeMgCl in THF at 0°C, then r.t. for 12 h., 39%. (iii) For **5**, **6** and **7**, [Zr($\eta\text{-C}_5\text{H}_5$)Cl₃ · DME] or [Hf($\eta\text{-C}_5\text{H}_5$)Cl₃ · DME] in toluene reflux for 12 h., 65% (**5**), 41% (**6**), 36% (**7**). (iv) For **14**, TiCl₄ in toluene at 0°C, then r.t. for 12 h., 69%. (v) For **10**, [Hf($\eta\text{-C}_5\text{H}_5$)Cl₃ · DME] in toluene reflux 2 days, 37%. (vi) For **1** and **2**, [Zr($\eta\text{-C}_5\text{H}_5$)Cl₃ · DME] or [Hf($\eta\text{-C}_5\text{H}_5$)Cl₃ · DME] in toluene at r.t. for 1 day, 67% (**1**), 45% (**2**). (vii) For **3** and **4**, MeMgCl in THF at -78°C, then r.t. for 12 h., 65% (**3**), 53% (**4**). (viii) For **12** and **13**, [Rh($\eta\text{-C}_8\text{H}_{12}$)Cl]₂ in toluene reflux for 12 h., 77% (**12**), 72% (**13**). (ix) For **15** and **16**, MeMgCl in THF at -78°C, then r.t. for 12 h. 89% (**15**), 79% (**16**).

its activity-lowering) effect of hafnium as compared with zirconium [17,25,27,39,40].

In conclusion, the reactions and the structure proposed for the new compounds **1–15** are shown in Scheme 1; moderate catalytic activity with these compounds is observed but none of these new compounds are ‘living’ catalysts.

3. Experimental

All preparations and manipulations of air and/or moisture sensitive materials were carried out under an atmosphere of dinitrogen or argon, using either standard Schlenk line techniques or in an inert atmosphere dry box containing dinitrogen. Inert gases were purified by passage through columns filled with molecular sieves (4 Å) and either manganese (II) oxide suspended on vermiculite for the vacuum line or BASF catalyst for the inert atmosphere box. Solvents and solutions were transferred through stainless steel cannulae, using a positive pressure of inert gas. Filtrations were performed in a similar manner using modified stainless steel cannulae which were fitted with glass fibre filter discs. All glassware and cannulae were thoroughly dried at 150°C, usually overnight, before use.

All solvents were thoroughly deoxygenated before use either by repeated evacuation followed by admission of dinitrogen, or by bubbling dinitrogen through the solvent for approximately 15 min. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled over sodium (toluene, petroleum ether (b.p. 100–120°C)), sodium/potassium alloy (diethyl ether, *n*-pentane and light petroleum ether (b.p. 40–60°C)), potassium (THF, benzene) or calcium hydride (dichloromethane, acetonitrile) under a mild, continuous stream of dinitrogen. Perdeuterated solvents for NMR spectroscopy were deoxygenated and dried over calcium hydride (dichloromethane, acetonitrile) or potassium (benzene, THF and toluene) and then distilled before use. Activated alumina (Al₂O₃,

neutral, Brockmann I, standard grade, ~150 mesh) was used for chromatography and deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Celite 545 filtration aid (Koch–Light) was pre-dried at 140°C and similarly deoxygenated before use.

Nuclear magnetic resonance (NMR) spectra were recorded on either a Varian UnityPlus 500: (¹H and ¹³C NMR spectra were recorded at 499.868 and 125.704 MHz, respectively), or a Bruker AM300 (¹H and ¹³C NMR spectra were recorded at 300.13 and 75.5 MHz, respectively). Indirect detection experiments were carried out on a Varian UnityPlus 500 fitted with a pulsed field gradient ID probe. The spectra were referenced internally using the residual protio solvent (¹H) and solvent (¹³C) resonances measured relative to TMS (¹H and ¹³C, δ = 0 ppm). All chemical shifts are quoted in δ (ppm) and coupling constants are given in Hz.

Mass spectra were recorded on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by mass spectrometry services. Fast atom bombardment mass spectra (FAB-MS) were obtained by the EPSRC mass spectrometry service centre at the University College of Swansea, under the supervision of Dr. J.A. Ballantine. The *m/z* values quoted are based on the most abundant isotope of each element.

Infra-red spectra were recorded on either a Perkin-Elmer 1710 FTIR spectrometer or a Mattson instruments Galaxy series FT-IR 6020 spectrometer in the range 400 cm⁻¹ to 4000 cm⁻¹ and a Perkin-Elmer 580B spectrometer in the range 200 to 600 cm⁻¹. Samples were prepared as either Nujol mulls between KBr or NaCl plates, or as KBr or CsI discs. All data given are in wavenumbers (cm⁻¹).

Elemental analyses were obtained by the microanalysis department of the Inorganic Chemistry Laboratory. Gel-permeation chromatography (GPC) of polymers were obtained at 135°C by using a Waters model 150C at Chisso Petrochemical, Japan.

The compounds [Zr(η-C₅H₅)Cl₃ · DME] [41]

and $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ [41] were prepared as described.

3.1. Preparation of 6,6-tetramethylenefulvene

A modified literature approach to the preparation of 6,6-dimethylfulvene [42], in which pyrrolidine is used to catalyse the condensation reaction between cyclopentadiene and cyclopentanone was used. To a solution of cyclopentanone (25.24 g, 300 mmol) and cyclopentadiene (24.72 cm³, 300 mmol) in reagent grade methanol (180 cm³), pyrrolidine (37.6 cm³, 450 mmol) was added at 0°C. On addition of pyrrolidine, the colourless solution immediately gave a yellow solution. After 2 min, aqueous acetic acid (25.7 cm³, 450 mmol) was added at 0°C to neutralise the reaction. The reaction mixture was diluted with ether and water and the organic phase washed with water and brine, and dried over MgSO₄. The solvent was removed under reduced pressure to give a yellow viscous oil which was purified by column chromatography on silica gel and eluted with light petroleum ether (b.p. 40–60°C) to give a pale yellow oil. Yield: 37 g (93%).

3.2. Preparation of $[(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_5)_2]$

Cyclopentadiene (9.9 cm³, 119.5 mmol) was added to a mixture of powdered NaOH (10 g, 250 mmol) in THF (100 cm³). After stirring for 30 min, the solution was cooled to 0°C and a solution of 6,6-tetramethylenefulvene (15.8 g, 119.5 mmol) in THF (50 cm³) was added dropwise over a period of 2 h. The mixture was then stirred overnight. The decanted solution was washed with water and brine, and dried over MgSO₄. The solvent was removed under reduced pressure to give a brown oil. The crude product (6.0 g) was purified using column chromatography on silica gel with petroleum ether (b.p. 40–60°C) to yield 2.6 g (34%) of a pale yellow oil, or 12.0 g was purified by distillation at 60–65°C, 0.04 Torr to yield 3.0 g (20%) target product.

3.3. Preparation of $[(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_5)(\text{C}_9\text{H}_7)]$

A solution of 6,6-tetramethylenefulvene (5.42 g, 41.0 mmol) in THF (80 cm³) was added dropwise over 1.5 h to a stirred solution of lithium indenide (5.0 g, 41.0 mmol) in THF (80 cm³) at 0°C. Stirring the brown reaction mixture overnight at 0°C led to a dark brown solution. Water (20 cm³) was added at 0°C. The THF was removed on a rotary evaporator. The resulting solution was then diluted by water (70 cm³) and ether (120 cm³). The ether layer was washed with water (3 × 100 cm³) and brine (2 × 100 cm³), and then dried over MgSO₄. The crude product was obtained as a red-orange oil after removal of the solvent on a rotary evaporator. This compound was purified by column chromatography on alumina (6% H₂O), and eluted with petroleum ether (b.p. 40–60°C) to give a yellow oil. Yield: 8.7 g (86%).

3.4. Preparation of $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)_2\}]$

A hexane solution of *n*-BuLi (33.54 cm³, 2.5 M 83.86 mmol) was added dropwise, with stirring, to a cooled solution (0°C) of $(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_5)_2$ (7.23 g, 36.46 mmol) in diethyl ether (170 cm³) to form a white precipitate. The reaction mixture was allowed to stir at room temperature for 2.5 h, then filtered and washed with diethyl ether (2 × 100 cm³). The solvent was removed under reduced pressure, and the product dried in vacuo to give a white pyrophoric solid. Yield: 7.5 g (98%).

3.5. Preparation of $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)\}]$

The compound 1-cyclopentadienyl-1-indenylcyclopentane (3.72 g, 15.0 mmol) in diethyl ether (60 cm³) was treated with a solution of *n*-BuLi in hexane (13.2 cm³ of a 2.5 M solution, 33.0 mmol), dropwise, at 0°C, and a white precipitate formed. The suspension was stirred overnight, then filtered, washed with diethyl ether (2 × 50 cm) and dried in vacuo to give a pyrophoric white solid. Yield: 3.7 g (96%).

3.6. Preparation of $[\text{Zr}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ **1**

The compounds $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ (4.23 g, 12.0 mmol) and $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)_2\}]$ (2.52 g, 12.0 mmol) were weighed into a Schlenk vessel and toluene (400 cm³) was added via cannula. The reaction mixture was stirred at room temperature for one day until yellow suspension formed. The solvent was removed under reduced pressure, and the residue washed three times with dry CH_2Cl_2 . The yellow CH_2Cl_2 extract was reduced to ca. 30 cm³, which gave a yellow precipitate, then stored at -20°C overnight. More precipitate formed which was filtered, washed with petroleum ether (40–60°C) and dried under vacuo to yield a yellow powder. Yield: 3.1 g (67%).

3.7. Preparation of $[\text{Hf}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ **2**

The compounds $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ (1.76 g, 4.0 mmol) and $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)_2\}]$ (0.85 g, 4.0 mmol) were weighed into a Schlenk vessel and toluene (100 cm³) was added via cannula. The reaction mixture was stirred at room temperature overnight to give a pale yellow suspension. After filtration, the solvent was removed under reduced pressure to a final volume of 5 cm³. A yellow powder was precipitated, cooling of the solution to -20°C overnight yielded more of this powder. The suspension was filtered, and the solid washed with petroleum ether (40–60°C) and dried in vacuo to yield a pale yellow solid which was recrystallised from CH_2Cl_2 at -20°C . Yield: 0.85 g (45%).

3.8. Preparation of $[\text{Zr}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Me}]$ **3**

A 3 M solution of MeMgCl (2.06 cm³, 6.18 mmol) in THF at 0°C , was reacted with the compound $[\text{Zr}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_4)\text{Cl}]$ (0.60 g, 1.55 mmol) in THF (50 cm³) (-78°C)

in a dropwise manner. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue was extracted with pentane (2×50 cm³). The resulting colourless solution was concentrated under reduced pressure to give white crystalline solid. This was filtered and dried in vacuo. Yield: 0.37 g (65%).

3.9. Preparation of $[\text{Hf}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Me}]$ **4**

A 3 M solution of MeMgCl (0.45 cm³, 1.35 mmol) in THF at 0°C was reacted with the compound $[\text{Hf}\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_4)\text{Cl}]$ (0.16 g, 0.34 mmol) in THF (30 cm³) (-78°C) in a dropwise manner. The solution was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure. The residue was extracted with pentane (2×50 cm³). After the solvent removal and dried in vacuo overnight, white powder was obtained, which was recrystallised from pentane at -80°C . Yield: 0.08 g (53%).

3.10. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ **5**

The solid compounds $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ (2.12 g, 6.0 mmol) and $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)_2\}]$ (0.63 g, 3.0 mmol) were mixed together in a Rotaflo ampoule and toluene (300 cm³) was then added. The reaction mixture was refluxed overnight to give a pale yellow suspension. The reaction was allowed to cool, and filtered and the residue was washed with toluene. The volume of filtrate was reduced to ca. 30 cm³ to give a white solid. This was filtered, washed with petroleum ether (b.p. 40–60°C) and then dried in vacuo. Yield: 1.27 g (65%).

3.11. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{HfCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ **6**

The compounds $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ (1.76 g, 4.0 mmol) and $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\text{C}_5\text{H}_4)_2\}]$

(0.42 g, 2.0 mmol) were mixed together in a Rotaflo ampoule and toluene (100 cm³) was added. The reaction mixture was refluxed overnight to give an off white suspension. This was allowed to cool, and was then filtered. The volume of the pale yellow filtrate was reduced to ca. 20 cm³ to give a white solid. This was filtered, washed with petroleum ether (b.p. 40–60°C) and then dried in vacuo for one day. Yield: 0.67 g (41%).

3.12. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2(\eta\text{-C}_9\text{H}_6)\}\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ 7

The compounds $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3 \cdot \text{DME}]$ (3.35 g, 10.0 mmol) and $[\text{Li}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2(\eta\text{-C}_9\text{H}_6)\}]$ (1.30 g, 5.0 mmol) were weighed into a 500 cm³ Rotaflo ampoule. The ampoule was cooled to –78°C in a dry ice/acetone bath, then toluene (200 cm³, –78°C) was added. The dry ice/acetone bath was removed and the reaction mixture allowed to warm to room temperature slowly, and then refluxed overnight. The reaction mixture was transferred into a Schlenk vessel and filtered. Upon reduction of the volume of toluene, some crystals formed, which proved to be mainly the starting material, $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_3 \cdot \text{DME}]$. The solution was filtered and the solvent removed to give a yellow solid. It was purified by recrystallisation from CH_2Cl_2 /petroleum ether (b.p. 40–60°C) at –20°C. Yield: 1.02 g (29%).

3.13. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{ZrMe}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{ZrMe}_2(\eta\text{-C}_5\text{H}_5)]$ 8

A 3 M solution of MeMgCl (8.6 cm³, 25.82 mmol) in THF at 0°C was treated with the compound $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ (2.10 g, 3.23 mmol) in THF (300 cm³, –78°C). The reaction mixture was warmed to room temperature and stirred overnight. The solvent was then removed under reduced pressure, and the residue was extracted with pentane (250 cm³ and 50 cm³). The resulting solution was reduced in volume to 40 cm³,

then filtered and dried in vacuo to give white fine needle microcrystals. Yield: 1.05 g (57%).

3.14. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{HfMe}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfMe}_2(\eta\text{-C}_5\text{H}_5)]$ 9

A solution of 3 M MeMgCl (1.0 cm³, 3.0 mmol) in THF at 0°C was treated with the compound $[(\eta\text{-C}_5\text{H}_5)\text{HfCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ (0.30 g, 0.36 mmol) in THF (30 cm³, –78°C) in a dropwise manner. The solution was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue extracted with pentane. The pentane was removed and the resulting white needle-like microcrystals were dried in vacuo overnight. Yield: 0.15 g (56%).

3.15. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ 10

The compounds $[(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ (0.48 g, 1.24 mmol) and $[(\eta\text{-C}_5\text{H}_5)\text{HfCl}_3 \cdot \text{DME}]$ (0.56 g, 1.24 mmol) were weighed into a 250 cm³ Rotaflo ampoule and toluene (100 cm³) was added. The reaction mixture was refluxed for two days to give an off-white suspension. The suspension was filtered and the resulting pale yellow filtrate was concentrated to 25 cm³ to give a white precipitate which was filtered, washed with petroleum ether (b.p. 40–60°C) and dried in vacuo. Yield: 0.34 g (37%).

3.16. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{ZrMe}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfMe}_2(\eta\text{-C}_5\text{H}_5)]$ 11

A solution of 3 M MeMgCl (0.72 cm³, 2.2 mmol) in THF at 0°C was treated with $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ (0.20 g, 0.27 mmol) in THF (30 cm³, –78°C) in a dropwise manner. The solution was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue extracted with pentane (2 × 50

cm³). The pentane was removed and the resulting solid dried in vacuo overnight to give white fine needle microcrystals. Yield: 0.07 g (39%).

3.17. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Rh}(\eta\text{-C}_8\text{H}_{12})]$ **12**

The compounds $[(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2]\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}$ (0.78 g, 2.0 mmol) and $[\text{Rh}(\eta\text{-C}_8\text{H}_{12})\text{Cl}]_2$ (0.49 g, 1.0 mmol) were weighed into a Schlenk vessel. Toluene (110 cm³) was added and the mixture was refluxed overnight. The reaction mixture was filtered and the volatile removed from the filtrate under reduced pressure to a volume of 20 cm³. A yellow solid was obtained, which was separated by filtration and washed with petroleum ether (b.p. 40–60°C) and dried in vacuo. Yield: 0.98 g (77%).

3.18. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{HfCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Rh}(\eta\text{-C}_8\text{H}_{12})]$ **13**

The compounds $[(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2]\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}$ (0.21 g, 0.446 mmol) and $[\text{Rh}(\eta\text{-C}_8\text{H}_{12})\text{Cl}]_2$ (0.11 g, 0.223 mmol) were weighed into a Rotaflo ampoule. Toluene (110 cm³) was added and the mixture was refluxed overnight. The cooled reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure to a volume of 5 cm³. The solution was stored at –20°C overnight to give a yellow precipitate. It was filtered, washed with petroleum ether (40–60°C) and dried in vacuo. Yield: 0.23 g (72%).

3.19. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{TiCl}_3]$ **14**

A suspension of $[(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2]\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}$ (0.33 g, 0.85 mmol) in toluene (50 cm³) was treated dropwise with TiCl_4 (0.85 cm³, 1.0 M in toluene) at 0°C. The solution rapidly became yellow-brown in colour. It was stirred overnight at room temperature, becoming darker with formation of a precipitate. The reaction mixture was filtered and the volume of the

filtrate was reduced to 10 cm³ under reduced pressure to give a yellow precipitate which was filtered, washed with pentane and dried in vacuo. Yield: 0.34 g (69%).

3.20. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{ZrMe}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Rh}(\eta\text{-C}_8\text{H}_{12})]$ **15**

A solution of 3 M MeMgCl (0.69 cm³, 1.9 mmol) in THF at 0°C was treated with $[(\eta\text{-C}_5\text{H}_5)\text{ZrCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Rh}(\eta\text{-C}_8\text{H}_{12})]$ (0.30 g, 0.47 mmol) in THF (30 cm³, –78°C) in a dropwise manner. The solution was warmed to room temperature and stirred overnight. The solvent was then removed under reduced pressure, and the residue extracted with pentane (100 cm³). The pentane was removed and the resulting solid dried in vacuo overnight to give yellow microcrystals. Yield: 0.25 g (89%).

3.21. Preparation of $[(\eta\text{-C}_5\text{H}_5)\text{HfMe}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Rh}(\eta\text{-C}_8\text{H}_{12})]$ **16**

A solution of 3 M MeMgCl (0.3 cm³, 0.84 mmol) in THF at 0°C was treated with $[(\eta\text{-C}_5\text{H}_5)\text{HfCl}_2\{(\text{CH}_2)_4\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Rh}(\eta\text{-C}_8\text{H}_{12})]$ (0.15 g, 0.21 mmol) in THF (20 cm³, –78°C) in a dropwise manner. The solution was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue was extracted with pentane (80 cm³). The pentane was removed and the resulting solid dried in vacuo overnight to give yellow microcrystals. Yield: 0.11 g (79%).

3.22. General details of polymerisation studies

All manipulations of catalysts and cocatalysts were performed under an inert atmosphere using either a dual vacuum/nitrogen line and standard Schlenk techniques or in an inert atmosphere dry box containing nitrogen. Ethene and propene (pure grade) were further purified by passage through columns of 4 Å molecular sieves and then over finely divided potassium metal supported on glass wool.

3.23. Polymerisation of ethene using metallocene/MAO catalysts

Polymerisations were carried out under similar conditions to those employed previously [17]. Methylaluminoxane (MAO) (850 mg) was weighed into the Fischer–Porter bottle, which was then connected to the ethene supply via the computer-controlled gas supply system. The flexible steel hose joining the Fischer–Porter bottle to the supply system was evacuated and filled with ethene three times, then the Fischer–Porter bottle was evacuated and filled with ethene. Toluene (200 cm³) was then added,

the ethene pressure increased to 2 bar (absolute pressure) and the mixture stirred at 30°C until saturated with ethene. Meanwhile, the metallocene (6.25×10^{-6} mol of transition metal in total) in 10 cm³ of toluene was added to 50 mg of MAO and stirred for 15 min for pre-activation. The metallocene/MAO mixture was added quickly to the reactor. The reaction mixture was stirred vigorously at 30°C under 2 bar pressure of ethene.

The polymerisation was quenched by venting the ethene and adding a small amount of ethanol. The contents of the reactor were transferred to a conical flask and 50 cm³ of 20% (by volume)

Table 9
Crystal data, data collection and refinement

| | Compound | | |
|---|--------------------------------------|---|--------------------------------------|
| | 1 | 12 | 15 |
| Formula | C ₂₀ H ₂₁ ZrCl | C ₂₈ H ₃₃ ZrRhCl ₂ | C ₃₀ H ₃₉ ZrRh |
| Formula weight | 388.06 | 634.60 | 593.76 |
| Crystal size (mm) | 0.18 × 0.145 × 0.145 | 0.19 × 0.25 × 0.28 | 0.15 × 0.22 × 0.23 |
| Crystal system | triclinic | monoclinic | monoclinic |
| Space group | P-1 | P 2 ₁ /n | P 2 ₁ /c |
| <i>a</i> (Å) | 7.129(1) | 8.1640(5) | 13.149(2) |
| <i>b</i> (Å) | 9.522(1) | 26.983(2) | 12.802(2) |
| <i>c</i> (Å) | 11.482(1) | 11.913(1) | 14.001(1) |
| α (°) | 87.23(1) | | |
| β (°) | 88.15(2) | 104.35(7) | 92.052(4) |
| γ (°) | 88.04(2) | | |
| Unit-cell volume (Å ³) | 777.70 | 2546.64 | 2523.55 |
| <i>Z</i> | 2 | 4 | 4 |
| <i>D_c</i> (g cm ⁻³) | 1.66 | 1.66 | 1.56 |
| Linear absorption | | | |
| Coeff. μ (cm ⁻¹) | 8.6 | 12.67 | 10.66 |
| Data collection: | | | |
| Diffractometer | FAST | CAD4 | DIP2020 |
| X-radiation ($\lambda = 0.71069$ Å) | Mo-K α | Mo-K α | Mo-K α |
| Scan mode | ω | $\omega - 2\theta$ | ω |
| θ_{\max} (°) | 25 | 27 | 26 |
| Reflections measured | 3285 | 7023 | 11441 |
| Independent reflections | 2153 | 5545 | 4893 |
| Total observed data [$I > 3\sigma(I)$] | 1876 | 3250 | 4233 |
| Merging <i>R</i> factor (%) | 16.5 | 2.35 | 2.4 |
| Temperature (K) | 150 | 298 | 150 |
| Number of parameters | 199 | 289 | 445 |
| Ratio data:parameters | 9.4:1 | 11:1 | 9.5:1 |
| Weighting scheme | Chebychev | Chebychev | Chebychev |
| Min, max residual peak (e Å ⁻³) | -1.42, 1.08 | -0.48, 0.65 | 0.65, 0.35 |
| <i>R</i> (%) | 8.38 | 3.41 | 2.4 |
| <i>R_w</i> (%) | 8.52 | 4.02 | 2.9 |

solution of concentrated HCl in ethanol was added and the mixture stirred overnight. The polymer was then separated from the solution using a sintered glass funnel (on a Buchner flask, connected to a water aspirator), washed with water and ethanol, then dried in vacuo at 60°C to constant weight.

3.24. Polymerisation of propene using metallocene / MAO catalysts

Polymerisation reactions were performed under the same conditions (2 bar monomer pressure, 30°C), and using the same procedure as for ethene, except: (i) 4.25 g of MAO and 160 cm³ of toluene were pre-saturated with propene at 2 bar and 30°C, (ii) metallocene (3.13×10^{-5} mol of transition metal in total) in 50 cm³ was added to 250 mg of MAO for 15 min pre-activation.

The polymerisation was quenched by venting the propene and adding a small amount of ethanol. The contents of the reactor were transferred to a conical flask and 250 cm³ of 20% (by volume) solution of concentrated HCl in ethanol was added and the mixture stirred overnight. As the polypropene was soluble in toluene the toluene layer was separated, washed with water (300 cm³) then stirred with anhydrous MgSO₄. After filtration, the toluene was removed under reduced pressure leaving the polypropene, typically a highly viscous liquid, which was then dried to constant weight in vacuo at 60°C.

3.25. Crystal structure determination

All crystals were mounted in Lindemann glass capillaries under nitrogen. Crystal data, data collection and refinement parameters for the compounds are given in Table 9. Data for all structures were corrected for Lorentz and polarization effects. Data for compound **12** were corrected for absorption using DIFABS ($T_{\min} = 0.98$, $T_{\max} = 1.01$) [43]. For **1** and **15** absorption effects were corrected by multi-frame scaling of

the image-plate data [44]. All structures were solved by direct methods [45] giving non-hydrogen atom positions. The structures were refined using full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. For **1** and **12** hydrogen atoms were placed in calculated positions during the final cycles of refinement. For **15** the hydrogen atoms were located in difference Fourier maps and refined isotropically. Three parameter Chebychev weighting schemes were applied to all structures. All crystallographic calculations were carried out using CRYSTALS [46]. Neutral atom scattering factors were taken from International Tables for X-ray Crystallography [47].

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