

Synthesis of heterobinuclear metallocenes containing bridging *ansa*-bis- η -cyclopentadienyl ligands †

Malcolm L. H. Green* and Neil H. Popham

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR.

E-mail: malcolm.green@chemistry.ox.ac.uk

Received 22nd December 1998, Accepted 5th February 1999

Binuclear metallocene derivatives have been prepared, exemplified by $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{-Rh}(\text{CO})_2]$, $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{PPh}_3)_2]$, $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{-Mn}(\text{CO})_3]$, $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Ru}(\text{CO})(\eta\text{-C}_4\text{H}_7)]$, $[\text{Fe}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$, $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Co}(\eta\text{-C}_5\text{Me}_5)]$, $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{-Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$, $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$. The tris- η -cyclopentadienyl compounds $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)_2(\eta\text{-C}_5\text{H}_4\text{Me})\text{Cl}]$ and the new η -indenyl compound $[\text{Zr}\{(4\text{-Bu}^t\text{C}_6\text{H}_9)(\eta\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ are also described. The activity of a selection of the binuclear compounds as co-catalysts for ethylene polymerisation has been demonstrated.

Metallocenes of the Group IV elements, especially of zirconocenes, are of considerable interest as homogeneous co-catalysts for the polymerisation of α -olefins.^{1,2} The use of ring-substituted η -cyclopentadienyl ligands in metallocenes has given rise to industrially useful isospecificities. For example, the ring substituents can control whether the polymerisation of propene gives iso- or syndio-tactic polymers.² There are claims that ring substituents can control the activity of substituted metallocene polymers.³ It is true that alkyl and other substituents on cyclopentadienyl rings of metallocenes can modify the activity of the metallocene catalyst and also they can alter the specificity of the mechanism for olefin polymerisation. However, there is a subtle interplay between the steric and electronic effects of ring substituents that at present does not allow accurate *a priori* prediction of ring-substitution effects and these can only be determined by experiment. Therefore, there is active research into a variety of ring-substituted cyclopentadienyl metallocenes in order to identify optimum compounds for use as catalyst precursors. In this context we have set out to synthesise and study the catalytic properties of binuclear metallocenes, as described below.

Previous studies on the synthesis of binuclear metallocenes were initiated by Petersen⁴ who reported that the reaction of the lithium salts $\text{Li}_2[\text{X}(\eta\text{-C}_5\text{H}_4)_2]$ (where $\text{X} = \text{CH}_2$ or SiMe_2) with $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]\cdot 2\text{THF}$ or $[\text{Zr}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_3]$ gave the binuclear compounds $[\{\text{Zr}(\eta\text{-C}_5\text{R}_5)\text{Cl}_2\}_2\{\text{X}(\eta\text{-C}_5\text{H}_4)_2\}]$ (where $\text{R} = \text{H}$ or Me). Reaction of this tetrachloride compound with $\text{LiAl}(\text{O}i\text{Bu})_3\text{H}$ yield the hydride-bridged complexes $[\{\text{Zr}(\eta\text{-C}_5\text{R}_5)\text{Cl}_2\}_2\{\text{X}(\eta\text{-C}_5\text{H}_4)_2\}(\mu\text{-H})_2]$.⁵ The related sulfide bridged compound $[\{\text{Zr}(\eta\text{-C}_5\text{R}_5)\}_2\{\text{X}(\eta\text{-C}_5\text{H}_4)_2\}(\mu\text{-S})_2]$ has been described.⁶ Binuclear zirconocenes with phenyl bridged *ansa*-ligands have been synthesized.⁷ The thallium salt $\text{Tl}_2[\text{Me}_2\text{Si}(\eta\text{-C}_5\text{H}_4)_2]$ with TiCl_4 yields the binuclear complex $[(\text{TiCl}_3)_2\{\text{Me}_2\text{Si}(\eta\text{-C}_5\text{H}_4)_2\}]$.^{8,9} Nifant'ev *et al.*¹⁰ reported the ligand exchange reaction between $[\text{TiCl}_2\{\text{Me}_2\text{X}(\eta\text{-C}_5\text{H}_4)_2\}]$ (where $\text{X} = \text{C}$ or Si) and TiCl_4 to give $[(\text{TiCl}_3)_2\{\text{Me}_2\text{X}(\eta\text{-C}_5\text{H}_4)_2\}]$. Related compounds in which the bridging system between the two cyclopentadienyl rings is $(\text{SiMe}_2)_2$ have been described.^{8,9,11}

Nifant'ev *et al.*¹² reported the monotransmetallation reaction of the *ansa*-bridged dimethyltin complex $[\text{SnMe}_2\{\text{Me}_2\text{Si}(\eta\text{-C}_5\text{H}_4)_2\}]$ with $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]\cdot 2\text{THF}$ or $[\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]$ to give $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{M}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{SnMe}_2\text{Cl}]$ ($\text{M} = \text{Ti}$ or Zr).

It has been shown that the reaction of the dilithium salt $[\text{Li}_2\{\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)\}]$ with one equivalent of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]\cdot \text{DME}$ produces a deep red mononuclear complex involving an indenyl ligand with an unprecedented η^2 mode of coordination confirmed by crystal structure determination.^{13,14} This complex reacts with $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]\cdot 2\text{THF}$ in refluxing toluene to afford the heterobinuclear complex $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\text{C}_9\text{H}_6)\}\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$ in good yield (80%).¹⁵

Nifant'ev *et al.*¹² reported that the compound $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Ti}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{SnMe}_2\text{Cl}]$ with $[\{\text{Rh}(\text{COD})\text{Cl}\}_2]$ gave the early-late heterobimetallic complex $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Ti}\{(\eta\text{-C}_5\text{H}_4)\text{SiMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{Rh}(\text{COD})]$.

Werner and co-workers have also reported a number of homo- and hetero-bimetallic complexes of the late transition metals using the ligand anion $[(\text{C}_5\text{H}_4)\text{CH}_2(\text{C}_5\text{H}_4)]^{2-}$ to give the complexes $[\text{M}(\text{CO})_2\{(\eta\text{-C}_5\text{H}_4)\text{CH}_2(\eta\text{-C}_5\text{H}_5)\}]$ ($\text{M} = \text{Rh}$ or Ir)^{16,17} and the heterobimetallic complexes $[(\text{OC})_2\text{M}\{(\eta\text{-C}_5\text{H}_4)\text{CH}_2(\eta\text{-C}_5\text{H}_4)\}\text{M}^*(\text{CO})_2]$ (where $\text{M}^* = \text{Rh}$ or Co) and $[(\text{OC})_2\text{M}\{(\eta\text{-C}_5\text{H}_4)\text{CH}_2(\eta\text{-C}_5\text{H}_4)\}\text{Ti}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$.^{17,18}

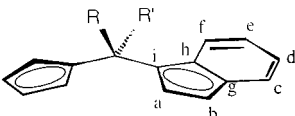
Preliminary reports of part of the present work have been published.^{13,15}

Results and discussion

Treatment of the previously described compound $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^2\text{-C}_9\text{H}_6)(\eta\text{-C}_5\text{H}_5)\text{Cl}\}]^{13-15}$ with $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ in diethyl ether gave orange crystalline $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ **1** in 60% yield. This complex is slightly air- and moisture-sensitive, fairly soluble in diethyl ether and soluble in toluene, THF and dichloromethane. The analytical and spectroscopic data for **1** and for all the other new compounds described in this work have been deposited (SUP) and selected illustrative data are given in Table 1. All these data will not be further discussed except where the interpretation is not straightforward. In many cases the assignments of the NMR data were assisted by COSY, heteronuclear decoupling and related experiments. When such experiments were carried out this is indicated either in the text or in SUP 57500. A fuller description of the data is available elsewhere.¹⁹

† *Supplementary data available:* full analytical and spectroscopic data. For direct electronic access see <http://www.rsc.org/suppdata/dt/1999/1049/>, otherwise available from BLDSC (No. SUP 57500, 12 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).

Table 1 Selected analytical and spectroscopic data

Compound and analysis ^a	Spectroscopic data ^b
3 [Cl ₂ (η-C ₅ H ₅)Hf{μ-(η-C ₅ H ₄)CMe ₂ (η-C ₉ H ₆)}Rh(CO) ₂] Yellow C, 41.5 (41.6) H, 3.0 (3.1) Cl, 10.4 (10.2)	¹ H: 7.34 [1 H, m, H _{c or f}], 7.25 [1 H, m, H _{c or f}], 7.11 [2 H, m, H _{d and e}], 6.58 [1 H, pseudo q, C ₅ H ₄], 6.42 [1 H, pseudo q, C ₅ H ₄], 6.36 [1 H, pseudo q, C ₅ H ₄ , partially obscured], 6.35 [5 H, s, C ₅ H ₅], 6.10 [1 H, pseudo q, C ₅ H ₄], 5.72 [1 H, t, J(HH) = J(RhH) 3, H _a], 5.59 [1 H, d, J(HH) 3, H _b], 2.08 [3 H, s, Me], 1.95 [3 H, s, Me] ¹³ C- ¹ H: 190.3 [d, J(RhC) 83, CO], 137.8 [s, C _{ipso}], 125.0 [s, C _{d or e}], 124.6 [s, C _{d or e}], 119.9 [s, C _{c or f}], 119.5 [s, C _{c or f}], 117.6 [s, C _{g, h or i}], 116.9 [s, C ₅ H ₄], 116.7 [s, C _{g, h or i}], 115.4 [s, C ₅ H ₄], 115.0 [s, C ₅ H ₅], 113.8 [s, C ₅ H ₄], 113.6 [s, C _{g, h or i}], 108.9 [s, C ₅ H ₄], 97.8 [d, J(RhC) 6, C _a], 71.0 [s, C _b], 37.5 [s, CMe ₂], 30.6 [s, Me], 30.3 [s, Me] Selected IR data; (CsI disc): ν(CO) 2037s, 1976s
	
7 [Cl ₂ (η-C ₅ H ₅ Zr){μ-(η-C ₅ H ₄)CMe ₂ (η-C ₉ H ₆)}Rh(PPh ₃) ₂] Orange C, 64.3 (64.9) H, 4.6 (4.7) Cl, 6.9 (6.6)	¹ H: 7.46 [1 H, partially obscured, H _{c or f}], 7.43 [12 H, m, PPh ₃], 7.02 [1 H, t, H _{d or e}], 6.95 [18 H, m, PPh ₃], 6.81 [1 H, t, J(HH) 8, H _{d or e}], 6.21 [1 H, d, J(HH) 8, H _{c or f}], 6.46 [1 H, pseudo q, C ₅ H ₄], 6.45 [1 H, pseudo q, C ₅ H ₄], 6.02 [1 H, pseudo q, C ₅ H ₄], 5.96 [1 H, t, J(RhH) = J(HH) 2.5, H _a], 5.84 [5 H, s, C ₅ H ₅], 5.54 [1 H, pseudo q, C ₅ H ₄], 4.25 [1 H, d, J(HH) 2.5, H _b], 2.21 [3 H, s, Me], 2.18 [3 H, s, Me] ¹³ C- ¹ H (125.7 MHz): 141.2 [s, C _{ipso} C ₅ H ₄], 123.1 [s, C _{d or e}], 122.7 [s, C _{d or e}], 118.8 [s, C _{c or f}], 118.3 [s, C _{c or f}], 117.3 [s, C ₅ H ₄], 116.8 [s, 2 × C ₅ H ₄], 116.2 [s, C ₅ H ₄], 116.0 [s, C ₅ H ₅], 110.5 [s, C ₅ H ₄], 98.4 [m, C _a], 76.7 [m, C _b], 31.8 [s, Me], 31.2 [s, Me] ³¹ P- ¹ H (200 MHz, C ₆ D ₆): 47.5 [d, J(RhP) 200]
10 [Cl ₂ (η-C ₅ H ₅)Zr{μ-(η-C ₅ H ₄)CMe ₂ (η-C ₉ H ₆)}Ru(η-C ₄ H ₇)(CO)] Yellow C, 50.7 (51.3) H, 3.9 (4.5)	¹ H: (500 MHz): 6.96 [1 H, d, J(HH) 8, H _{c or f}], 6.64 [1 H, d, J(HH) 8, H _{c or f}], 6.43 [1 H, t, J(HH) 8, H _{d or e}], 6.41 [1 H, t, J(HH) 8, H _{d or e}], 6.38 [1 H, pseudo q, C ₅ H ₄], 6.28 [1 H, pseudo q, C ₅ H ₄], 5.88 [5 H, s, C ₅ H ₅], 5.81 [1 H, pseudo q, C ₅ H ₄], 5.57 [1 H, pseudo q, C ₅ H ₄], 5.49 [1 H, d, J(HH) 3, H _a], 4.92 [1 H, d, J(HH) 3, H _b], 3.47 [1 H, m, H _{syn} , (CH ₂) ₂ CMe], 3.40 [1 H, m, H _{syn} , (CH ₂) ₂ CMe], 2.07 [3 H, s, Me], 1.97 [3 H, s, Me], 1.66 [3 H, s, (CH ₂) ₂ CMe], -0.29 [1 H, s, H _{anti} , (CH ₂) ₂ CMe], -0.31 [1 H, s, H _{anti} , (CH ₂) ₂ CMe] ¹³ C- ¹ H (125.7 MHz): 204.3 [br s, CO], 139.7 [s, C _{ipso}], 124.8 [s, C _{d or e}], 124.6 [s, C _{c or f}], 124.5 [s, C _{d or e}], 124.3 [s, C _{c or f}], 117.4 [s, C ₅ H ₄], 116.9 [s, C ₅ H ₄], 115.9 [s, C ₅ H ₅], 113.8 [s, C ₅ H ₄], 112.0 [s, C _{g, h or i}], 110.9 [s, C ₅ H ₄], 110.5 [s, C _{g, h or i}], 106.3 [s, C _{g, h or i}], 86.4 [s, C _a], 64.8 [s, C _b], 49.8 [s, (CH ₂) ₂ CMe], 49.1 [s, (CH ₂) ₂ CMe], 37.7 [s, CMe ₂ or (CH ₂) ₂ CMe], 37.4 [s, CMe ₂ or (CH ₂) ₂ CMe], 31.3 [s, Me], 31.1 [s, Me], 24.6 [s, (CH ₂) ₂ CMe] Selected IR data (CsI disc): ν(CO) 1912s
13 [Cl ₂ (η-C ₅ H ₅)Zr{μ-(η-C ₅ H ₄)C(CH ₂) ₂ (η-C ₉ H ₆)}Zr(η-C ₅ H ₅)Cl ₂] Yellow C, 50.2 (50.4) H, 4.2 (4.2) Cl, 20.0 (19.8)	¹ H (500 MHz): 7.90 [1 H, d, J(HH) 8, H _{c or f}], 7.56 [1 H, d, J(HH) 8, H _{c or f}], 7.31 [1 H, t, J(HH) 8, H _{d or e}], 7.19 [1 H, t, J(HH) 8, H _{d or e}], 7.04 [1 H, d, J(HH) 3, H _a], 6.87 [1 H, pseudo q, J(HH) 3, C ₅ H ₄], 6.77 [1 H, d, J(HH) 3, H _b], 6.71 [1 H, pseudo q, J(HH) 3, C ₅ H ₄], 6.50 [1 H, pseudo q, J(HH) 3, C ₅ H ₄], 6.36 [5 H, s, ZrCp], 6.35 [1 H, pseudo q, J(HH) 3, C ₅ H ₄], 5.87 [5 H, s, Cp of Zr(C ₉ H ₆)], 2.94 [1 H, m, cyclohexyl], 2.71 [2 H, m, cyclohexyl], 2.35 [1 H, m, cyclohexyl], 1.78 [1 H, m, cyclohexyl], 1.68 [1 H, m, cyclohexyl], 1.47 [2 H, m, cyclohexyl], 1.40 [1 H, m, cyclohexyl], 0.84 [1 H, m, cyclohexyl] ¹³ C- ¹ H (125.7 MHz): 143.8 [s, C _{ipso} of C ₅ H ₄], 127.1 [s, C _{g, h or i}], 126.9 [s, C _{c or f}], 126.4 [s, C _{d or e}], 126.0 [s, C _{c or f}], 125.7 [s, C _a], 124.9 [s, C _{d or e}], 123.9 [s, C _{g, h or i}], 117.7 [s, Cp of Zr(C ₉ H ₆) and C ₅ H ₄], 117.3 [s, C ₅ H ₄], 116.7 [s, ZrCp], 116.2 [s, C ₅ H ₄], 112.0 [s, C ₅ H ₄], 103.3 [s, C _b], 95.3 [s, C _{g, h or i}], 42.9 [s, C(CH ₂) ₂], 36.6 [s, cyclohexyl], 35.8 [s, cyclohexyl], 25.5 [s, cyclohexyl], 23.7 [s, cyclohexyl], 22.7 [s, cyclohexyl]
19 [Cl(η-C ₅ H ₅)Hf{μ-(η-C ₅ H ₄)CMe ₂ (η-C ₉ H ₆)}(μ-O)Zr(η-C ₅ H ₅)Cl] White C, 46.3 (45.9) H, 3.6 (3.7) Cl, 8.7 (10.0)	¹ H: 8.08 [1 H, d, J(HH) 9, H _{c or f}], 7.91 [1 H, d, J(HH) 9, H _{c or f}], 7.90 [1 H, d, J(HH) 9, H _{c or f}], 7.70 [1 H, d, J(HH) 9, H _{c or f}], 7.34 [1 H, t, J(HH) 9, H _{d or e}], 7.29 [1 H, m, H _{d or e}], 7.28 [1 H, m, H _{d or e}], 7.15 [1 H, d, J(HH) 9, H _{d or e}], 6.77 [1 H, d, J(HH) 2.5, H _a], 6.75 [1 H, pseudo q, C ₅ H ₄], 6.56 [1 H, d, J(HH) 2.5, H _a], 6.54 [1 H, pseudo q, C ₅ H ₄], 6.45 [1 H, pseudo q, C ₅ H ₄], 6.41 [1 H, pseudo q, C ₅ H ₄], 6.39 [1 H, pseudo q, C ₅ H ₄], 6.33 [1 H, d, J(HH) 3, H _b], 6.31 [5 H, s, Cp], 6.26 [5 H, s, Cp], 6.22 [1 H, m, C ₅ H ₄], 6.21 [1 H, m, H _b], 6.18 [5 H, s, Cp], 5.93 [1 H, m, C ₅ H ₄], 5.92 [1 H, m, C ₅ H ₄], 5.64 [5 H, s, Cp], 1.81 [3 H, s, Me], 1.80 [3 H, s, Me], 1.62 [3 H, s, Me], 1.58 [3 H, s, Me] ¹³ C- ¹ H (125.7 MHz): 126.3 [s, C _{c or f}], 126.2 [s, C _{c or f}], 124.5 [s, 2x C _{c or f}], 125.2 [s, C _{d or e}], 125.1 [s, C _{d or e}], 124.9 [s, 2x C _{d or e}], 122.7 [s, C _a], 122.2 [s, C _a], 117.6 [s, C ₅ H ₄], 116.4 [s, Cp], 113.6 [s, Cp], 113.2 [s, Cp], 113.1 [s, Cp], 113.1 [s, C ₅ H ₄], 110.9 [s, C ₅ H ₄], 109.7 [s, C ₅ H ₄], 108.0 [s, C ₅ H ₄], 106.5 [s, C ₅ H ₄], 106.4 [s, C ₅ H ₄], 104.0 [s, C ₅ H ₄], 98.9 [s, C _i], 95.3 [s, C _b], 32.9 [s, 2x CMe ₂], 31.8 [s, CMe ₂], 3.06 [s, CMe ₂] Selected IR data: (M-O-M) 768s, 748s; bridging ligand 808s

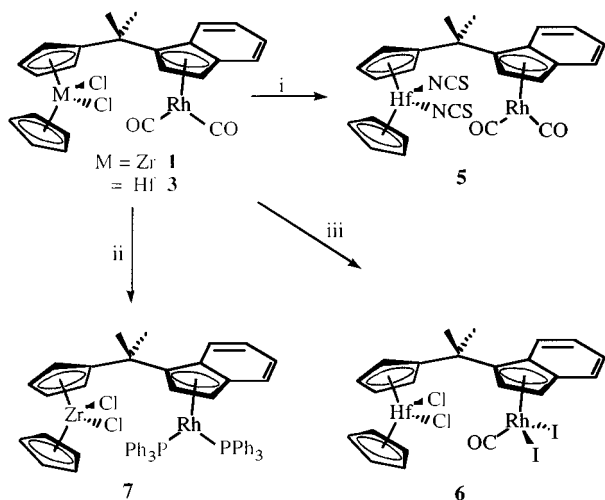
^a Analytical data given as: found (required) %. ^b ¹H NMR data given for 300 MHz, ¹³C NMR at 72.5 MHz unless otherwise stated. All at room temperature. Data given as: chemical shift (δ) [relative intensity, multiplicity *J* in Hz, assignment]. Cp indicates η-C₅H₅. ^c In CD₂Cl₂. ^d In C₆H₆.

The ¹H NMR spectrum of compound **1** shows two resonances at δ 2.08 and 1.95 assignable to the two inequivalent methyl groups of the bridging ligand. The infrared spectrum shows the expected two strong bands at 2038 and 1985 cm⁻¹ in good agreement with those at 2050 and 1989 cm⁻¹ observed for [Rh(η-C₉H₇)(CO)₂].²⁰

The reaction of [{Rh(CO)₂Cl}]₂ with [Zr{(4-Bu^t-C₆H₉)(η-C₅H₄)(η²-C₉H₆)}(η-C₅H₅)Cl] (see below) gives [Cl₂(η-C₅H₅)Zr{μ-(η-C₅H₄)(4-Bu^t-C₆H₉)(η-C₉H₆)}Rh(CO)₂] **2** as an orange solid in 62% yield. The compound is slightly air- and moisture-sensitive. Treatment of [Hf{(η-C₅H₄)CMe₂(η²-C₉H₆)}(η-C₅H₅)Cl] with [{Rh(CO)₂Cl}]₂ in diethyl ether gave a yellow precipitate of [Cl₂(η-C₅H₅)Hf{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Rh(CO)₂] **3** in an overall yield of 72%. Similarly, addition of [{Rh(CO)₂Cl}]₂ in toluene to [Zr{Me₂C(η-C₅H₄)₂}(η-C₅H₅)Cl] in toluene gave dark orange [Cl₂(η-C₅H₅)Zr{μ-(η-C₅H₄)CMe₂(η-C₅H₄)}Rh(CO)₂] **4** in 76% yield.

A suspension of [{Rh(CO)₂Cl}]₂ in diethyl ether was added to an ether solution of [Zr{(η-C₅H₄)CMe₂(η³-C₁₃H₈)}(η-C₅H₅)Cl]¹³ at room temperature. The solution gradually darkened over several days and a brown precipitate appeared. The reaction mixture was filtered and the precipitate dried *in vacuo*. This material was shown to be the complex [Zr{(η-C₅H₄)CMe₂(C₁₃H₉)}(η-C₅H₅)Cl]₂ by comparison of the ¹H NMR spectrum with that of an authentic sample.¹³

The compound [Cl₂(η-C₅H₅)Hf{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Rh(CO)₂] **3** in dichloromethane was treated with a suspension of two equivalents of KNCS, also in dichloromethane at 0 °C. This gave orange microcrystalline [(SCN)₂(η-C₅H₅)(Hf){μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Rh(CO)₂] **5** in 67% yield (Scheme 1). The IR spectrum shows three bands near 2000 cm⁻¹, at 2040, 2002 and 1974 cm⁻¹. The starting compound **3** has two carbonyl bands at 2037 and 1976 cm⁻¹, and the values for the ν(CN) stretch in dichloromethane solution for the complex



Scheme 1 i, KCNs in dichloromethane at room temperature (r.t.) and for 24 h, yield 67%; ii, PPh₃ in toluene at r.t. for 24 h, 54%; iii, I₂ in THF at r.t. for 3 h, 51%.

[Hf(η-C₅H₅)₂(NCS)₂] are 2049 and 2011 cm⁻¹.²¹ It thus appears that the IR spectrum can be understood by the superimposition of these two spectra, assuming there is an overlap of the two highest wavenumber bands.

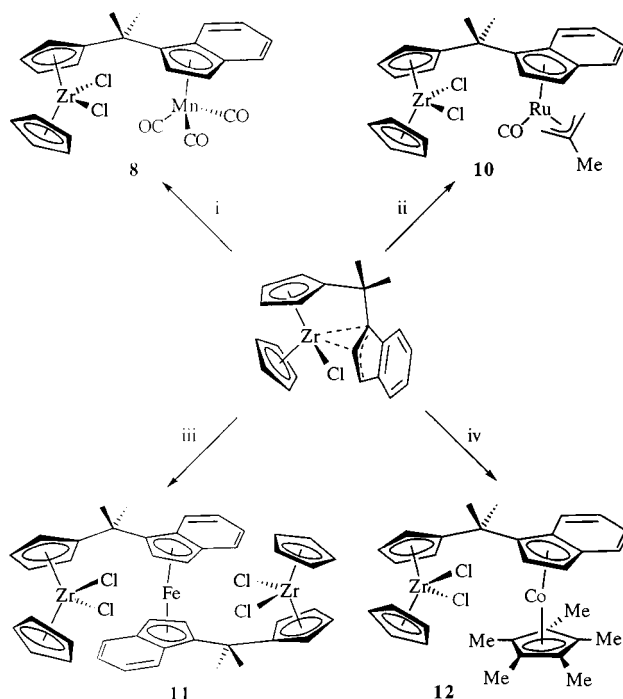
Compound **3** in THF was treated with iodine to give black microcrystalline [Cl₂(η-C₅H₅)Hf{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}-Rh(CO)I₂] **6** in 51% yield. The presence of the carbonyl ligand in **6** was confirmed by a single band in the IR spectrum, ν(CO) 2063 cm⁻¹.

A toluene solution of [Cl₂(η-C₅H₅)Zr{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Rh(CO)₂] **1** was treated with two equivalents of PPh₃ at room temperature to give orange [Cl₂(η-C₅H₅)Zr{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Rh(PPh₃)₂] **7** in 54% yield. The ³¹P NMR spectrum showed a doublet (*J* = 200 Hz) at δ 47.5 due to coupling with the ¹⁰³Rh nucleus. As expected, the IR spectrum showed no bands assignable to the presence of CO ligands.

The compound [Mn(CO)₅Cl] in THF was added dropwise to a THF solution of [Zr{Me₂C(η-C₅H₄)(η²-C₉H₆)}(η-C₅H₅)Cl]¹³ at room temperature to give orange-yellow [Cl₂(η-C₅H₅)Zr{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Mn(CO)₃] **8** in 66% yield (Scheme 2). The compound **8** is slightly air and moisture sensitive. The infrared spectrum showed strong bands assignable to ν(CO) at 2012, 1935 and 1920 cm⁻¹. This indicates that the two e symmetry vibrations are not degenerate in this molecule, contrary to the expectation for local C_{3v} molecular symmetry. This implies that there is a degree of asymmetry in the indenyl-metal bonding, in a similar fashion to that found for some rhodium compounds [Rh(η-C₉H₇)L₂]. Three carbonyl stretching frequencies are also observed for the compound [Mn(η-C₉H₇)(CO)₃],²² at 2023, 1950 and 1930 cm⁻¹, and they are all between 10 and 15 cm⁻¹ higher than those for compound **8**, suggesting that in the bimetallic system there is greater metal-ligand back donation into the antibonding CO orbitals.

When the hafnium complex [Hf{μ-(η-C₅H₄)CMe₂(η²-C₉H₆)}(η-C₅H₅)Cl]¹³ was treated with [Mn(CO)₅Cl] in THF the yellow compound [Cl₂(η-C₅H₅)Hf{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Mn(CO)₃] **9** was formed.

Addition of [Ru(η-C₄H₇)(CO)₃Cl] in THF to [Zr{(η-C₅H₄)CMe₂(η²-C₉H₆)}(η-C₅H₅)Cl] yielded the yellow binuclear compound [Cl₂(η-C₅H₅)Zr{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Ru(CO)(η-CH₂CMeCH₂)] **10** in 39% yield. The NMR assignments were confirmed by a COSY spectrum, and a ¹³C-¹H heteronuclear shift correlation spectrum. These data are all indicative of there being only one isomer formed in this reaction. In the case of both [Ru(η-C₅H₅)(η-C₃H₅)(CO)] and its methylallyl analogue, the *exo* isomer was characterised by a CO stretching



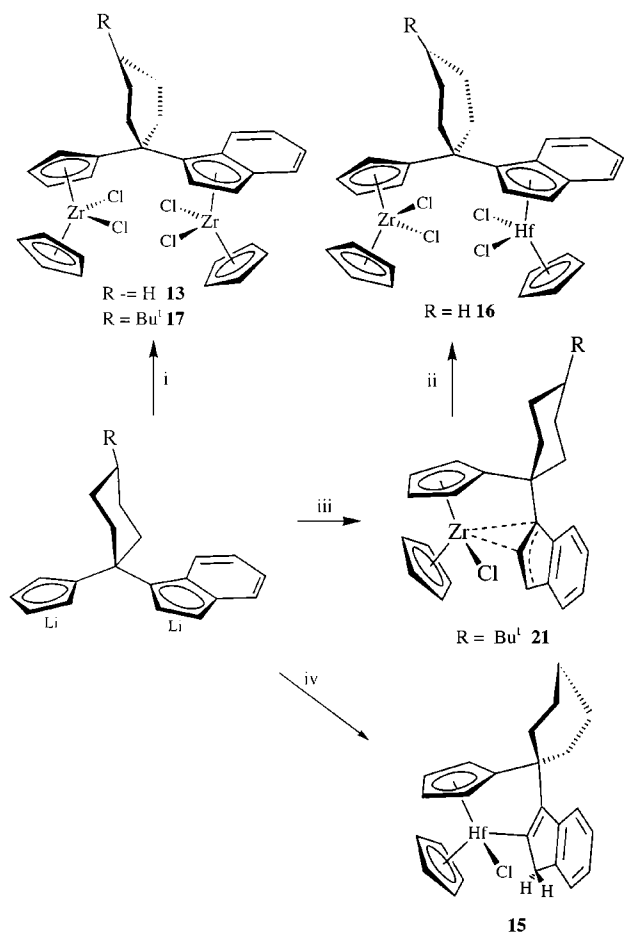
Scheme 2 i, [Mn(CO)₅Cl] in THF at 60 °C for 5 h, yield 66%; ii, [Ru(η-C₄H₇)(CO)₃Cl] in THF at 60 °C for 3 h, 39%; iii, FeCl₂·1.5THF, reflux for 3 h, 42%; iv, [Co(η-C₅Me₅)Cl]₂ in THF at -78 °C, warm to r.t. for 4 h, 58%.

frequency in hexane solution of around 1955–1960 cm⁻¹, whilst the *endo*-isomer was characterised by one of around 1930–1935 cm⁻¹.²³ The IR spectrum of **10** as a CsI disc shows a peak at 1912 cm⁻¹ indicative of an *endo* isomer. In order to attempt to confirm this assignment a NOESY spectrum was obtained. This allowed assignment of the methyl resonance of the allyl ligand at δ 1.66, and the magnitude of the correlations confirmed the assignment of the *syn*- and *anti*- protons of the allyl ligand. However, no correlations were observed between any of the signals of the indenyl ligand and those of the allyl ligand. Although not definitive evidence for the *endo* isomer, a close proximity of the methyl group of the allyl ligand to the indenyl ring in the *exo* isomer would be expected to result in the appearance of a correlation in a NOESY spectrum.

The compounds [Zr{(η-C₅H₄)CMe₂(η²-C₉H₆)}(η-C₅H₅)Cl]¹³ and FeCl₂·1.5THF in THF gave brown microcrystalline [Fe{μ-(η-C₉H₆)CMe₂(η-C₅H₄)Zr(η-C₅H₅)Cl₂}₂] **11** in 42% yield. The compound **11** appears to decompose slowly in solution at room temperature. The ¹H NMR spectrum showed that only one isomer was present and a COSY spectrum allowed the assignment of all the resonances but not the determination of which isomer was present. Addition of [Zr{(η-C₅H₄)CMe₂(η²-C₉H₆)}(η-C₅H₅)Cl]¹³ in THF at -78 °C to a solution of one equivalent of [Co(η-C₅Me₅)Cl]₂ in THF gave black microcrystals of [Cl₂(η-C₅H₅)Zr{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Co(η-C₅Me₅)] **12** in 58% yield. The ESR spectrum of a solid sample of this compound at room temperature shows an isotropic lineshape, though with a small degree of asymmetry, which, by comparison with the position of the diphenylpicrylhydrazyl standard gives *g*_{iso} = 2.01. Cobaltocene²⁴ and decamethylcobaltocene²⁵ gave no ESR spectra at room temperature and this was attributed to rapid relaxation from the degenerate electronic ground state e⁴a²e¹. The observation of a spectrum at room temperature for **12** may reflect the low symmetry of the indenyl ligand with a consequential lifting of the degeneracy of the ground state. The ESR spectrum of **12** in toluene solution at room temperature had a lineshape characteristic of an axially

symmetric system;²⁵ $g_1 = 2.131$ and $g_2 = 1.915$. The spectrum was complicated by poorly resolved hyperfine coupling, with a coupling constant, $A = 50$ G.

The dilithium salt $\text{Li}_2[(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)] \cdot 0.8\text{Et}_2\text{O}$ ¹⁴ when added to two equivalents of $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot \text{DME}$ gave the yellow bimetallic complex $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{-C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$ **13** in 62% yield (Scheme 3).



Scheme 3 i, For complex **13**, $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot \text{DME}$ at -78°C , add toluene at -78°C , warm to r.t., heat to 105°C for 24 h, yield 62%; ii, $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$ at r.t., then 105°C for 24 h, 58%; iii, $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot \text{DME}$ at -78°C , add toluene at -78°C , warm to r.t. for 14 h, 86%; iv, $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$ in toluene at r.t., then heat to 120°C for 16 h, ca. 20%.

Addition of toluene to a mixture of the dilithium salt $\text{Li}_2[(\text{C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\text{C}_9\text{H}_6)] \cdot 0.8\text{Et}_2\text{O}$ and slightly less than two equivalents of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$ at -78°C gave pale yellow $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{HfCl}_2(\eta\text{-C}_5\text{H}_5)]$ **14** in 68% yield. The ^1H NMR spectrum is extremely similar to that of the dizirconium complex **13**. The low field region of the ^{13}C NMR spectrum is also similar to that of the dizirconium analogue: the resonances assigned to the C_5H_5 ligands occur at δ 116.3 and 115.8. The C_5H_4 carbons give rise to bands at δ 115.4, 115.0, 114.6 and 110.8, with those of the C_5 ring of the indenyl ligand being at δ 125.6 and 114.8. The bands due to the carbons of the C_6 ring of the indenyl ligand lie at 127.1, 126.5, 125.9 and 124.7: these signals were assigned with the aid of a $^{13}\text{C}\text{-}^1\text{H}$ heteronuclear shift correlation spectrum.

In an attempted preparation of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$ toluene was added to a mixture of dilithium salt $\text{Li}_2[(\text{C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\text{C}_9\text{H}_6)] \cdot 0.8\text{Et}_2\text{O}$ and $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$ at room temperature. The resulting mixture was heated to 120°C for 16 h by which time a pale yellow solution was formed with a pale precipitate. The ^1H

NMR spectrum of the yellow product was different from that found for the expected bimetallic complex. It was complicated by the presence of a small amount of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$. Nonetheless the most obvious feature was the presence of two roofed doublets at δ 3.62 and 3.32. These signals were very closely similar to those observed from the product of the reaction between $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ and $[\text{Y}(\eta\text{-C}_5\text{H}_5)_2]$ namely the compound $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^1\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$. In this reaction a hydrogen has been transferred from the bonding CH group of the η^2 -indenyl ligand to the second and adjacent CH group. This results in the formation of a CH_2 group and an η^1 -vinylic system.²⁶

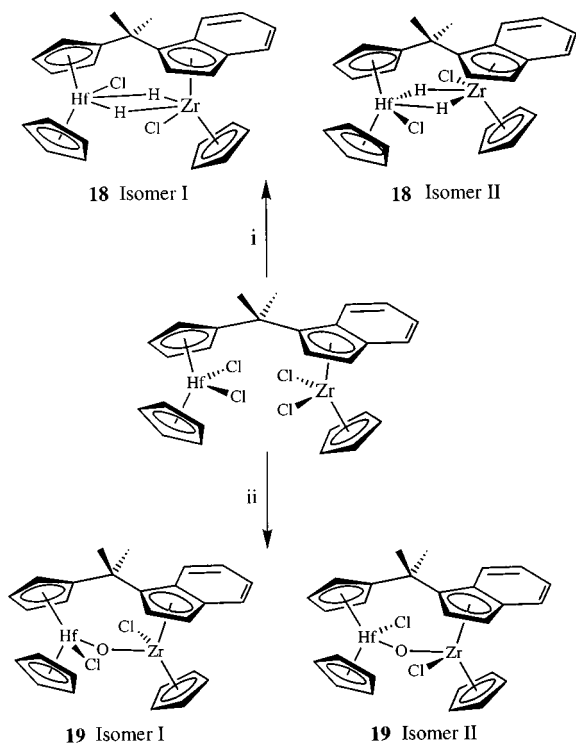
The spectrum of complex **15** shows the presence of a band assignable to the $\eta\text{-C}_5\text{H}_5$ ligand at δ 6.26 and four signals assigned to the C_5H_4 ligand at δ 6.43, 6.20, 6.08 and 5.72, the latter being at rather high field for such a proton. The resonances assignable to the C_6 ring of the indenyl ligand are a pair of doublets at δ 7.68 and 7.39 and a pair of triplets at δ 7.23 and 7.14. In the high field region of the spectrum the resonances consisted of two broad multiplets at δ 1.42 and 1.67, two doublets at δ 1.96 and 2.25 and two triplets at δ 2.38 and 2.54. The structure proposed for the compound $[\text{Hf}\{(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta^1\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ **15** is illustrated in Scheme 3.

The complex $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ ¹⁵ was treated with one equivalent of $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$ to give the yellow heterobimetallic compound $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$ **16** in 58% yield. The ^1H NMR spectrum is similar to those of the homobimetallic complexes **13** and **14**. In particular, the resonance assignable to the C_5H_5 ligand bonded to the zirconium atom occurs at δ 6.36, identical to the low field C_5H_5 resonance of the dizirconium complex **13**; and the resonance assignable to the $\eta\text{-C}_5\text{H}_5$ ligand bonded to the hafnium atom occurs at δ 5.71, virtually identical to that of the high field resonance observed for the dihafnium complex **14**. This is strong evidence that compound **16** is indeed the heterobimetallic analogue of **13** and **14**, with the zirconium exclusively bonded to the C_5H_4 ring of the bridging ligand and the hafnium bonded exclusively to the indenyl ligand. The other resonances in the ^1H NMR spectrum also correspond closely to those of **13** and **14**. The ^{13}C NMR spectrum was also very similar to those of the homobimetallic complexes described earlier; the resonances assigned to the C_5H_5 ligands are at δ 116.8, almost identical to the value of the C_5H_4 ring bound to the zirconium in **13**, and δ 116.3, identical to that found for the indenyl ring bound to the hafnium in **14**. This further confirms the analogous nature of compounds **13**, **14** and **16**.

It was decided to investigate the effect of increasing bulk of the bridging system on the polymerisation behaviour of these bimetallic species. The dilithium salt $\text{Li}_2[(\eta\text{-C}_5\text{H}_4)(4\text{-Bu}^t\text{-C}_6\text{H}_{10})(\eta\text{-C}_9\text{H}_6)] \cdot 0.8\text{Et}_2\text{O}$ was prepared and added to the compound $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot \text{DME}$ at -78°C . Yellow crystals of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)(4\text{-Bu}^t\text{-C}_6\text{H}_9)(\eta\text{-C}_9\text{H}_6)\}\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$ **17** was formed in 74% yield.

A solution of two equivalents of $\text{LiAl}(\text{O}i\text{Bu})_3\text{H}$ in THF was slowly added to a solution of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$ ¹⁵ also in THF, at room temperature giving the pale binuclear dihydride $[\text{Cl}(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}(\mu\text{-H})_2\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ **18**. The ^1H NMR spectrum of **18** shows that only one of the possible isomers of this compound is present (see Scheme 4). The IR spectrum shows a broad band centred around 1490 cm^{-1} which can be assigned to vibrations of the hydride ligands. A similar band centred at 1390 cm^{-1} is observed for the species $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{H}(\text{Cl})]$.²⁷

A solution of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$ ¹⁵ in dichloromethane was treated, at room temperature, with an equimolar quantity of water followed by a further equimolar quantity of aniline. The addition of the



Scheme 4 i, $\text{LiAl}(\text{OBu}^t)_3\text{H}$ in THF at r.t. for 3 h, yield 25%, two possible isomers are shown; ii, in dichloromethane, add degassed water and aniline; stir for 1 h at r.t., 77%, two possible isomers are shown.

aniline gave an immediate white precipitate of $[\text{Cl}(\eta\text{-C}_5\text{H}_5)\text{-Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\{\mu\text{-O}\}\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ **19**. The ^1H NMR spectrum shows the presence of four peaks assignable to $\eta\text{-C}_5\text{H}_5$ ligands and this is indicative of the presence of two isomers of the complex. The proposed isomers are shown in Scheme 4. The ^{13}C NMR spectrum is complicated by the presence of two isomers. Four signals assigned to cyclopentadienyl rings are observed, at δ 116.4, 113.6, 113.2 and 113.1. Examination of the $^{13}\text{C}\text{-}^1\text{H}$ heteronuclear shift correlation spectrum shows that the low field resonance of these four is the one which correlates to the high field cyclopentadienyl resonance in the ^1H spectrum. The IR spectrum shows bands at 768 and 748 cm^{-1} assignable to the vibrations of the bridging oxo-ligand.²⁸

The *ansa*-bridged zirconocene $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)_2\}\text{Cl}_2]$ was treated with a suspension of $\text{K}(\text{C}_5\text{H}_4\text{Me})$ in THF to give the desired tris- η -cyclopentadienyl compound $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_4\text{Me})\text{Cl}]$ **20**, as a very pale yellow solid. The assignments for **20** were confirmed by a COSY NMR spectrum, and 500 MHz inverse-detection $^1\text{H}\text{-}^{13}\text{C}$ heteronuclear shift correlation spectrum in C_6D_6 at r.t. Variable temperature ^1H and ^{13}C NMR spectra in solution revealed no slowing of any fluxional processes down to -90°C . The dilithium salt of the *ansa*-ligand $\text{Li}_2[(4\text{-Bu}^t\text{-C}_6\text{H}_9)(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]$ was prepared and one equivalent was mixed with the pure compound $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]\cdot\text{DME}$. Toluene was added at -78°C to give a deep red reaction mixture from which air- and moisture-sensitive red crystals of $[\text{Zr}\{(4\text{-Bu}^t\text{-C}_6\text{H}_9)(\eta\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ **21** were obtained. The ^1H NMR spectrum showed that only one diastereomer was present. The $^{13}\text{C}\text{-}^1\text{H}$ heteronuclear shift correlation spectrum allows the assignment of the signals of the bridging cyclohexyl system and the ^{13}C DEPT spectrum shows clearly the presence of the carbon atoms of the four CH_2 groups of the cyclohexyl ring and allows easy assignment of the carbon atom to which the Bu^t group is bonded; this resonance is at δ 48.3. The $^{13}\text{C}\text{-}^1\text{H}$ heteronuclear shift correlation spectrum shows a large correlation between the signals assigned to the Bu^t ligand, four carbon resonances with correlations to two proton resonances and a carbon resonance with a single correlation in the proton spectrum.

Polymerisation studies

Eleven of the new metallocenes described above have been examined as catalyst precursors for ethylene polymerisation. The polymerisation experiments were carried out under the conditions described by Kaminsky *et al.*²⁹ namely, using 2 bar monomer pressure at 30°C in toluene solvent and 6.25×10^{-6} mol of catalyst with a $[(\text{MeAlO})_n]$ (MAO): metallocene ratio of 830:1. They were performed at least twice and found to be reproducible.

The data show that the relative activities of the rhodium and manganese carbonyl-containing complexes [Table 2(a)] are all lower than those of both the dizirconium complexes and very much lower than the $60900 \text{ kg PE mol}^{-1} \text{ h}^{-1} \text{ C}_{\text{mon}}^{-1}$ found by Kaminsky *et al.*²⁹ for the $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]\text{-MAO}$ system under the same conditions. There was no appreciable deactivation of the catalytic systems over the 1 h period of each experiment.

Table 2(c) shows that the early-late binuclear complexes **11** and **12** have activities approaching those of the $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]\text{-MAO}$ system. Indeed, the polymerisation was so rapid that the experiment had to be abandoned after a short time since the quantity of polymer produced caused the stirring of the reaction to stop. The viscous nature of the solution may also cause a slowing of the diffusion of the monomer to the catalytic centres and a reduction of the magnitude and speed of dissolution of ethene in the toluene, and the activities for these very active catalysts are likely to be underestimates.

The data in Table 2(d) also show that replacing the CMe_2 bridging system by a cyclohexyl system causes a rise in the polymerisation activity. In the case of the dihafnium and zirconium-hafnium binuclear compounds the increase in the activity is between 40 and 50%, whereas the increase in the dizirconium system is almost 100%. In addition, the dizirconium compound with a $4\text{-Bu}^t\text{-C}_6\text{H}_9$ bridging system is more active than the cyclohexyl complex, with a relative activity of $3530 \text{ kg PE mol}^{-1} \text{ h}^{-1} \text{ C}_{\text{mon}}^{-1}$. This is more than twice that observed for the mononuclear *ansa*-bridged complex with the same bridging ligand, namely $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)(\eta\text{-C}_9\text{H}_6)\}\text{Cl}_2]$, with a relative activity of $1550 \text{ kg PE mol}^{-1} \text{ h}^{-1} \text{ C}_{\text{mon}}^{-1}$.²⁹ The higher activity of the zirconium with respect to the hafnium-containing species is interpreted in terms of the increased bond enthalpy of a Hf-C ($\approx 306 \text{ kJ mol}^{-1}$) compared with a Zr-C bond ($\approx 284 \text{ kJ mol}^{-1}$), which results in the insertion being more difficult for hafnium catalysts.³⁰

Propene. Polymerisation conditions were identical to those for ethene (210 cm^3 toluene solvent, 30°C , 2 bar monomer pressure). Previous studies on binuclear catalysts of this type for the polymerisation of propene revealed that only a very small quantity of polymer was produced when a similar quantity of catalyst and MAO were used (6.25×10^{-6} mol and 0.3 g respectively).¹⁴ To improve the yield of polymer, eight times this amount of catalyst was used. This increase, whilst allowing direct comparison with the previously studied binuclear catalysts, does make direct comparison with the results of Kaminsky's study somewhat less valid, although cautious comparisons can still be made.²⁹

The yields and activities of the carbonyl-containing complexes for the polymerisation of propene are given in Table 3. The data show that the relative activities exhibited by the new complexes are very low. The relative activity for propene polymerisation of the $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2]\text{-MAO}$ system is $140 \text{ kg PP mol}^{-1} \text{ h}^{-1} \text{ C}_{\text{mon}}^{-1}$, and values of over $1000 \text{ kg PP mol}^{-1} \text{ h}^{-1} \text{ C}_{\text{mon}}^{-1}$ have been obtained for some of the highly stereospecific mononuclear *ansa*-zirconocene complexes.²⁹

The new complexes listed in Table 3 all show a similar activity with the exception of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{-CMe}_2(\eta\text{-C}_5\text{H}_4)\}\text{Rh}(\text{CO})_2]$ which shows a surprisingly higher activity for the polymerisation of propene, the reason for which is not clear.

Table 2 Polymerisation of ethylene

Compound	X	Ring	Yield/g	Activity/ kg PE mol ⁻¹ h ⁻¹	Relative activity/ kg PE mol ⁻¹ h ⁻¹ C _{mon} ⁻¹
(a) [Cl ₂ (η-C ₅ H ₅)Zr(η-C ₅ H ₄)X(Ring)] Rh(CO) ₂					
1	CMe ₂	C ₉ H ₆	0.85	136	580
2	^t BuC ₆ H ₉	C ₉ H ₆	0.28	45	191
4	CMe ₂	η-C ₅ H ₅	0.75	120	512
(b) [Cl ₂ (η-C ₅ H ₅){(η-C ₅ H ₄)CMe ₂ (C ₉ H ₆)}X]					
8^a	Mn(CO) ₃		1.37	219	935
10	Ru(C ₄ H ₇)(CO)		1.55	248	1060
^a	ZrCl ₂ (η-C ₅ H ₅)		2.14	342	1460
^a	H		4.94	790	3360
(c) [{Cl ₂ (η-C ₅ H ₅)Zr{(η-C ₅ H ₄)CMe ₂ (C ₉ H ₆)} _n X]					
11^b	Fe	<i>n</i> = 2	1.76	3137	13350
12^b	Co(η-C ₅ Me ₅)	<i>n</i> = 1	1.52	4168	17730
^b	H	<i>n</i> = 1	4.94	790	3360
CoCp ₂ ^b			0.03	5	20
(d) [Cl ₂ (η-C ₅ H ₅)Zr{(η-C ₅ H ₄)X(C ₉ H ₆)}Zr(η-C ₅ H ₅)Cl ₂]					
^a	Zr Zr	CMe ₂	2.14	342	1460
13^a	Zr Zr	(CH ₂) ₅	4.20	671	2870
17^a	Zr Zr	^t BuC ₆ H ₉	5.18	828	3530
^a	Hf Hf	CMe ₂	0.59	94	400
14^a	Hf Hf	(CH ₂) ₅	0.96	153	655
^a	Zr Hf	CMe ₂	1.69	270	1150
16^a	Zr Hf	(CH ₂) ₅	2.27	363	1550

^a At 2 bar absolute monomer pressure, 30 °C, 210 cm³ toluene solution, 1 h, 6.25 × 10⁻⁶ mol of compound, 0.3 g MAO, C_{mon} = 0.235 mol dm⁻³. ^b Ar 2 bar absolute pressure, 30 °C, 210 cm³ toluene solvent, 1 h, except 5 min for compound **17** and 3½ min for compound **18**, 6.25 × 10⁻⁶ mol of compound, 0.3 g MAO, C_{mon} = 0.235 mol dm⁻³.

Table 3 Polymerisation of propylene

Compound	X	Ring	Yield/g	Activity/ kg PP mol ⁻¹ h ⁻¹	Relative activity/ kg PP mol ⁻¹ h ⁻¹ C _{mon} ⁻¹
(a) [Cl ₂ (η-C ₅ H ₅)Zr{(η-C ₅ H ₄)X(Ring)}Rh(CO) ₂]					
1^a	CMe ₂	C ₉ H ₆	0.22	1.1	0.9
2^a	^t BuC ₆ H ₉	C ₉ H ₆	0.42	2.1	1.7
4^a	CMe ₂	Cp	3.9	19.5	15.5
(b) [(η-C ₅ H ₅)ZrCl ₂ {(η-C ₅ H ₄)CMe ₂ (C ₉ H ₆)}X]					
8^a	Mn(CO) ₃		0.26	1.3	1
^a	Zr(η-C ₅ H ₅)Cl ₂		2.22	11.1	8.8
^a	H		0.36*	7.2	5.7
(c) [(η-C ₅ H ₅)ZrCl ₂ {(η-C ₅ H ₄)CMe ₂ (C ₉ H ₆)} _n]					
11^a	Fe	<i>n</i> = 2	43.3	216	171
12^a	Co(η-C ₅ Me ₅)	<i>n</i> = 1	38.4	192	152
^a	H	<i>n</i> = 1	0.36*	7.2	5.7
(d) [Cl ₂ (η-C ₅ H ₅)M{(η-C ₅ H ₄)X(C ₉ H ₆)}M*(η-C ₅ H ₅)Cl ₂]					
	M M*	X			
^b	Zr Zr	CMe ₂	2.22	11.1	8.8
13^b	Zr Zr	(CH ₂) ₅	2.74	13.7	10.9
17^b	Zr Zr	^t BuC ₆ H ₉	9.25	46.3	36.7
^b	Hf Hf	CMe ₂	1.33	6.7	5.3
14^b	Hf Hf	(CH ₂) ₅	2.03	10.2	8.1
^b	ZrHf	CMe ₂	0.42	2.1	1.7
16^b	Zr Hf	(CH ₂) ₅	2.28	11.4	9.0

^a At 2 bar monomer pressure, 30 °C, 210 cm³ toluene solvent, 4 h (* 1 h), 5 × 10⁻⁵ mol of compound, 2.4 g MAO, C_{mon} = 1.26 mol dm⁻³. ^b At 2 bar monomer pressure, 30 °C, 10 cm³ toluene solvent, 4 h, 5 × 10⁻⁵ mol of compound, 2.4 g MAO, C_{mon} = 1.26 mol dm⁻³.

The polymerisation behaviour of the early-late transition metal metallocenes towards propene is shown in Table 3(c). These catalysts are far more active than the other multimetallic complexes, as was the case for ethene polymerisation. The ratio of the polymerisation activity of complexes **11** and **12** with respect to the mononuclear zirconocene [Zr{μ-(η-C₅H₄)-

CMe₂(η-C₉H₇)}(η-C₅H₅)Cl₂] is greater for propene polymerisation than for ethene.

The polymerisation behaviour of the binuclear Group IV metallocene derivatives is given in Table 3(d). The pattern of activity is essentially similar to that for the polymerisation of ethene. For example, the cyclohexyl bridged compounds have

Table 4 Determination of M_n
(a) For early-late bimetallic compounds from NMR spectroscopy

Compound (metals)	Chain length	Molecular weight, M_n
1 (Zr, Rh)	22.0	920
2 (Zr, Rh)	42.7	1797
4 (Zr, Rh)	37.3	1571
8 (Zr, Mn)	28.9	1216
11 (Zr, Fe)	39.6	1666
12 (Zr, Co)	29.9	1258

(b) For the polymers produced by binuclear Group IV catalysts, together with dyad functions

Compound	Bridge	$[m]$	$[r]$	Chain length	Molecular weight, M_n
13	Cyclohexyl	0.50	0.50	45.2	1900
17	¹ BuC ₆ H ₆	0.51	0.49	39.3	1650
14	Cyclohexyl	0.67	0.33	136.1	5730
16	Cyclohexyl	0.55	0.45	57.5	2420

higher activities than the corresponding Me₂C bridged complexes and the compound with a 4-Bu¹C₆H₆ bridge is more active still.

Several workers have noted interesting relationships between the activity of propene polymerisation and the stereoregularity and molecular weight of the polymer produced.^{29,31–34} In view of this, the nature of the polypropene samples produced above was investigated.

The polypropenes produced by the new compounds described above were viscous liquids or gummy solids soluble in toluene. The ¹³C NMR spectra were recorded in 1,2,4-trichlorobenzene-d₆-benzene (80:20 v/v) at 130 °C. The spectra also show the chain-end structures of the polymer indicative of low molecular weights.^{35–37} The methyl region of the spectrum between δ 23 and 19 shows a number of features typical for atactic polypropenes.^{37,38} The protons of the vinylidene chain-end group can also be seen in the ¹H NMR spectrum of the polymer. The ¹³C NMR spectrum shows that the signals of the two chain-end groups occur in approximately equal intensity. The main chain transfer process is likely to involve β -hydride elimination from a monomer which has inserted in a regio-regular manner, with the new polymer chain being initiated from a metal-hydrogen bond, from which a primary insertion will yield the *n*-propyl group.

The ¹³C NMR spectra of the polypropene samples formed from the zirconium compounds in Table 3 were all very similar, the main differences being in the intensity of the chain-end signals with respect to those of the main chain. Polymers from the hafnium-containing binuclear complexes were of higher molecular weight. Some polymer data are shown in the Table 4(a) and 4(b), and further discussion may be found in ref. 19. Molecular weight determinations and the values of M_w , M_n and the ratio M_w/M_n are shown in Table 5. In most cases the number-average molecular weight of the polymer, M_n , was slightly higher than the corresponding value obtained from NMR spectroscopy.

It can be seen that use of the early-late heterobimetallic metallocene complexes **11** and **12** gave the smallest value of the ratio M_w/M_n indicating that these provide the most uniform polymers. In contrast, the values of this ratio from the hafnium-containing Group IV bimetallic complexes are the largest. The molecular weight distribution curves show two components. From the dihafnium complex **14** there is a small region to

Table 5 Determination of M_w and M_n from GPC analysis

Compound (metals)	M_w	M_n	M_w/M_n
2 (Zr, Rh)	5178	2052	2.5
4 (Zr, Rh)	3355	1707	2.0
11 (Zr, Fe)	2611	1554	1.7
12 (Zr, Co)	2170	1340	1.6
13 (Zr, Zr)	4800	2083	2.3
17 (Zr, Zr)	3719	1697	2.2
14 (Hf, Hf)	35601	10329	3.5
16 (Zr, Hf)	7690	2082	3.7

the low molecular weight side of the main peak, whereas the zirconium-hafnium complex **16** resulted in a small region to the high side of the main peak of the envelope. This is consistent with the notion that hafnium centres yield higher molecular weight polymers than zirconium ones,^{29,33–36} and that the polymerisation activity of the metal centre at the cyclopentadienyl site is larger than that of the metal at the indenyl site. In addition, the zirconium-rhodium complex **2**, with a bulky 4-Bu¹-C₆H₆ bridging ligand, resulted in a molecular weight envelope with a considerably flatter peak than the others.

In conclusion the polymerisation experiments show that the early-late heterometallic bis(metallocene) complexes [Cl₂Zr(η -C₅H₅)₂]{(η -C₅H₄)CMe₂(η -C₉H₆)}Co(η -C₅Me₅)] **12** and Cl₂Zr-[Fe{ μ -(η -C₉H₆)CMe₂(η -C₈H₄)Zr(η -C₅H₅)Cl₂}₂] **11** are much more active catalysts than previously described compounds of this type, giving activities approaching those obtained for [Zr(η -C₅H₅)₂Cl₂]-MAO. However, early-late heterobimetallic complexes involving carbonyl ligands have been shown to be poor catalysts. This investigation showed that the bulkier bridging systems resulted in greater polymerisation activity, with higher molecular weight polymer being produced, although no enhancement of the stereoregularity of the polypropene was observed.

Experimental

All manipulations, with the exception of the preparation of purely organic chemicals, were carried out in an inert atmosphere using either a dual vacuum/nitrogen line and standard Schlenk techniques, or in an inert atmosphere dry-box under dinitrogen. The nitrogen was purified by passage over 4 Å molecular sieves and either MnO, for the Schlenk line, or BASF catalyst, for the dry-box. Solvents and solutions were transferred, using a positive pressure of nitrogen, through stainless steel cannulae. Filtrations were performed using stainless steel cannulae fitted with glass fibre filter discs. All glassware and cannulae were dried overnight in an oven at over 150 °C before use. Solvents were pre-dried by standing over 4 Å molecular sieves and then refluxed and distilled, under an inert atmosphere, from the appropriate drying agent: sodium-potassium alloy (1:3 w/w) [*n*-pentane, light petroleum (bp 40–60 °C) and diethyl ether]; sodium [light petroleum (bp 100–120 °C), 1,2-dimethoxyethane, toluene]; potassium (THF, benzene); or calcium hydride (dichloromethane). All solvents were degassed by bubbling nitrogen or by repeated evacuation followed by admission of nitrogen. Solvents for polymerisation experiments were additionally stored over a potassium mirror. Deuteriated solvents for NMR studies were stored in Young's ampoules over 4 Å molecular sieves under a nitrogen atmosphere. The were transferred using a teat pipette in a dry-box and the tubes either

sealed under vacuum or capped and the caps wrapped with Labfilm and Teflon tape.

The NMR spectra were recorded on either a Bruker AM300 (^1H , 300 MHz; ^{13}C , 75.43 MHz) or a Varian UnityPlus spectrometer (^1H , 500 MHz; ^{31}P , 200 MHz; ^{13}C , 125.7 MHz). Spectra were referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) signals relative to tetramethylsilane (δ 0), or externally using trimethyl phosphate in D_2O (^{31}P). The IR spectra were recorded on either a Perkin-Elmer 1710 or a Mattson Polaris FTIR spectrometer. ESR spectra on an X-band Varian E109 spectrometer with an operating field of 3300 G referenced externally to 1,1-diphenyl-2-picrylhydrazyl and with samples prepared in high-purity Spectrosil quartz tubes sealed with a Young's tap.

Gel-permeation chromatography (GPC) experiments were performed by Dr Lilge of BASF AG. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory.

The complexes $[\text{M}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3]\cdot\text{DME}$ (where $\text{M} = \text{Zr}$ or Hf) and $[\text{Zr}(\eta\text{-C}_5\text{Me}_3\text{Cl}_3)\cdot 2\text{THF}]$ were prepared according to the literature methods and were recrystallised from tetrahydrofuran.^{39,40} The co-catalyst MAO was prepared by following the literature preparations of Kaminsky *et al.*³⁹ and Giannetti *et al.*,⁴⁰ or purchased as a 30% w/v solution in toluene from Witco PLC. The compound $[\text{Hf}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ was synthesized as described.⁴¹

Preparations

$\text{Li}_2\{[(4\text{-Bu}^t\text{C}_6\text{H}_9)(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]\}$. A solution of 6,6-(4-*tert*-butylcyclohexylene)fulvene (1.32 g, 6.5 mmol) in diethyl ether (50 cm^3) was added to $\text{Li}(\text{C}_9\text{H}_7)$ (0.797 g, 6.5 mmol) in diethyl ether (100 cm^3) at 0 °C, allowed to warm to room temperature and stirred for 24 h. The solution was cooled to 0 °C and *n*-BuLi (7.65 cm^3 of a 1.7 M solution in hexane) was added in small portions. The solution was again allowed to warm to room temperature and a white precipitate formed. This suspension was stirred for 14 h at room temperature. The precipitate was then allowed to settle and isolated *via* filtration. The resulting white solid was washed with diethyl ether (20 cm^3) and dried *in vacuo*. Yield 2.4 g (95%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ 2. A solution of $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ (0.285 g, 0.7 mmol)¹³ in diethyl ether (50 cm^3) at room temperature was treated dropwise with a solution of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ (0.135 g, 0.35 mmol)⁷ in diethyl ether (30 cm^3). The solution changed to orange immediately. Stirring was continued for 2 h. The mixture was filtered to remove a small quantity of dark material and concentrated to 20 cm^3 . Cooling this solution to -20 °C afforded an orange-yellow solid. Yield 0.25 g (60%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)(4\text{-Bu}^t\text{C}_6\text{H}_9)(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ 2. A solution of $[\text{Zr}\{(4\text{-Bu}^t\text{C}_6\text{H}_9)(\eta\text{-C}_5\text{H}_4)(1\text{-}\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ (0.250 g, 0.5 mmol) in diethyl ether (50 cm^3), at room temperature, was treated dropwise with a solution of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ (0.1 g, 0.25 mmol) in diethyl ether (30 cm^3). The solution changed to orange immediately. Stirring was continued for 2 h to ensure complete reaction. The solution was filtered to remove a small quantity of dark material and the filtrate concentrated to 25 cm^3 . Cooling this to -20 °C afforded an orange-yellow solid. The supernatant was decanted from this solid, and the solid dried *in vacuo*. Yield, 0.22 g (62%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ 3. A solution of $[\text{Hf}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ (0.500 g, 1 mmol) in diethyl ether (50 cm^3)⁶ at room temperature was treated with a solution of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ (0.200 g, 0.5 mmol) in diethyl ether (20 cm^3) in a dropwise manner. The solution lightened immediately. Stirring was continued for 10 min,

during which time a yellow precipitate was obtained. The solid was isolated *via* filtration and dried *in vacuo* as the pure product. Yield 0.45 g. A further small quantity of product could be obtained by concentration of the filtrate under reduced pressure to 20 cm^3 and cooling this solution to -20 °C. Combined yield 0.50 g (72%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ 4. A suspension of $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)_2\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ (0.205 g, 0.57 mmol) in diethyl ether (80 cm^3) at room temperature was treated with a solution of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ (0.110 g, 0.28 mmol) in diethyl ether (30 cm^3), in several small portions. The suspension was stirred at room temperature. As the reaction progressed the starting material gradually dissolved. After 3 h the solution was yellow, with only a very small amount of dark precipitate. The solution was filtered and concentrated to 40 cm^3 . Cooling to -80 °C gave an orange solid. Yield 0.22 g (70%). The reaction in toluene proceeded within 1 h and the yield was 76%.

$[(\text{SCN})_2(\eta\text{-C}_5\text{H}_5)(\text{Hf})\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ 5. A solution of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ (0.15 g, 0.22 mmol) in dichloromethane (30 cm^3) was cooled to 0 °C. To this was added, dropwise, a solution of KCNS (0.042 g, 0.44 mmol), also in dichloromethane (40 cm^3). The solution was allowed to warm to room temperature and stirred for 24 h, during which it changed from yellow to orange. The solvent was removed under reduced pressure and the residue extracted with toluene (30 cm^3), leaving a small quantity of pale residue. After filtration the filtrate was concentrated to 20 cm^3 under reduced pressure and cooled to -20 °C, affording a dark orange powder. The supernatant was decanted, and the resulting solid washed with light petroleum (bp 40–60 °C) (5 cm^3) and dried *in vacuo*. Yield 0.11 g (67%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ 6. A solution of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ 3 (0.200 g, 0.29 mmol) in THF (20 cm^3) was added to a solution of I_2 (0.073 g, 0.29 mmol), also in THF (20 cm^3), at room temperature. The solution was stirred at room temperature for 3 h, changing from purple to black. The solvent was removed under reduced pressure and the black residue washed with toluene (30 cm^3), yielding a purplish solution and a black solid. The supernatant was decanted and the resulting solid dried *in vacuo*. Yield 0.13 g (51%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{PPh}_3)_2]$ 7. A solution of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Rh}(\text{CO})_2]$ 4 (0.200 g, 0.33 mmol) in toluene (20 cm^3) was treated with PPh_3 (0.17 g, 0.66 mmol) in toluene (20 cm^3) at room temperature in a dropwise manner. The solution lightened slightly and was stirred for 24 h. It was concentrated under reduced pressure to 10 cm^3 and cooled to -20 °C. After several weeks an orange solid separated. The solution was decanted and the solid dried *in vacuo*. Yield 0.19 g (54%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Mn}(\text{CO})_3]$ 8. A mixture of $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ ¹³ (0.500 g, 1.2 mmol) and $[\text{Mn}(\text{CO})_5\text{Cl}]$ (0.280 g, 1.2 mmol)⁸ was treated with THF (50 cm^3). The reaction vessel was evacuated and heated to 60 °C for 5 h. During this time the reaction mixture became orange. The solvent was removed under reduced pressure, yielding an orange oily solid. This was washed with *n*-pentane (70 cm^3) and extracted with toluene (30 cm^3). After filtration the filtrate was concentrated to 15 cm^3 and light petroleum (bp 40–60 °C) added (15 cm^3). The solution was cooled to -20 °C giving a yellow solid. Yield 0.47 g (66%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Mn}(\text{CO})_3]$ 9. A mixture of $[\text{Hf}\{(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ ¹³ (0.325

g, 0.65 mmol) and $[\text{Mn}(\text{CO})_5\text{Cl}]$ (0.150 g, 0.65 mmol) was treated with THF (50 cm³). The reaction vessel was evacuated and heated to 60 °C for 5 h. During this time the reaction mixture became orange. The solvent was removed under reduced pressure yielding an orange oily solid. This was washed with *n*-pentane (50 cm³) and extracted with toluene (50 cm³). The filtrate was concentrated to 10 cm³ and light petroleum (bp 40–60 °C) added (15 cm³). The solution was cooled to –20 °C, affording the product as a yellow solid. Yield 0.19 g (43%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Ru}(\eta\text{-C}_4\text{H}_7)(\text{CO})]$ 10. A mixture of $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ (0.450 g, 1.1 mmol) and $[\text{Ru}(\eta\text{-C}_4\text{H}_7)(\text{CO})_3\text{Cl}]$ (0.300 g, 1.1 mmol)⁹ was treated with THF (70 cm³). The reaction vessel was evacuated and heated at 60 °C for 3 h. The reaction mixture changed to bright orange. The solvent was removed under reduced pressure, yielding an orange oily solid. This was washed with *n*-pentane (40 cm³) and extracted with toluene (30 cm³). The solution was cooled to –20 °C, yielding a yellow powder. This was shown to be a mixture of complexes. Further recrystallisation from diethyl ether (40 cm³) afforded the pure product as a yellow solid. Yield 0.27 g (39%).

$[\text{Fe}\{\mu\text{-}(\eta\text{-C}_9\text{H}_6)\text{CMe}_2(\eta\text{-C}_5\text{H}_4)\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2\}_2]$ 11. A mixture of $[\text{Zr}\{\eta\text{-C}_5\text{H}_4\}\text{CMe}_2(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ ¹³ (0.412 g, 1 mmol) and $\text{FeCl}_2 \cdot 1.5\text{THF}$ (0.117 g, 0.5 mmol) were treated with THF (50 cm³) and the ampoule evacuated. The solution was then heated to reflux for 3 h. During this time the reaction mixture changed to red-brown. The solvent was removed under reduced pressure to yield a brown oily solid. The solid was washed with *n*-pentane (30 cm³) and extracted with toluene (50 cm³). The filtrate was concentrated to 35 cm³ and the solution cooled to –20 °C, affording the product as a brown solid. Yield 0.20 g (42%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Co}(\eta\text{-C}_5\text{Me}_5)]$ 12. A solution of $[\text{Zr}\{\text{Me}_2\text{C}(\eta\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ ¹³ (0.412 g, 1 mmol) in THF (40 cm³) was cooled to –78 °C and treated with $[\{\text{Co}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\}]$ (0.230 g, 0.5 mmol) in THF (30 cm³), in a dropwise manner over 30 min. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Although it remained black when viewed with reflected light, the solution changed from deep purple to green when viewed with transmitted light. The solvent was removed under reduced pressure, yielding a green-black residue. The residue was washed with *n*-pentane (50 cm³) to give a dark solution and black residue. The solution was decanted and the residue extracted with toluene (30 cm³). After filtration the filtrate was concentrated to 15 cm³ and cooled to –20 °C giving a black solid. The supernatant was decanted and the solid washed with cold *n*-pentane (5 cm³) and dried *in vacuo*. Yield 0.37 g (58%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{ZrCl}_2(\eta\text{-C}_5\text{H}_5)]$ 13. A mixture of $\text{Li}_2\{[(\text{CH}_2)_5\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]\} \cdot 0.8 \text{Et}_2\text{O}$ (0.5 g, 1.5 mmol) and $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot \text{DME}$ (1 g, 2.9 mmol) was cooled to –78 °C. Toluene (150 cm³) at 70 °C was added to give an orange suspension. The reaction mixture was allowed to warm to room temperature, during which time it gradually darkened to deep red. When the solution had reached room temperature the reaction vessel was partially evacuated and heated to 105 °C for 24 h. After this time the reaction mixture was light red. It was allowed to cool and filtered leaving a pale residue. The light red filtrate was concentrated under reduced pressure to 60 cm³ and cooled to –20 °C yielding a bright yellow crystalline solid. An analytically pure sample was obtained by recrystallisation from dichloromethane (40 cm³). The supernatant was decanted and the solid dried *in vacuo*. Further concentration of the filtrate followed by cooling afforded more product, but this was contaminated with large red crystals of

the mononuclear complex $[\text{Zr}\{(\text{CH}_2)_5\text{C}(\eta\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$. Yield 0.63 g (62%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{-Cl}_2]$ 14. A mixture of $\text{Li}_2\{[(\text{CH}_2)_5\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]\} \cdot 0.8 \text{Et}_2\text{O}$ (0.5 g, 1.5 mmol) and $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$ (1.45 g, 2.9 mmol) was cooled to –78 °C. Toluene (150 cm³) at 70 °C was added to give an orange suspension. The reaction mixture was allowed to warm to room temperature and became dark orange. When the solution had reached room temperature the reaction vessel was partially evacuated and heated to 105 °C for 24 h. The reaction mixture became yellow. It was cooled and filtered from a pale residue. The yellow filtrate was concentrated to 50 cm³ under reduced pressure and cooled to –20 °C, yielding a pale yellow crystalline solid. An analytically pure sample, off-white, was obtained by recrystallisation from dichloromethane (40 cm³). Yield 0.86 g (68%).

$[\text{Hf}\{(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta^1\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$ 15. The reaction was undertaken in a similar manner to that described for the synthesis of complex 14 using identical quantities of chemicals. In this case, however, the solvent was added to the reagents at room temperature and the reaction mixture heated to 120 °C for 16 h. A yellow solution was obtained, from which an off-white solid was obtained after concentrating the toluene solution to 50 cm³ and cooling to –20 °C. Yield *ca.* 20%.

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H}_5)\text{C}(\text{CH}_2)_5(\eta\text{-C}_9\text{H}_6)\}\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{-Cl}_2]$ 16. (i) *Preparation of $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}]$* This complex was synthesized in a modification of the literature preparation.¹³ A mixture of $\text{Li}_2\{[(\text{CH}_2)_5\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]\} \cdot 0.8 \text{Et}_2\text{O}$ (0.5 g, 1.5 mmol) and $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{-Cl}_3] \cdot \text{DME}$ (0.53 g, 1.5 mmol) at –78 °C was treated with toluene (150 cm³) –78 °C to give an orange suspension. The reaction mixture was allowed to warm to room temperature and became deep red. It was stirred for 14 h then filtered, leaving a pale residue. The filtrate was concentrated under reduced pressure to 20 cm³ and cooled to –20 °C. Red crystals of the toluene solvate were obtained, from which the supernatant was decanted and the solid dried *in vacuo*. Yield 0.64 g (86%).

(ii) *Reaction of $[\text{Zr}\{(\eta\text{-C}_5\text{H}_4)\text{C}(\text{CH}_2)_5(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{-Cl}]$ with $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$.* A mixture of $[\text{Zr}\{(\text{CH}_2)_5\text{-}(\eta\text{-C}_5\text{H}_4)(\eta^2\text{-C}_9\text{H}_6)\}(\eta\text{-C}_5\text{H}_5)\text{Cl}] \cdot 0.5 \text{C}_6\text{H}_5\text{CH}_3$ (0.23 g, 0.46 mmol) and $[\text{Hf}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot 2\text{THF}$ (0.228 g, 0.46 mmol) was treated with toluene (100 cm³) at room temperature to give a deep red solution. The mixture was heated to 105 °C and stirred for 24 h and became light red. The cooled mixture was filtered from a very small quantity of pale solid and the filtrate concentrated to 40 cm³. Cooling to –20 °C afforded a yellow solid, which was isolated *via* filtration, washed with diethyl ether (10 cm³) and dried *in vacuo*. Yield 0.215 g (58%).

$[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Zr}\{\mu\text{-}(\eta\text{-C}_5\text{H})\text{(4-Bu}^t\text{C}_6\text{H}_9)(\eta\text{-C}_9\text{H}_6)\}\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{-Cl}_2]$ 17. A mixture of $\text{L}_2\{[(4\text{-Bu}^t\text{C}_6\text{H}_9)_4(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]\} \cdot 0.8 \text{Et}_2\text{O}$ (0.5 g, 1.28 mmol) and $[\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_3] \cdot \text{DME}$ (0.88 g, 2.5 mmol) at –78 °C was treated with toluene (100 cm³) at 78 °C to give an orange suspension. The mixture was allowed to warm to room temperature and became deep red. It was heated to 105 °C for 24 h becoming light red and was cooled and filtered, leaving a pale residue. The light red filtrate was concentrated under reduced pressure to 20 cm³ and left to stand at room temperature, yielding a bright yellow crystalline solid. The supernatant was decanted and the solid dried *in vacuo*. Yield 1.43 g (74%).

$[\text{Cl}(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}(\mu\text{-H})_2\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{-Cl}]$ 18. A stirred solution of $\text{LiAl}(\text{O}^t\text{Bu})_3\text{H}$ (0.167 g, 0.66 mmol) in THF (30 cm³) was added dropwise over 1 h to a solution of $[\text{Cl}_2(\eta\text{-C}_5\text{H}_5)\text{Hf}\{\mu\text{-}(\eta\text{-C}_5\text{H}_4)\text{CMe}_2(\eta\text{-C}_9\text{H}_6)\}\text{Zr}(\eta\text{-C}_5\text{H}_5)\text{Cl}_2]$ (0.250 g, 0.33 mmol), in THF (50 cm³) at room temperature.

The mixture was stirred at room temperature for 3 h and became dark yellow. The solvent was removed under reduced pressure and 30 cm³ light petroleum (bp 40–60 °C) were added. This gave a yellow solution and a pale residue. The pale residue was extracted with toluene (30 cm³) to yield a very pale yellow solution and a very small amount of pale residue. After filtration the toluene solution was concentrated under reduced pressure to 20 cm³ and cooling to –20 °C yielded a slightly grey solid. The supernatant was decanted from the precipitate and the solid dried *in vacuo*. Yield 0.057 g (25%).

[Cl(η-C₅H₅)Hf{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}(μ-O)Zr(η-C₅H₅-Cl)] 19. A stirred solution of [Cl₂(η-C₅H₅)Hf{μ-(η-C₅H₄)CMe₂(η-C₉H₆)}Zr(η-C₅H₅)Cl₂] (0.25 g, 0.33 mmol) in dichloromethane (30 cm³) was treated with degassed water (6 μl, 0.33 mmol) *via* a microlitre syringe. Aniline (60 μl, 0.66 mmol) was added giving an immediate white precipitate. The solution was stirred for 1 h at room temperature. It was then filtered and concentrated under reduced pressure to 15 cm³. Pentane (20 cm³) was added giving a white precipitate which was isolated *via* filtration and dried *in vacuo*. Yield 0.18 g (77%).

[Zr{Me₂C(η-C₅H₄)}(η-C₅H₄Me)Cl] 20. A solution of [Zr{Me₂C(η-C₅H₄)₂}Cl₂] (0.50 g, 1.5 mmol) in THF (75 cm³) was cooled to –78 °C and a solution of K(C₅H₄Me) (0.18 g, 1.5 mmol) in THF (50 cm³) added dropwise. The mixture was allowed to warm to room temperature and stirred for 12 h. The solvent was removed under reduced pressure and the residue extracted with toluene (2 × 30 cm³). The filtrate was concentrated under reduced pressure to 30 cm³ and cooled to –20 °C. A pale yellow solid separated and was isolated *via* filtration and dried *in vacuo*. Yield 0.35 g (62%).

[Zr{(4-Bu^tC₆H₉)(η-C₅H₄)(η²-C₉H₆)}(η-C₅H₅)Cl] 21. Toluene (100 cm³) was added to a stirred mixture of Li₂[(4-Bu^tC₆H₉)(C₅H₄)(C₉H₆)]·0.8 Et₂O (0.50 g, 1.28 mmol) and [Zr(η-C₅H₅)Cl₃]·DME (0.45 g, 1.28 mmol) at –78 °C. The solution was allowed to warm to room temperature, during which time it darkened, through orange to deep red. The reaction mixture was then stirred at room temperature for 16 h and filtered. Concentration of the solution under reduced pressure, to 15 cm³, and cooling to –20 °C gave red crystals. Yield 0.57 g (56%).

Polymerisation studies

All manipulations of catalysts and co-catalysts were carried out under an inert atmosphere, using Schlenk techniques or a dry-box. Pure grade ethene and propene were further purified by passage through a column of 4 Å molecular sieves and then over finely divided potassium, which was supported on glass wool. Polymerisation reactions were carried out in a Fischer–Porter reactor, stirred using a magnetic stirrer and maintained at the required temperature by the use of a thermostatically heated bath.

Of ethene. The conditions used were those as close as possible to the ones employed by Kaminsky *et al.*²⁹ A Fischer–Porter reactor was loaded with MAO (0.250 g) and then connected to the computer-controlled gas supply system *via* a flexible steel hose. The hose was then repeatedly evacuated and filled with ethene. Toluene (200 cm³) was then added to the reactor under nitrogen, the reactor was evacuated and filled with ethene three times. The ethene pressure was then increased to 2 bar and the solution stirred at 30 °C. The gas supply was switched on so as to allow the solution to become saturated with ethene at the required temperature and pressure.

Standard solutions of the catalysts were prepared by dissolving 1.125 × 10^{–4} mol of catalyst (18 times the quantity used in each ethene polymerisation experiment) in 90 cm³ of toluene. A 5 cm³ portion of this solution was diluted with 5 cm³ of toluene,

added to a Schlenk tube containing MAO (0.05 g), and this mixture was stirred for 15 min to pre-activate the catalyst.

After the solution in the Fischer–Porter reactor had become saturated with ethene, illustrated by the computer showing no further pressure loss, stirring was stopped so as to minimise the loss of ethene when the pressure was released to allow the catalyst/MAO to be added quickly to the contents of the reactor *via* a cannula. Care was taken to avoid the introduction of excessive amounts of nitrogen whilst adding the catalyst by inserting the cannula into the catalyst solution immediately on releasing the pressure, and withdrawing the cannula from the reactor immediately after the addition was complete. The ethene pressure in the reactor was then increased to 2 bar again, stirring was recommenced and the experiment started.

After exactly 1 h, the polymerisation was quenched by venting the ethene, followed by the addition of a small amount of ethanol. The reactor contents were then transferred to a conical flask containing a solution of concentrated HCl in ethanol (300 cm³ of a 30% v/v solution) and stirred overnight. The polymer was then collected on a sintered glass funnel using a Buchner flask and a water aspirator. The polymer was washed with deionised water, ethanol and finally diethyl ether. At least three 50 cm³ portions of each solvent were used. The polymer was then dried *in vacuo* at 50 °C to constant weight.

Of propene. A similar procedure was used for the polymerisation of propene. Eight times the quantity of catalyst and co-catalyst were used. The pre-activation of the catalyst was performed using 80 cm³ of toluene and 130 cm³ of toluene were initially introduced into the Fischer–Porter reactor. The polymerisation was allowed to proceed for 4 h at 30 °C under a monomer pressure of 2 bar.

After 4 h, the polymerisation was quenched by venting the propene and adding a small quantity of ethanol. The contents were transferred to a conical flask containing a solution of concentrated HCl in ethanol (300 cm³ of a 30% v/v solution) and stirred overnight. All the polypropenes produced by the catalysts were soluble in toluene, so the toluene layer was separated, washed well with water (5 × 100 cm³) and stirred over MgSO₄. The solution was then filtered and the toluene removed leaving the polypropene as, typically, a viscous liquid. The polymer was dried *in vacuo* at 50 °C to constant weight.

Acknowledgements

We thank the EPSRC for financial support (to N. H. P.).

References

- 1 M. Arndt, W. Kaminsky, A. M. Schauwienold and U. Weingarten, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, 1998, **199**, 1135; W. Kaminsky, *J. Chem. Soc., Dalton Trans.*, 1998, 1413; *Pure Appl. Chem.*, 1998, **70**, 1229; *Polimery*, 1997, **42**, 587; O. Olabisi, M. Atiqullah and W. Kaminsky, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, 1997, **C37**, 519; W. Kaminsky, H. Sinn and H. G. Zachmann, *Makromol. Chem. Rapid Commun.*, 1982, **3**, 327; W. Kaminsky, M. Miri, H. Sinn and R. Woldt, *Makromol. Chem. Rapid Commun.*, 1983, **4**, 417.
- 2 J. A. Ewen, *J. Am. Chem. Soc.*, 1984, **106**, 6355; J. A. Ewen, R. L. Jones, J. A. Razavi and J. D. Ferrara, *J. Am. Chem. Soc.*, 1988, **110**, 6255; J. A. Ewen, *J. Mol. Cat. A. Chem.*, 1998, **128**, 103; M. K. Leclerc and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 922; A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587; G. M. Diamond, R. P. Jordan and J. L. Petersen, *Organometallics*, 1996, **15**, 4045; Z. Y. Guo, D. C. Swenson and R. F. Jordan, *Organometallics*, 1994, **13**, 1424; X. J. Song, M. Thornton-Pett and M. Bochmann, *Organometallics*, 1998, **17**, 1004; M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255; M. Bochmann and S. J. Lancaster, *J. Organomet. Chem.*, 1995, **497**, 55; G. G. Hlatky, H. W. Turner and R. R. Eckman, *J. Am. Chem. Soc.*, 1989, **111**, 2728.
- 3 H. Welborn, Jr. and J. A. Ewen, *US Pat.*, 5 324 800, 28th Jun. 1994.
- 4 K. P. Reddy and J. L. Petersen, *Organometallics*, 1989, **8**, 2107.

- 5 K. P. Reddy and J. L. Petersen, *Organometallics*, 1989, **8**, 547.
- 6 J. Cacciola, K. P. Reddy and J. L. Petersen, *Organometallics*, 1992, **11**, 665.
- 7 S. Jungling, R. Mulhaupt and H. Plenio, *J. Organomet. Chem.*, 1993, **460**, 191.
- 8 S. Ciruelos, T. Cuenca, J. C. Flores, R. Gomez, P. Gomez-Sal and P. Royo, *Organometallics*, 1993, **12**, 944.
- 9 R. Gomez, T. Cuenca, P. Royo, W. A. Herrmann and E. Herdtweck, *J. Organomet. Chem.*, 1990, **382**, 103.
- 10 I. E. Nifant'ev, K. A. Butakov, Z. G. Aliev and I. F. Urazovskii, *Organomet. Chem. USSR*, 1991, **4**, 622.
- 11 U. Siemeling and P. Jutzi, *Chem. Ber.*, 1992, **125**, 31.
- 12 I. E. Nifant'ev, M. V. Borsov, A. V. Churakov, S. G. Mkoyan and L. O. Atovmyan, *Organometallics*, 1992, **11**, 3942.
- 13 G. M. Diamond, M. L. H. Green, P. Mountford, N. A. Popham and A. N. Chernega, *J. Chem. Soc., Chem. Commun.*, 1994, 103.
- 14 G. M. Diamond, A. N. Chernega, P. Mountford and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1996, 921.
- 15 G. M. Diamond, M. L. H. Green, N. A. Popham and A. N. Chernega, *J. Chem. Soc., Chem. Commun.*, 1994, 727.
- 16 H. Werner, M. Treiber, A. Nessel, F. Lippert, P. Betz and C. Kruger, *Chem. Ber.*, 1992, **125**, 337.
- 17 H. Werner, D. Schneider and M. Schulz, *Chem. Ber.*, 1992, **125**, 1017.
- 18 D. Schneider and H. Werner, *Organometallics*, 1993, **12**, 4420.
- 19 N. A. Popham, D.Phil. Thesis, Oxford, 1995.
- 20 H. Eshtiagh-Hosseini and J. F. Nixon, *J. Less-Common Met.*, 1978, **61**, 107.
- 21 J. L. Burmeister, E. A. Deardorff, A. Jensen and V. H. Christiansen, *Inorg. Chem.*, 1970, **9**, 58.
- 22 R. B. King and A. Efraty, *J. Organomet. Chem.*, 1970, **23**, 527.
- 23 D. H. Gibson, W.-L. Hsu, A. L. Steinmetz and B. V. Johnson, *J. Organomet. Chem.*, 1981, **208**, 89.
- 24 J. H. Ammeter, *J. Magn. Reson.*, 1978, **30**, 299.
- 25 J. L. Robbins, N. Edelstein, B. Spencer and J. C. Smart, *J. Am. Chem. Soc.*, 1982, **104**, 1882; F. F. Kneubuhl, *J. Chem. Phys.*, 1960, **33**, 1074.
- 26 V. C. Williams and M. L. H. Green, unpublished work.
- 27 B. C. Wailes and H. Weigold, *Inorg. Synth.*, 1990, **28**, 259.
- 28 E. Samuel and R. Setton, *C. R. Hebd. Seances Acad. Sci.*, 1963, **256**, 443.
- 29 W. Kaminsky, R. Engehausen, R. Zoumis, W. Spalek and J. Rohrmann, *Makromol. Chem.*, 1992, **193**, 1643.
- 30 L. E. Schock and T. J. Marks, *J. Am. Chem. Soc.*, 1988, **110**, 7701.
- 31 W. Spalek, M. Antberg, V. Dolle, R. Klein, J. Rohrmann and A. Winter, *New J. Chem.*, 1990, **14**, 499.
- 32 J. A. Ewen, L. Haspeslagh, J. L. Attwood and H. Zhang, *J. Am. Chem. Soc.*, 1987, **109**, 6544.
- 33 J. A. Ewen, M. J. Elder, R. L. Jones, L. Haspeslagh, J. L. Attwood, S. G. Bott and K. Robinson, *Makromol. Chem., Makromol. Symp.*, 1991, **48/49**, 253.
- 34 M. L. H. Green and N. Ishihara, *J. Chem. Soc., Dalton Trans.*, 1994, 657.
- 35 H. N. Cheng and D. A. Smith, *Macromolecules*, 1986, **19**, 2065.
- 36 H. N. Cheng and J. A. Ewen, *Makromol. Chem.*, 1989, **190**, 1931.
- 37 T. Tsutsui, A. Mizuno and N. Kashiwa, *Polymer*, 1989, **30**, 428.
- 38 A. Zambelli, P. Localetti, G. Bajo and F. A. Bovey, *Macromolecules*, 1975, **8**, 687.
- 39 W. Kaminsky, M. Miri, H. Sinn and R. Woldt, *Makromol. Chem., Rapid Commun.*, 1983, **4**, 417.
- 40 E. Giannetti, G. M. Nicoletti and R. Mazzochi, *J. Poly. Sci., Polym. Chem. Ed.*, 1985, **23**, 2117.
- 41 I. E. Nifant'ev, P. V. Ivchenko and M. V. Borzov, *J. Chem. Res. (S)*, 1992, 162.

Paper 8/09944H