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New mono- and bi-nuclear *ansa*-metallocenes of zirconium and hafnium as catalysts for the polymerisation of ethene and propene†

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The new *ansa*-metallocenes $[M\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ [M = Zr (crystal structure) or, Hf], $[M\{(CH_2)_5C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]\cdot 0.5C_6H_5Me$ [M = Zr (crystal structure) or Hf], $[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)\}(\eta\text{-}C_5H_5)Cl]$ (crystal structure), $[M\{Me_2C(\eta\text{-}C_5H_4)_2\}(\eta\text{-}C_5H_5)Cl]$ [M = Zr or Hf (crystal structures)], $[X_2(\eta\text{-}C_5H_5)M\{C_5H_4(CMe_2)C_9H_6)\}M^*(\eta\text{-}C_5H_5)X_2\}]$ (X = Cl, M, M* = Zr, Zr; Hf, Hf; Zr, Hf; or Hf, Zr; X = Me, M, M* = Zr, Zr; Zr, Hf; Hf, Zr; or Hf, Hf), $[Cl_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}\text{-}Zr(\eta\text{-}C_5Me_5)Cl_2]$, $[\{M(C_5H_4CMe_2(C_9H_7))\}(\eta\text{-}C_5H_5)Cl_2]$ (M = Zr or Hf) and $[Zr\{C_5H_4CMe_2(C_9H_7\}\text{-}(\eta\text{-}C_5H_5)Me_2]$ have been prepared and characterised. The activity of the metallocenes as cocatalysts for the polymerisation of ethene and propene has been evaluated.

It was decided to study the synthesis of a variety of new *ansa*-bridged homo- and hetero-binuclear Group IV metallocenes, and to examine their catalytic properties towards olefin polymerisation. In 1989 Reddy and Petersen[1] described the metathesis of $Li_2[SiMe_2(C_5H_4)_2]$ with 2 equivalents of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot 2thf$ (thf = tetrahydrofuran) to give the *ansa*-bridged homobinuclear zirconocene derivative $[Cl_2(\eta\text{-}C_5H_5)Zr\{\mu\text{-}C_5H_4(SiMe_2)C_5H_4\}Zr(\eta\text{-}C_5H_5)Cl_2]$. It was decided to extend this strategy to prepare *ansa*-bridged homo- and hetero-binuclear Group 4 metallocenes. Recent independent reports have described the binuclear *ansa*-cyclopentadienyl compounds $[Cl_2(\eta\text{-}C_5H_5)Ti\{\mu\text{-}C_5H_4(SiMe_2)C_5H_4\}Ti(\eta\text{-}C_5H_5)Cl_2]$,[2] $[Cl_3Ti\{\mu\text{-}C_5H_4(SiMe_2)C_5H_4\}TiCl_3]$,[3] $[Cl_2(\eta\text{-}C_5H_5)Ti\{\mu\text{-}C_5H_4(SiMe_2)C_5H_4\}Zr(\eta\text{-}C_5H_5)Cl_2]$,[4] $[Cl_2(\eta\text{-}C_5H_5)Ti\{\mu\text{-}C_5H_4(SiMe_2)C_5H_4\}Zr(\eta\text{-}C_5Me_5)Cl_2]$,[4] $[Cl_2(\eta\text{-}C_5H_5)Zr\{\mu\text{-}C_5H_4(SiMe_2)C_5H_4\}Zr(\eta\text{-}C_5H_5)Cl_2]$,[5] $[(OC)_2M(\mu\text{-}C_5H_4CH_2C_5H_4)M(CO)_2]$ (M = Rh or Ir)[6] and $[Cl_2(\eta\text{-}C_5H_5)Zr\{\mu\text{-}C_5H_4(1,4\text{-}C_6H_4)C_5H_4\}Zr(\eta\text{-}C_5H_5)Cl_2]$.[7] We surmised that the metathesis reaction of $Li_2[SiMe_2(C_5H_4)_2]$ with 2 equivalents of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot 2thf$ would proceed *via* a mononuclear intermediate and that this intermediate might provide a route to heterobinuclear metallocene compounds. The first compound chosen for study was the previously described[8,9] $Li_2[Me_2C(C_5H_4)(C_9H_6)]$, since the envisaged binuclear complexes bridged by it would be chiral, and the two metals would have different ligand environments. Part of this work has been the subject of preliminary communications.[5,10,11]

Results and Discussion

The reaction of $Li_2[Me_2C(C_5H_4)(C_9H_6)]$[8,12,13] with 1 equivalent of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot dme$ (dme = 1,2-dimethoxyethane) in toluene at −78 °C gave red crystals of the *ansa*-bridged mononuclear compound $[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ **1**. Compound **1** is air- and moisture-sensitive, readily soluble in benzene, toluene and thf, but decomposes slowly in dichloromethane. The analytical and spectroscopic data which characterise it and all other new compounds described in this work are given in Table 1 and will not be further discussed except where interpretation is not straightforward.

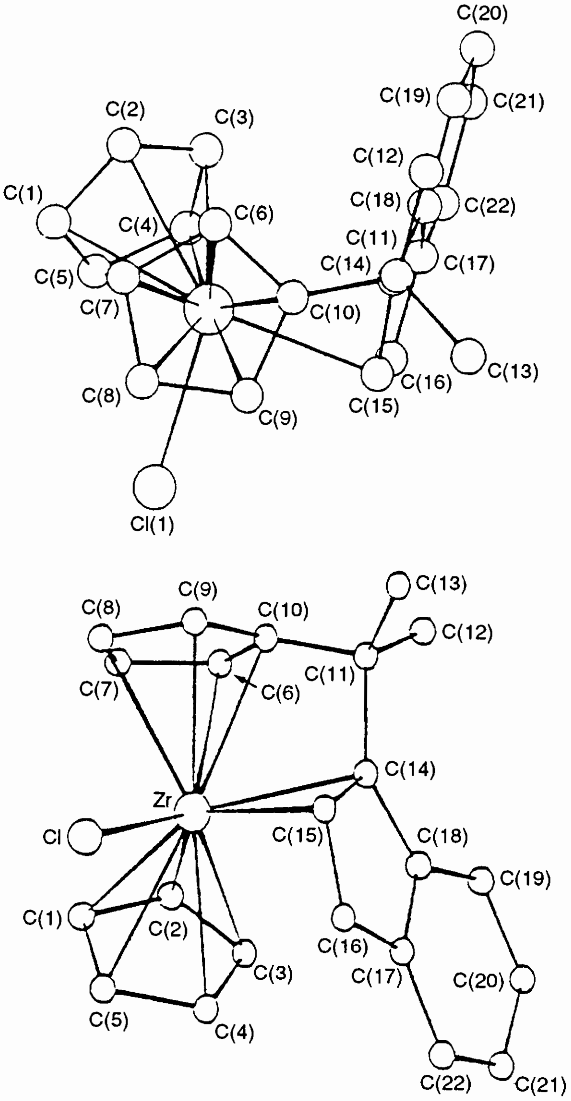

Fig. 1 Two views of the molecular structure of complex **1**

The crystal structure of complex **1** has been determined. The enantiomers of **1** crystallise separately, in the non-centrosymmetric space group $P\bar{4}2_1c$. The molecular structure is shown in Fig. 1 and selected interatomic distances and angles are listed in Table 2. Compound **1** adopts a bent-metallocene type structure

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† *Non-SI unit employed:* bar = 10^5 Pa.

Table 1 Analytical and spectroscopic data[a]

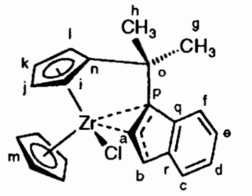
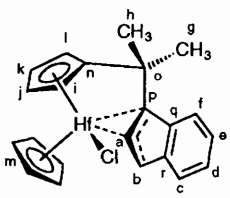
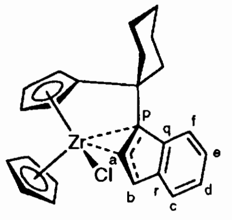
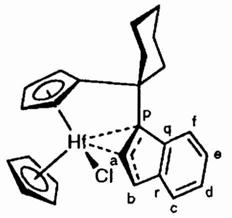
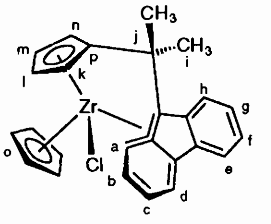
Compound	Spectroscopic data
1 $[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ Red crystals C, 64.1 (64.1); H, 5.2 (5.1); Cl, 8.8 (8.6); *m/z* 410 (M^+)	^{1}H and ^{13}C data in ref. 10 
2 $[Hf\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ Orange C, 53.2 (52.9); H, 4.2 (4.2); Cl, 7.15 (7.1) 	^{1}H:[b] 7.60 [1 H, d, $J(H_fH_e)$ 8, H_f], 7.53 [1 H, d, $J(H_cH_d)$ 8, H_c], 7.29 [1 H, d, $J(H_bH_a)$ 4, H_b], 7.07 [1 H, pseudo t, $J(H_eH_{d,f})$ 8, H_e], 6.78 [1 H, pseudo t, $J(H_dH_{c,e})$ 8, H_d], 6.27 [1 H, d, $J(H_aH_b)$ 4, H_a], 6.25 (1 H, m, H_k), 6.22 (1 H, m, H_i), 6.00 [1 H, pseudo q, $J(H_jH_{i,k,l})$ 3, H_j], 5.67 [1 H, pseudo q, $J(H_lH_{i,j,k})$ 3, H_l], 5.32 (5 H, s, H_m), 2.06 (3 H, s, H_g), 1.66 (3 H, s, H_h) ^{13}C:[b] 141.6 (s, C_n), 138.2 (s, C_q or C_r), 129.4 (s, C_b), 127.9 (s, C_q or C_r), 123.2 (s, C_e), 122.6 (s, C_c), 120.7 (s, C_j), 120.6 (s, C_d), 120.5 (s, C_f), 113.0 (s, C_m), 110.5 (s, C_k), 108.6 (s, C_a), 106.1 (s, C_i), 98.0 (s, C_l), 85.1 (s, C_p), 39.0 (s, C_o), 32.3 (s, C_h), 27.0 (s, C_g)[c]
3 $[Zr\{(CH_2)_5C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]\cdot 0.5C_6H_5Me$ Red C, 68.7 (68.7); H, 5.9 (5.9); Cl, 7.4 (7.1) 	^{1}H:[d] 7.43 [1 H, d, $J(H_cH_d)$ 8, H_c or $J(H_fH_e)$ 8, H_f], 7.42 [1 H, d, $J(H_bH_a)$ 4, H_b], 7.40 [1 H, d, $J(H_cH_d)$ 8, H_c or $J(H_fH_e)$ 8, H_f], 7.10 [1 H, pseudo t, $J(H_dH_{c,e})$ 8, H_d or $J(H_eH_{d,f})$ 8, H_e], 6.91 [1 H, pseudo t, $J(H_dH_{c,e})$ 8, H_d or $J(H_eH_{d,f})$ 8, H_e], 6.35 [1 H, d, $J(H_aH_b)$ 4, H_a], 5.82 [1 H, pseudo q, $J(HH)$ 3, C_5H_4], 5.72 [1 H, pseudo q, $J(HH)$ 3, C_5H_4], 5.37 [1 H, pseudo q, $J(HH)$ 3, C_5H_4], 5.15 (5 H, s, C_5H_5), 4.77 [1 H, pseudo q, $J(HH)$ 3, C_5H_4], 2.28 (2 H, m, CH_2), 2.02 (1 H, m, CH_2), 1.7–1.2 (7 H, br m, CH_2) ^{13}C:[d] 140.6 (s, C_{ipso} of C_5H_4), 137.0 (s, C_q or C_r), 128.9 (coupling obscured by solvent, C_b), 126.8 (s, C_q or C_r), 123.8 [d, $J(CH)$ 155, C_d or C_e], 123.3 [d, $J(CH)$ 165, C_c or C_f], 120.5 [d, $J(CH)$ 159, C_d or C_e], 119.9 [d, $J(CH)$ 157, C_c or C_f], 119.7 [d, $J(CH)$ 172, C_5H_4], 114.1 [d, $J(CH)$ 174, C_5H_5], 112.0 [d, $J(CH)$ 171, C_5H_4], 111.0 [d, $J(CH)$ 152, C_a], 107.5 [d, $J(CH)$ 179, C_5H_4], 97.8 [d, $J(CH)$ 172, C_5H_4], 85.7 (s, C_p), 43.8 [s, $C(CH_2)_5$], 39.2 [t, $J(CH)$ 127, CH_2], 34.8 [t, $J(CH)$ 125, CH_2], 26.3 [t, $J(CH)$ 130, CH_2], 23.2 [t, $J(CH)$ 121, CH_2], 22.0 [t, $J(CH)$ 130, CH_2][e]
4 $[Hf\{(CH_2)_5C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]\cdot 0.5C_6H_5Me$ Orange C, 59.0 (58.5); H, 5.0 (5.0); Cl, 6.4 (6.1) 	^{1}H:[d] 7.55 [1 H, d, $J(H_cH_d)$ 8, H_c or $J(H_fH_e)$ 8, H_f], 7.48 [1 H, d, $J(H_bH_a)$ 4, H_b], 7.44 [1 H, d, $J(H_cH_d)$ 8, H_c or $J(H_fH_e)$ 8, H_f], 7.20 [1 H, pseudo t, $J(H_dH_{c,e})$ 8, H_d or $J(H_eH_{d,f})$ 8, H_e], 6.94 [1 H, pseudo t, $J(H_dH_{c,e})$ 8, H_d or $J(H_eH_{d,f})$ 8, H_e], 6.19 [1 H, d, $J(H_aH_b)$ 4, H_a], 5.84 [1 H, pseudo q, $J(HH)$ 3, C_5H_4], 5.67 [1 H, pseudo q, $J(HH)$ 3, C_5H_4], 5.30 [1 H, pseudo q, $J(HH)$ 3, C_5H_4], 5.03 (5 H, s, C_5H_5), 4.64 [1 H, pseudo q, $J(HH)$ 3, C_5H_4], 2.28 (2 H, m, CH_2), 2.02 (1 H, m, CH_2), 1.66 (1 H, m, CH_2), 1.5 (4 H, br m, CH_2), 1.30 (1 H, m, CH_2), 1.18 (1 H, m, CH_2) ^{13}C:[d] 141.3 (s, C_{ipso} of C_5H_4), 137.8 (s, C_q or C_r), 129.5 (coupling obscured by solvent, C_b), 125.6 (s, C_q or C_r), 123.2 [d, $J(CH)$ 161, C_d or C_e], 122.9 [d, $J(CH)$ 156, C_c or C_f], 120.6 [d, $J(CH)$ 162, C_d or C_e], 120.5 [d, $J(CH)$ 162, C_c or C_f], 119.4 [d, $J(CH)$ 179, C_5H_4], 112.3 [d, $J(CH)$ 178, C_5H_5], 110.0 [d, $J(CH)$ 174, C_5H_4], 108.0 [d, $J(CH)$ 156, C_a], 105.7 [d, $J(CH)$ 174, C_5H_4], 96.5 [d, $J(CH)$ 180, C_5H_4], 84.9 (s, C_p), 43.7 [s, $C(CH_2)_5$], 40.4 [t, $J(CH)$ 128, CH_2], 35.1 [t, $J(CH)$ 128, CH_2], 26.4 [t, $J(CH)$ 123, CH_2], 23.3 [t, $J(CH)$ 126, CH_2], 22.3 [t, $J(CH)$ 126, CH_2][f]
5 $[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)\}(\eta\text{-}C_5H_5)Cl]$ Red C, 67.5 (67.6); H, 5.0 (5.0); Cl, 7.8 (7.7)	^{1}H and ^{13}C data in ref. 10 
6 $[Zr\{Me_2C(\eta\text{-}C_5H_4)_2\}(\eta\text{-}C_5H_5)Cl]$ Pale yellow C, 60.2 (59.7); H, 5.3 (5.3); Cl, 9.85 (9.8)	^{1}H and ^{13}C data in ref. 11

Table 1 (*continued*)

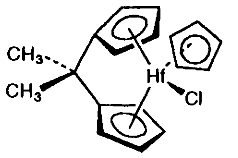
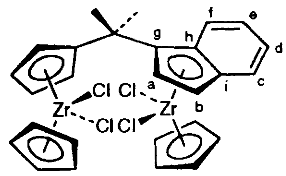
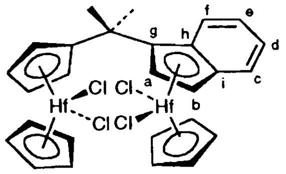
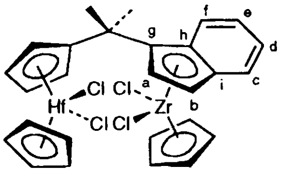
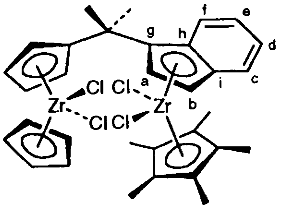
7 $[Hf\{Me_2C(\eta-C_5H_4)_2\}(\eta-C_5H_5)Cl]$ Pale yellow C, 48.3 (48.1); H, 4.3 (4.3); Cl, 7.9 (7.9) 	^1H:[b] 6.09 (2 H, m, C_5H_4), 5.94 (2 H, m, C_5H_4), 5.93 (5 H, s, C_5H_5), 5.82 [2 H, pseudo q, *J*(CH) 2.5, C_5H_4], 5.66 [2 H, pseudo q, *J*(CH) 2.5, C_5H_4], 1.64 (3 H, s, CH_3), 1.55 (3 H, s, CH_3);[g] 5.99 (2 H, m, C_5H_4), 5.75 (2 H, m, C_5H_4), 5.58 (5 H, s, C_5H_5), 5.52 (2 H, m, C_5H_4), 5.18 (2 H, m, C_5H_4), 1.34 (3 H, s, CH_3), 1.30 (3 H, s, CH_3)
8 $[Cl_2(\eta-C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta-C_5H_5)Cl_2]$ Yellow C, 48.0 (48.1); H, 4.1 (3.9); Cl, 21.3 (21.0) 	^1H data in ref. 9 $^{13}C-\{^1H\}$:[h] 139.9 (s, C_{ipso} of C_5H_4), 127.6 (s, $C_{g,h,i}$), 126.1 (s, C_c), 125.8 (s, C_e), 125.4 (s, $C_{g,h,i}$), 125.2 (s, C_f), 124.9 (s, C_d), 122.7 (s, $C_{g,h,i}$), 122.2 (s, C_a), 116.9 (s, C_5H_4), 115.5 (s, C_5H_4), 115.3 [s, $(C_9H_6)Zr(\mathit{C}_5H_5)$], 115.0 [s, $(C_5H_4)Zr(\mathit{C}_5H_5)$], 112.8 (s, C_5H_4), 110.2 (s, C_5H_4), 99.6 (s, C_b), 39.1 (s, *C*Me_2), 29.1 (s, CH_3), 28.2 (s, CH_3)[j]
9 $[Cl_2(\eta-C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta-C_5H_5)Cl_2]$ Yellow C, 38.6 (38.2); H, 3.1 (3.1); Cl, 16.6 (16.7) 	^1H data in ref. 9 $^{13}C-\{^1H\}$:[h] 139.9 (s, C_{ipso} of C_5H_4), 127.6 (s, $C_{g,h,i}$), 126.1 (s, C_c), 125.8 (s, C_e), 125.4 (s, $C_{g,h,i}$), 125.2 (s, C_f), 124.9 (s, C_d), 122.7 (s, $C_{g,h,i}$), 122.2 (s, C_a), 116.9 (s, C_5H_4), 115.5 (s, C_5H_4), 115.3 [s, $(C_9H_6)Hf(\mathit{C}_5H_5)$], 115.0 [s, $(C_5H_4)Hf(\mathit{C}_5H_5)$], 112.8 (s, C_5H_4), 110.2 (s, C_5H_4), 99.6 (s, C_b), 39.1 (s, *C*Me_2), 29.1 (s, CH_3), 28.2 (s, CH_3)[j]
10 $[Cl_2(\eta-C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta-C_5H_5)Cl_2]$ Yellow C, 42.4 (42.6); H, 3.5 (3.4); Cl, 18.7 (18.6)	^1H and ^{13}C data in ref. 9
11 $[Cl_2(\eta-C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta-C_5H_5)Cl_2]$ Yellow C, 42.4 (42.6); H, 3.5 (3.4); Cl, 18.6 (18.6) 	^1H data in ref. 14 $^{13}C-\{^1H\}$:[h] 139.6 (s, C_{ipso} of C_5H_4), 130.1 (s, $C_{g,h,i}$), 128.6 (s, $C_{g,h,i}$), 125.9 (s, C_c), 125.8 (s, C_e), 125.3 (s, C_f), 124.8 (s, C_d), 123.4 (s, $C_{g,h,i}$), 122.3 (s, C_a), 117.1 (s, C_5H_4), 116.6 [s, $Zr(C_5H_5)$], 115.8 (s, C_5H_4), 115.0 [s, $Hf(C_5H_5)$], 112.5 (s, C_5H_4), 110.2 (s, C_5H_4), 100.7 (s, C_b), 39.3 (s, *C*Me_2), 29.1 (s, CH_3), 28.2 (s, CH_3)[j]
12 $[Cl_2(\eta-C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta-C_5Me_5)Cl_2]$ Yellow C, 51.5 (51.6); H, 4.8 (4.9); Cl, 18.6 (19.0)	^1H and ^{13}C data in ref. 9 

Table 1 *(continued)*

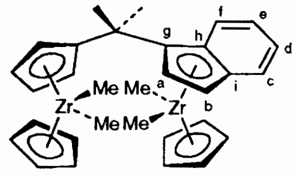
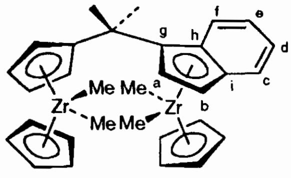
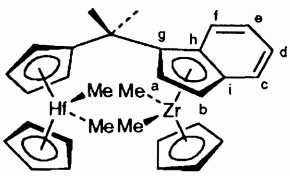
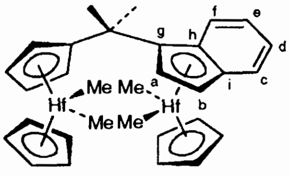
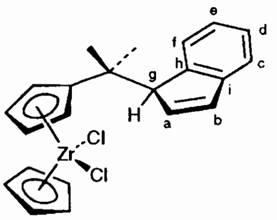
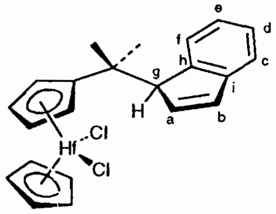
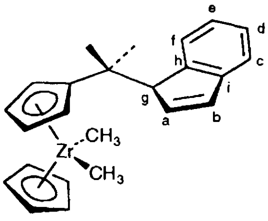
13 $[Me_2(\eta\text{-}C_5H_5)Zr\text{-}\{C_5H_4(CMe_2)C_9H_6\}\text{-}Zr(\eta\text{-}C_5H_5)Me_2]$ Pale orange C, 62.6 (62.8); H, 6.4 (6.5) 	^{1}H:^{d} 7.43 [1 H, d, $J(H_fH_e)$ 9, H_f], 7.09 [1 H, d, $J(H_cH_d)$ 8, H_c], 6.79 (1 H, m, H_e), 6.67 (1 H, m, H_d), 6.41 (2 H, m, H_a and H_b), 5.95 (1 H, m, C_5H_4), 5.79 (1 H, m, C_5H_4), 5.75 [5 H, s, $(C_5H_4)Zr(C_5H_5)$], 5.48 [5 H, s, $(C_9H_6)Zr(C_5H_5)$], 5.46 (1 H, m, C_5H_4), 5.40 (1 H, m, C_5H_4), 1.56 [3 H, s, $C(CH_3)$], 1.43 [3 H, s, $C(CH_3)$], 0.05 [3 H, s, $(C_9H_6)Zr(CH_3)$], 0.00 [3 H, s, $(C_5H_4)Zr(CH_3)$], −0.01 [3 H, s, $(C_5H_4)Zr(CH_3)$], −0.22 [3 H, s, $(C_9H_6)Zr(CH_3)$] ^{13}C:^{d} 138.1 (s, C_{ipso} of C_5H_4), 125.3 [d, J(CH) 161, C_c and C_f], 125.3 (s, $C_{g,h,i}$), 124.0 (s, $C_{g,h,i}$), 123.1 [d, J(CH) 159, C_e], 122.6 [d, J(CH) 160, C_d], 120.3 (s, $C_{g,h,i}$), 116.9 [d, J(CH), C_a], 112.4 [d, J(CH) 172, $(C_9H_6)Zr(C_5H_5)$], 110.8 [d, J(CH) 172, $(C_5H_4)Zr(C_5H_5)$], 110.5 [d, J(CH) 164, C_5H_4], 109.5 [d, J(CH) 170, C_5H_4], 109.1 [d, J(CH) 163, C_5H_4], 108.6 [d, J(CH) 164, C_5H_4], 100.9 [d, J(CH) 175, C_b], 37.9 (s, CMe_2), 35.3 [q, J(CH) 117, $(C_9H_6)Zr(CH_3)$], 32.9 [q, J(CH) 117, $(C_9H_6)Zr(CH_3)$], 31.6 [q, J(CH) 117, $(C_9H_6)Zr(CH_3)$], 31.4 [q, J(CH) 116, $(C_5H_4)Zr(CH_3)$], 30.1 [q, J(CH) 125, $C(CH_3)_2$]^{k}
14 $[Me_2(\eta\text{-}C_5H_5)Zr\text{-}\{C_5H_4(CMe_2)C_9H_6\}\text{-}Hf(\eta\text{-}C_5H_5)Me_2]$ Pale yellow C, 54.4 (54.7); H, 5.5 (5.6) 	^{1}H:^{d} 7.42 [1 H, d, $J(H_fH_e)$ 9, H_f], 7.09 [1 H, d, $J(H_cH_d)$ 8, H_c], 6.80 (1 H, m, H_e), 6.69 (1 H, m, H_d), 6.36 [1 H, d, $J(H_aH_b)$ 4, H_a], 6.32 [1 H, d, $J(H_bH_a)$ 4, H_b], 5.93 [1 H, pseudo q, J(HH) 3, C_5H_4], 5.78 (1 H, m, C_5H_4), 5.75 [5 H, s, $Zr(C_5H_5)$], 5.46 [1 H, pseudo q, J(HH) 3, C_5H_4], 5.41 (1 H, m, C_5H_4), 5.39 [5 H, s, $Hf(C_5H_5)$], 1.57 [3 H, s, $C(CH_3)$], 1.43 [3 H, s, $C(CH_3)$], 0.00 [3 H, s, $Zr(CH_3)$], −0.01 [3 H, s, $Zr(CH_3)$], −0.11 [3 H, s, $Hf(CH_3)$], −0.39 [3 H, s, $Hf(CH_3)$] ^{13}C-{^{1}H}:^{d} 138.1 (s, C_{ipso} of C_5H_4), 125.5 (s, C_c), 125.2 (s, C_f), 123.4 (s, C_e), 123.0 (s, $C_{g,h,i}$), 122.7 (s, C_d), 120.6 (s, $C_{g,h,i}$), 117.2 (s, C_a), 111.6 [s, $Hf(C_5H_5)$], 110.8 [s, $Zr(C_5H_5)$], 110.5 (s, C_5H_4), 109.9 (s, C_5H_4), 109.0 (s, C_5H_4), 108.6 (s, C_5H_4), 100.2 (s, C_b), 41.1 [s, $Hf(CH_3)$], 38.5 [s, $Hf(CH_3)$], 37.9 (s, CMe_2), 31.5 [s, $Zr(CH_3)$], 31.4 [s, $Zr(CH_3)$], 30.1 [s, $C(CH_3)$], 30.0 [s, $C(CH_3)$]^{k,l}
15 $[Me_2(\eta\text{-}C_5H_5)Hf\text{-}\{C_5H_4(CMe_2)C_9H_6\}\text{-}Zr(\eta\text{-}C_5H_5)Me_2]$ Pale yellow C, 53.2 (54.7); H, 5.4 (5.6) 	^{1}H:^{d} 7.42 [1 H, d, $J(H_fH_e)$ 9, H_f], 7.09 [1 H, d, $J(H_cH_d)$ 8, H_c], 6.78 (1 H, m, H_e), 6.66 (1 H, m, H_d), 6.41 (2 H, m, H_a and H_b), 5.87 [1 H, pseudo q, J(HH) 3, C_5H_4), 5.72 (1 H, m, C_5H_4), 5.68 [5 H, s, $Hf(C_5H_5)$], 5.47 [5 H, s, $Zr(C_5H_5)$], 5.37 (2 H, m, C_5H_4), 1.56 [3 H, s, $C(CH_3)$], 1.45 [3 H, s, $C(CH_3)$], 0.05 [3 H, s, $Zr(CH_3)$], −0.18 [3 H, s, $Hf(CH_3)$], −0.19 [3 H, s, $Hf(CH_3)$], −0.22 [3 H, s, $Zr(CH_3)$] ^{13}C-{^{1}H}:^{g} 136.7 (s, C_{ipso} of C_5H_4), 125.3 (s, C_c and C_f), 124.0 (s, $C_{g,h,i}$), 123.1 (s, C_e), 122.6 (s, C_d), 120.3 (s, $C_{g,h,i}$), 117.0 (s, C_a), 112.4 [s, $Zr(C_5H_5)$], 110.3 [s, $Hf(C_5H_5)$], 109.9 (s, C_5H_4), 108.8 (s, C_5H_4), 108.7 (s, C_5H_4), 108.5 (s, C_5H_4), 101.0 (s, C_b), 37.9 (s, CMe_2), 37.7 [s, $Hf(CH_3)$], 37.5 [s, $Hf(CH_3)$], 35.2 [s, $Zr(CH_3)$], 32.8 [s, $Zr(CH_3)$], 30.0 [s, $C(CH_3)_2$]^{k,l}
16 $[Me_2(\eta\text{-}C_5H_5)Hf\text{-}\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta\text{-}C_5H_5)Me_2]$ Pale yellow C, 48.9 (48.5); H, 4.9 (5.0) 	^{1}H: 7.43 [1 H, d, $J(H_fH_e)$ 9, H_f], 7.08 [1 H, d, $J(H_cH_d)$ 8, H_c], 6.80 (1 H, m, H_e), 6.68 (1 H, m, H_d), 6.36 [1 H, d, $J(H_aH_b)$ 4, H_a], 6.31 [1 H, d, $J(H_bH_a)$ 4, H_b], 5.86 [1 H, pseudo q, J(HH) 3, C_5H_4], 5.70 (1 H, m, C_5H_4), 5.67 [5 H, s, $(C_5H_4)Hf(C_5H_5)$], 5.39 [5 H, s, $(C_9H_6)Hf(C_5H_5)$], 5.36 (2 H, m, C_5H_4), 1.58 [3 H, s, $C(CH_3)$], 1.46 [3 H, s, $C(CH_3)$], −0.11 [3 H, s, $(C_9H_6)Hf(CH_3)$], −0.18 [3 H, s, $(C_5H_4)Hf(CH_3)$], −0.19 [3 H, s, $(C_5H_4)Hf(CH_3)$], −0.39 [3 H, s, $(C_9H_6)Hf(CH_3)$] ^{13}C-{^{1}H}:^{d} 136.7 (s, C_{ipso} of C_5H_4), 125.5 (s, C_c), 125.3 (s, C_f), 123.4 (s, C_e), 123.0 (s, $C_{g,h,i}$), 122.7 (s, C_d), 120.5 (s, $C_{g,h,i}$), 117.2 (s, C_a), 111.6 [s, $(C_9H_6)Hf(C_5H_5)$], 110.3 [s, $(C_5H_4)Hf(C_5H_5)$], 109.8 (s, C_5H_4), 108.7 (s, $2C_5H_4$), 108.4 (s, C_5H_4), 100.2 (s, C_b), 41.1 [s, $(C_9H_6)Hf(CH_3)$], 38.4 [s, $(C_9H_6)Hf(CH_3)$], 37.9 (s, CMe_2), 37.7 [s, $(C_5H_4)Hf(CH_3)$], 37.5 [s, $(C_5H_4)Hf(CH_3)$], 29.9 [s, $C(CH_3)_2$]^{k,l}
17 $[Zr\{C_5H_4CMe_2(C_9H_7)\}\text{-}(\eta\text{-}C_5H_5)Cl_2]$ White C, 59.0 (58.9); H, 5.0 (5.0); Cl, 15.9 (15.8) 	^{1}H:^{h} 7.25 [1 H, d, $J(H_fH_e)$ 7, H_f or $J(H_cH_d)$ 7, H_c], 7.19 [1 H, pseudo t, $J(H_dH_{c,e})$ 7, H_d, or $J(H_eH_{d,f})$ 7, H_e], 7.02 [1 H, pseudo t, $J(H_dH_{c,e})$ 7, H_d, or $J(H_eH_{d,f})$ 7, H_e], 6.73 [1 H, dd, $J(H_aH_b)$ 6, $J(H_{a,b}H_g)$ 2, H_a or H_b], 6.65 [1 H, d, $J(H_fH_e)$ 7, H_f or $J(H_cH_d)$ 7, H_c], 6.49 (5 H, s, C_5H_5), 6.46 (2 H, m, C_5H_4), 6.39 (1 H, m, C_5H_4), 6.33 [1 H, dd, $J(H_aH_b)$ 6, $J(H_{a,b}H_g)$ 2, H_a or H_b], 6.28 (1 H, m, C_5H_4), 3.46 (1 H, m, H_g), 1.56 (3 H, s, CH_3), 1.34 (3 H, s, CH_3) ^{13}C-{^{1}H}:^{h} 145.6 (s, C_h or C_i), 144.5 (s, C_h or C_i), 142.0 (s, C_{ipso} of C_5H_4), 137.0 (s, C_a or C_b), 132.3 (s, C_a or C_b), 126.9 (s, C_d or C_e), 124.8 (s, C_c or C_f), 124.5 (s, C_d or C_e), 121.0 (s, C_c or C_f), 117.3 (s, C_5H_4), 117.3 (s, C_5H_4), 116.3 (s, C_5H_5), 114.3 (s, C_5H_4), 111.0 (s, C_5H_4), 64.0 (s, C_g), 39.4 (s, CMe_2), 27.0 (s, CH_3), 23.4 (s, CH_3)^{c}
18 $[Hf\{C_5H_4CMe_2(C_9H_7)\}\text{-}(\eta\text{-}C_5H_5)Cl_2]$ White C, 49.2 (49.3); H, 4.0 (4.1); Cl, 13.4 (13.2) 	^{1}H:^{h} 7.24 [1 H, d, $J(H_fH_e)$ 7, H_f or $J(H_cH_d)$ 7, H_c], 7.18 [1 H, pseudo t, $J(H_dH_{c,e})$ 7, H_d, or $J(H_eH_{d,f})$ 7, H_e], 7.00 [1 H, pseudo t, $J(H_dH_{c,e})$ 7, H_d, or $J(H_eH_{d,f})$ 7, H_e], 6.73 [1 H, dd, $J(H_aH_b)$ 6, $J(H_{a,b}H_g)$ 2, H_a or H_b], 6.57 [1 H, d, $J(H_fH_e)$ 7, H_f or $J(H_cH_d)$ 7, H_c], 6.39 (5 H, s, C_5H_5), 6.39 (1 H, m, C_5H_4), 6.36 (1 H, m, C_5H_4), 6.33 [1 H, dd, $J(H_aH_b)$ 6, $J(H_{a,b}H_g)$ 2, H_a or H_b], 6.28 (1 H, m, C_5H_4), 6.19 (1 H, m, C_5H_4), 3.46 (1 H, m, H_g), 1.56 (3 H, s, CH_3), 1.30 (3 H, s, CH_3) ^{13}C-{^{1}H}:^{h} 145.6 (s, C_h or C_i), 144.6 (s, C_h or C_i), 139.8 (s, C_{ipso} of C_5H_4), 137.1 (s, C_a or C_b), 132.3 (s, C_a or C_b), 126.9 (s, C_d or C_e), 125.0 (s, C_c or C_f), 124.5 (s, C_d or C_e), 121.0 (s, C_c or C_f), 116.0 (s, C_5H_4), 115.7 (s, C_5H_4), 114.9 (s, C_5H_5), 113.4 (s, C_5H_4), 109.5 (s, C_5H_4), 64.3 (s, C_g), 39.3 (s, CMe_2), 27.0 (s, CH_3), 23.1 (s, CH_3)^{c}

Table 1 (*continued*)

19 $[Zr\{C_5H_4CMe_2(C_9H_7)\}(\eta\text{-}C_5H_5)Me_2]$ Pale yellow C, 70.6 (70.7); H, 7.1 (6.9)  	^{1}H:^{d} 7.24 [1 H, d, $J(H_fH_e)$ 7, H_f or $J(H_cH_d)$ 7, H_c], 7.21 [1 H, m (coupling obscured by solvent), H_d, or H_e], 7.09 [1 H, pseudo t, $J(H_dH_{c,e})$ 7, H_d, or $J(H_eH_{d,f})$ 7, H_e], 6.74 [1 H, d, $J(H_fH_e)$ 7, H_f or $J(H_cH_d)$ 7, H_c], 6.69 [1 H, d, $J(H_aH_b)$ 6, H_a or H_b], 6.22 [1 H, d, $J(H_aH_b)$ 6, H_a or H_b], 5.88 (1 H, m, C_5H_4), 5.80 (5 H, s, C_5H_5), 5.75 (1 H, m, C_5H_4), 5.64 (1 H, m, C_5H_4), 5.61 (1 H, m, C_5H_4), 3.39 (1 H, br s, H_g), 1.05 [3 H, s, $C(CH_3)$], 0.98 [3 H, s, $C(CH_3)$], −0.03 [3 H, s, $Zr(CH_3)$], −0.05 [3 H, s, $Zr(CH_3)$] $^{13}C\text{-}\{^1H\}$:^{d} 145.6 (s, C_h or C_i), 145.1 (s, C_h or C_i), 137.6 (s, C_{ipso} of C_5H_4), 137.3 (s, C_a or C_b), 132.5 (s, C_a or C_b), 127.0 (s, C_d or C_e), 125.3 (s, C_c or C_f), 124.7 (s, C_d or C_e), 121.2 (s, C_c or C_f), 110.8 (s, C_5H_4), 110.8 (s, C_5H_5), 110.1 (s, C_5H_4), 109.2 (s, C_5H_4), 107.9 (s, C_5H_4), 64.6 (s, C_g), 38.4 (s, CMe_2), 31.6 [s, $Zr(CH_3)$], 31.2 [s, $Zr(CH_3)$], 27.4 [s, $C(CH_3)$], 22.9 [s, $C(CH_3)$]^c
$Li[C_5H_4CMe_2(C_9H_7)]$ Pale orange C, 85.6 (89.5); H, 7.8 (7.5); Li, 3.0 (2.9)	^{1}H:^{b} 7.15 [1 H, d, $J(H_fH_e)$ 7, H_f or $J(H_cH_d)$ 7, H_c], 7.02 [1 H, pseudo t, $J(H_dH_{c,e})$ 7, H_d, or $J(H_eH_{d,f})$ 7, H_e], 6.78 [1 H, pseudo t, $J(H_dH_{c,e})$ 7, H_d, or $J(H_eH_{d,f})$ 7, H_e], 6.71 [1 H, d, $J(H_aH_b)$, 6, H_a or H_b], 6.54 [1 H, d, $J(H_aH_b)$ 6, H_a or H_b], 6.17 [1 H, d, $J(H_fH_e)$ 7, H_f or $J(H_cH_d)$ 7, H_c], 5.64 (2 H, m, C_5H_4), 5.60 (2 H, m, C_5H_4), 3.69 (1 H, br s, H_g), 1.47 (3 H, s, CH_3), 0.98 (3 H, s, CH_3) $^{13}C\text{-}\{^1H\}$:^{b} 147.7 (s, C_h or C_i), 145.9 (s, C_h or C_i), 139.9 (s, C_a or C_b), 131.0 (s, C_a or C_b), 130.0 (s, C_{ipso} of C_5H_4), 126.7 (s, C_c or C_f), 125.9 (s, C_d or C_e), 124.3 (s, C_d or C_e), 120.1 (s, C_c or C_f), 102.5 (s, C_5H_4), 101.8 (s, C_5H_4), 65.5 (s, C_g), 38.4 (s, CMe_2), 31.3 (s, CH_3), 24.5 (s, CH_3)^m

[a] Analytical data given as: found (calculated) %. ^{1}H NMR at 300 MHz, ^{13}C at 75 MHz. Data given as: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), relative intensity, coupling constant (in Hz) and assignment. [b] In $[^2H_8]$thf. [c] Proton and ^{13}C assignments from selective ^{1}H decoupling experiments, $^{13}C\text{–}^1H$ shift correlation experiment and comparison with compound **1**. [d] In C_6D_6. [e] Proton assignments from selective decoupling experiments, ^{13}C assignments from comparison with compound **4**. [f] Proton assignments from selective decoupling experiments, ^{13}C assignments from $^{13}C\text{–}^1H$ shift correlation experiment. [g] Proton assignments from selective decoupling, COSY and NOESY experiments, ^{13}C assignments from $^{13}C\text{–}^1H$ shift correlation experiment. [h] In CD_2Cl_2. [i] Proton assignments from selective decoupling, COSY 45 and NOESY experiments, ^{13}C assignments from $^{13}C\text{–}^1H$ shift correlation experiment. [j] Proton and ^{13}C assignments from selective ^{1}H decoupling experiments, $^{13}C\text{–}^1H$ shift correlation experiment and comparison with compounds **9–11**. [k] Proton and ^{13}C assignments from selective ^{1}H decoupling experiments, $^{13}C\text{–}^1H$ shift correlation experiment and comparison with compounds **14–16**. [l] One of the quaternary signals (g, h or i) is not observed, presumably obscured by another signal. [m] Proton assignments from selective decoupling experiments, ^{13}C assignments from $^{13}C\text{–}^1H$ shift correlation experiment and by comparison with ^{13}C NMR spectrum of indene (C_9H_8). Lithium-7 NMR (116.6 MHz, $[^2H_6]$thf, room temperature): δ −4.0 (relative to 1.0 mol dm $^{-3}$ LiCl in D_2O).

Table 2 Selected interatomic distances (Å) and angles (°) for compound **1**

Zr–C(14)	2.587(8)	Zr–Cl	2.489(2)
Zr–C(15)	2.497(8)	Zr–C (C_5H_5)	2.51 (mean)
Zr • • • C(16)	3.141(9)	Zr–C (C_5H_4)	2.47 (mean)
Zr • • • C(17)	3.589(8)	Zr–Cp	2.212
Zr • • • C(18)	3.329(7)	Zr–Cp′	2.165
C(14)–C(15)	1.43(1)	C(15)–C(16)	1.40(1)
C(10)–C(11)–C(14)	101.5(6)	Cp–Zr–Cp′	129.1
C(11)–C(14)–C(18)	131.8(8)	Cl–Zr–Cp	105.5
Zr–C(14)–C(15)	70.2(4)	Cl–Zr–Cp′	104.7
C(14)–Zr–Cl(1)	117.1(2)		

Cp and Cp′ denote the centroids of the C_5H_5 and C_5H_4 rings respectively.

with a centroid–Zr–centroid angle of 129.1°. The η-C_5H_5 and η-C_5H_4 rings are planar (deviations from best least-squares plane less than 0.008 and 0.003 Å respectively) and their zirconium–carbon and –centroid distances are similar to those reported for $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$.[13–15] During the course of this work the crystal structure of $[Ti\{C_5H_4(CMe_2)C_9H_6\}Cl_2]$ was reported.[16] The most interesting feature of the molecular structure of **1** is the mode of co-ordination of the indenyl ligand to the zirconium atom. It is planar (to within 0.04 Å) and bonded in an η^2 fashion, *via* C(14) and C(15). The Zr, Cl, C(14) and C(15) atoms are approximately coplanar (deviations from best least-squares plane less than 0.11 Å), whilst C(16) lies well outside this plane. The angle between the line Zr–Cl and the plane Zr, C(14), C(15) is 11.2°, whilst the deviation of the Cl atom from the Zr, C(14) and C(15) plane is 0.48 Å.

Since the frontier molecular orbitals of a bent metallocene lie in the equatorial plane between the cyclopentadienyl ligands,[17–19] the ligand plane Zr, Cl, C(14) would normally be expected to coincide with the equatorial plane. For compound **1** this is not quite the case, which presumably reflects the constraints imposed on the molecular geometry by the *ansa* bridge. The Zr–C(14) bond length of 2.587(8) Å is about 0.09 Å longer than the Zr–C(15) bond length of 2.497(8) Å. It may be that C(14) is constrained from closer approach to the metal by the *ansa* bridge [bond strain in the *ansa* bridge is indicated by the rather small C(10)–C(11)–C(14) angle of 101.5°]. The short Zr–C(15) distance and acute Zr–C(14)–C(15) angle (70.2°) suggest a pronounced bonding interaction between the electrophilic zirconium atom and C(15). The Zr • • • C(16) separation of 3.141(9) Å is outside the range of strong, direct covalent bonding.

The C(14)–C(15) bond length [1.43(1) Å] is only about 0.03 Å longer than C(15)–C(16) [1.40(1) Å], whilst the almost coplanar disposition of carbon atoms around C(14) is consistent with the hybridisation of C(14) being closer to sp^2 than sp^3. Thus the C(14)–C(16) bonding situation is closer to that expected for a delocalised π-allyl system than a σ,π system with sp^3 hybridisation at C(14) and a double bond between C(15) and C(16).[20]

The Zr–Cl bond length in zirconocene chloride derivatives is highly sensitive to the extent of electronic saturation of the metal centre.[21] The Zr–Cl bond lengths found in 16-valence-electron compounds $[Zr(\eta\text{-}C_5H_5)_2Cl(R)]$ typically lie in the range 2.44–2.45 Å,[22,23] whilst the Zr–Cl bond lengths of 18-electron compounds $[Zr(\eta\text{-}C_5H_5)_2Cl(R)L]$ are typically around 2.55–2.58 Å.[24] For compound **1** the Zr–Cl bond length of 2.489(2) Å is intermediate between the values typical of 16- and 18-electron zirconocene derivatives. This is consistent with electron donation from the η^2-indenyl group being intermediate between η^1 (σ) and η^3 (π) co-ordination. A similar Zr–Cl bond length of 2.480 Å has been reported for the zirconocene alkenyl $[Zr(\eta\text{-}C_5H_5)_2Cl\{C(Ph){=}CMe_2\}]$.[22] The molecular structure of this compound suggests significant π donation, from the p_π orbital of C_{ipso} of the phenyl group, to the vacant orbital of the zirconium atom which lies in the Zr–R–Cl plane. It seems reasonable to propose that the *ansa* bridge also prevents the indenyl ligand from adopting an η^3-allyl type co-ordination mode. This mode would give the favourable 18-valence-electron configuration for the metal.[25] Evidence for strain in the *ansa* ligand is the acute C(10)–C(11)–C(14) angle of 101.5(6)° and a large C(11)–C(14)–C(18) angle of 131.8(8)°. These bond angles would have to be further distorted if the C(16) atom was to move closer to the equatorial plane.

A similar η^2 co-ordination is observed in benzyl complexes[26] and in a zirconocene–η^2-butadiene complex.[27] Extended-Hückel molecular orbital calculations, performed on the model compounds $[MH_3(CH_2CH{=}CH_2)]$ and $[MH_3\{C(=CH_2)-CH{=}CH_2\}]$, suggest there is an energetically favourable p_π–d_π interaction causing acute M–C–*C* angles for the zirconium species.[20] A d^2 *ansa*-η^2-indene–zirconium compound somewhat similar to **1** has been described.[28] The η^2-bonding mode explains the formation of the observed diastereomer. For the alternative diastereomer to adopt a similar mode one of the methyl groups of the *ansa* bridge would be brought very close to the C_5H_5 ligand, resulting in significant steric crowding.

The ^1H NMR spectrum of complex **1** is consistent with a solution structure similar to the molecular structure in Fig. 1. Detailed NMR studies including selective ^1H decoupling, correlation (COSY) and nuclear Overhauser effect spectroscopy (NOESY) experiments allowed the individual assignment of all the hydrogens. Full details of the NMR studies are available elsewhere.[25] Compound **1** possesses two chiral elements and inversion of the configuration at the zirconium atom would result in a diastereomer, as would co-ordination of the alternative face of the indenyl group to the metal, thus two possible diastereomers are possible. These are shown in Fig. 2. The ^1H NMR spectrum confirms that only one diastereomer (one pair of enantiomers) is present.

Two NOESY experiments were performed. The first[29] spectrum using a mixing time of 2 s and a recycle delay of 3 s shows that one of the methyl signals h is correlated with one of the indenyl C_5 ring signals a and one of the C_5H_4 signals i whilst the other methyl group g is correlated with one of the indenyl C_6 ring signals f and a different C_5H_4 signal l. These correlations are consistent with a stereorigid molecular structure without free rotation about the bridging C–C bonds of the *ansa* ligand. The second NOESY spectrum employed a mixing time and recycle delay of 8 s and showed that the C_5H_5 signal m is correlated with two of the C_5H_4 signals k and l. Hydrogen l is correlated with methyl group g, which in turn is correlated with the indenyl C_6 ring signal f. This suggests that the diastereomer present is that which has the indenyl C_6 ring and the C_5H_5 ring on the same side of the molecule (the top pair of enantiomers shown in Fig. 2). The observed correlation of the C_5H_5 signal m with the indenyl signals b and c is also consistent with this structure. The NOESY spectrum also allows assignment of the C_5H_4 signals j and k as the β-protons next to the α-protons i and l, respectively.

The ^{13}C NMR spectrum of complex **1** provides clear support for the η^2 mode of co-ordination of the indenyl ring, indeed this bonding mode was proposed on the basis of the NMR studies before the crystal structure was determined.[25] The assignments of the CH and CH_3 signals were based on a ^{13}C–^1H shift correlation experiment. The signal n was assigned to the *ipso*-carbon of the C_5H_4 ring by comparison with those of many other *ansa*-bridged complexes. Similarly, the signals q and r were assigned as the C_6–C_5 ring-junction carbons of the indenyl ligand by comparison with other spectra, as was the assignment of signal o to the CMe_2 bridging carbon atom.

The ^1H and ^{13}C NMR spectra of complex **1** are consistent with η^5 co-ordination of the C_5H_5 and C_5H_4 ligands to zirconium. The bridgehead quaternary carbon signal C_q lies at δ 84.4 compared with δ 111.7 for C_a and δ 129.8 for C_b. These chemical shifts are not consistent with those expected for η^1 or η^3 co-ordination of the indenyl group to the metal. For example, the relevant ^{13}C chemical shifts for the η^3-indenyl complex $[Ni(\eta^3\text{-}C_9H_7)_2]$ are δ 106.6 (central) and 67.6 (terminal).[30] We note that for the η^3-allyl derivative $[Zr\{(\eta\text{-}C_5Me_4)CH_2CH_2(\eta^3\text{-}CHCHCH_2)\}(\eta\text{-}C_5Me_5)]^+$ (in which the allyl fragment is joined to the C_5Me_4 ring by a CH_2CH_2 bridge) the ^{13}C chemical shifts of the η^3-$CHCHCH_2$ fragment are δ 85.5, 143.1 and 83.7 respectively.[31] If the indenyl group of compound **1** was co-ordinated in an η^3 fashion to the metal one would expect the chemical shift of C_a to be considerably higher than those of both C_p and C_b. The NMR data for the few η^1-indenyl complexes that have been reported show ^1H and ^{13}C chemical shifts corresponding to H_a and C_a at significantly higher values than for H_b and C_b,[14,32] whilst the opposite is found for compound **1**. The chemical shift of C_a is about 20 ppm lower than the shifts of the C_5 ring, C–C double-bonded carbon atoms of indene, both around δ 133, whilst that of C_b is quite close to these values.[30]

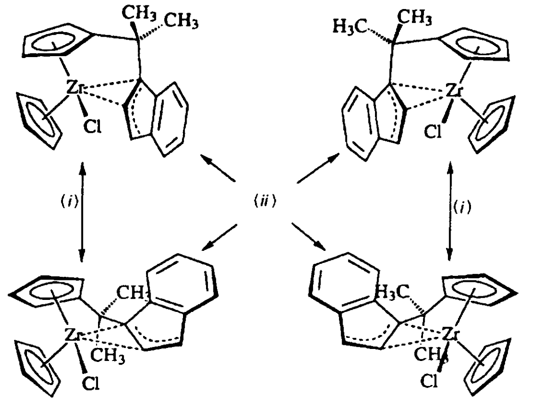
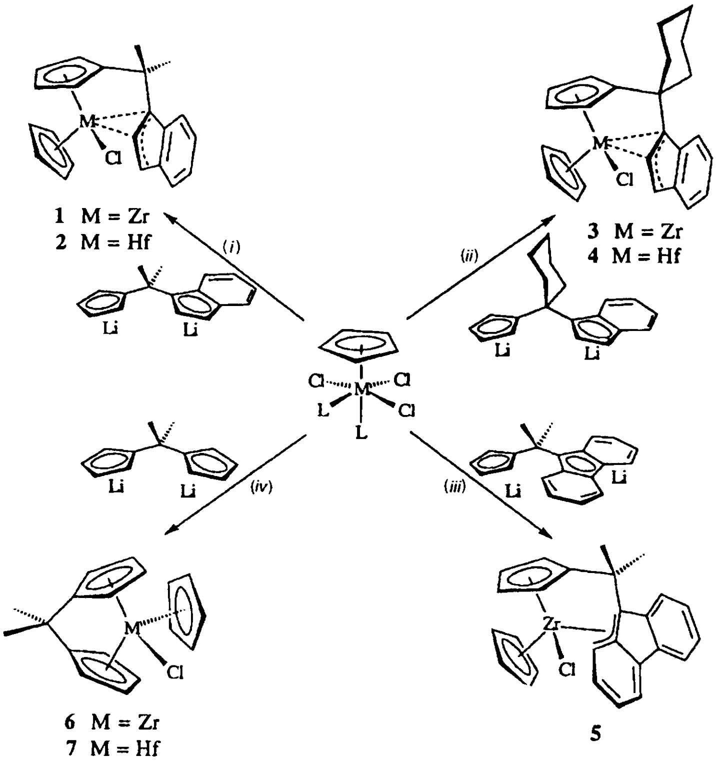


Fig. 2 Diastereomers (top and bottom pairs) and enantiomers (left and right pairs) of complex **1**. (i) Co-ordination of alternative indenyl faces; (*ii*) inversion of configuration at zirconium

The structure of complex **1** provides the first example of η^2 co-ordination of an indenyl ligand to a transition-metal centre, although such co-ordination of cyclopentadienyl has been observed in the neutral, paramagnetic compound $[Ti(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_5H_5)]$.[33] It was described in terms of a three-centre, four-electron bonding model.

Addition of toluene at −78 °C to a stirred mixture of $Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot 0.75Et_2O$ and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$dme gave air- and moisture-sensitive orange crystals of $[Hf\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ **2** in 81% yield. The ^1H and ^{13}C NMR spectra of **2** (Table 1) are very similar to those of **1**, and clearly indicate analogous molecular structures. In particular, the ^{13}C chemical shifts corresponding to C_p, C_a, and C_b lie at δ 85.1, 108.6 and 129.4 respectively, and this suggests there is a similar η^2 co-ordination of the indenyl ligand to the hafnium.

The dilithium salt $Li_2[(CH_2)_5C(C_5H_4)(C_9H_6)]\cdot 0.8Et_2O$ was prepared as a pyrophoric pale yellow solid by treatment of 6,6-pentamethylenefulvene with lithium indenide followed by *n*-butyllithium, in 92% yield.[8] Addition of toluene to a mixture of this salt and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme gave red needle crystals of the air- and moisture-sensitive *ansa*-bridged compound $[Zr\{(CH_2)_5C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]\cdot 0.5C_6H_5Me$ **3**. The ^1H NMR spectrum shows that only one diastereomer is present, and the close resemblance to the spectrum of **1** suggests an analogous diastereomeric structure. The ^{13}C NMR spectrum shows chemical shifts corresponding to C_p, C_a and C_b lie at δ 85.7, 111.0 and 128.9 respectively, suggesting an η^2 co-ordination of the indenyl ligand.



Scheme 1 L = thf or L_2 = dme. (*i*) In toluene at −78 °C, then at room temperature (r.t.) for 16 h, yield 75 (**1**) or 81% (**2**); (*ii*) as (*i*) yield 79 (**3**) or 58% (**4**); (*iii*) in toluene at r.t. for 16 h, 57%; (*iv*) in toluene at r.t. for 60 h, yield 41 (**6**) or 43% (**7**)

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

Zr–C(17)	2.564(4)	Zr–Cl	2.500(1)
Zr–C(18)	2.508(5)	Zr–C (C_5H_5)	2.51 (mean)
Zr · · · C(19)	3.170(5)	Zr–C (C_5H_4)	2.49 (mean)
Zr · · · C(21)	3.335(4)	Zr–Cp	2.214
C(17)–C(18)	1.439(7)	Zr–Cp′	2.174
C(18)–C(19)	1.376(7)		
Cl–Zr–C(17)	117.5(1)	Cp–Zr–Cp′	130.4
Zr–C(17)–C(18)	71.4(2)	C(10)–C(11)–C(17)	101.5(3)
C(11)–C(17)–C(21)	130.7(5)		

The crystal structure of complex **3** has been determined and the molecular structure shown in Fig. 3 corresponds to the diastereomer indicated by the NMR data. Selected interatomic distances and angles are given in Table 3. The centroid–Zr–centroid angle is 130.4°. The indenyl group is planar (to within 0.02 Å) and is bonded in an η^2 fashion to the metal, *via* C(17) and C(18). The Zr, Cl, C(17) and C(18) atoms are approximately coplanar (deviations from best least-squares plane less than 0.12 Å), whilst C(19) lies well outside this plane. The angle between the indenyl plane and the Zr, C(17) and C(18) plane is 76.6°. The Zr–C(17) and C(18)–C(19) bond lengths of **3** are slightly shorter than the corresponding bond lengths in **1**, while Zr–C(18) and C(17)–C(18) are slightly longer than the corresponding distances in **1**. These differences are consistent with **3** having slightly more σ,π character than **1**. The Zr–Cl distance for **3** is slightly (0.01 Å) longer than in **1**.

The hafnium analogue of compound **3** is formed by addition of toluene to a mixture of $Li_2[(CH_2)_5C(C_5H_4)(C_9H_6)]\cdot0.8Et_2O$ and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot2thf$ as dark orange crystals of $[Hf\{(CH_2)_5C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]\cdot0.5C_6H_5Me$ **4**. The ^1H and ^{13}C NMR spectra closely resemble those of **3** and show that only one diastereomer is present. Careful integration of the ^1H signals indicates the presence of 0.5 equivalent of toluene, and the elemental analysis is consistent with an empirical formula $C_{28.5}H_{29}ClHf$. The ^{13}C chemical shifts for the signals corresponding to C_p, C_a and C_b, are δ 84.9, 108.0 and 129.5 respectively, suggesting an η^2 co-ordination of the indenyl ligand.

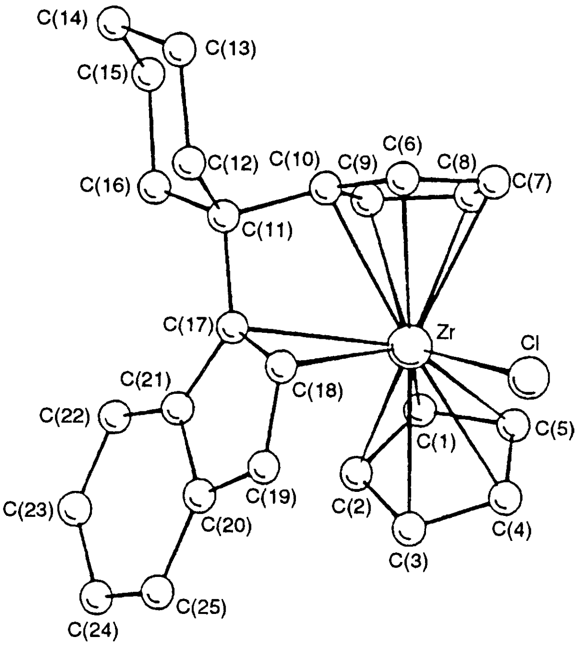


Fig. 3 Molecular structure of complex **3**

The *ansa*-bridged compound $Li_2[Me_2C(C_5H_4)(C_{13}H_8)]\cdot0.75Et_2O$ (Scheme 1) was prepared in high yield (90%) *via* 6,6-dimethylfulvene and lithium fluorenide.[32] The addition of toluene to a mixture of it and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot dme$ gave red crystals of $[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)\}(\eta\text{-}C_5H_5)Cl]$ **5**, in 57% yield. Compound **5** is air- and moisture-sensitive but is less air-sensitive than is **1**. Single crystals suitable for a structure analysis were obtained by cooling a concentrated toluene solution. The molecular structure is shown in Fig. 4 and selected interatomic distances and angles are listed in Table 4.

Compound **5** adopts a bent-metallocene structure with mean zirconium–carbon and –centroid distances similar to those of **1**, **3** and $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$.[13,15] However, the Zr–Cl bond length [2.560(1) Å] is considerably longer than those of **1** and **3** and is typical for 18-electron zirconocene derivatives.[13,15] The most interesting feature is the unusual η^3 co-ordination of the fluorenyl group to the metal *via* C(7), C(6) and C(5). The fluorenyl group is not planar, but curves gently around the metal atom; the dihedral angle between the least-squares planes C(1)–C(6) and C(7)–C(13) is 11.8°. The co-ordination of the fluorenyl group resembles η^3-allyl type bonding, with the atoms C(5)–C(7) lying close to the equatorial plane between the cyclopentadienyl ligands, as would be required for good p-orbital overlap.[17–19]

The Zr–C(7), Zr–C(6) and Zr–C(5) bond lengths [2.649(5), 2.633(5) and 2.692(5) Å respectively] are about 0.2 Å longer than typical π-allyl Zr–C bond lengths,[20] possibly due to steric crowding in **5** and the constraints imposed by the *ansa* bridge. The C(5)–C(6) and C(6)–C(7) bond lengths [1.406(7) and 1.445(7) Å respectively] are consistent with some tendency towards an η^3 σ,π-type co-ordination mode. The other C–C bond lengths of the fluorenyl group all lie in the range 1.37–1.41 Å, except C(7)–C(8) [1.489(7)], C(1)–C(6) [1.460(6)] and C(1)–C(13) [1.440(7) Å]. The bond lengths of the C(8)–C(13) ring appear to be largely unperturbed by the co-ordination of the fluorenyl group.

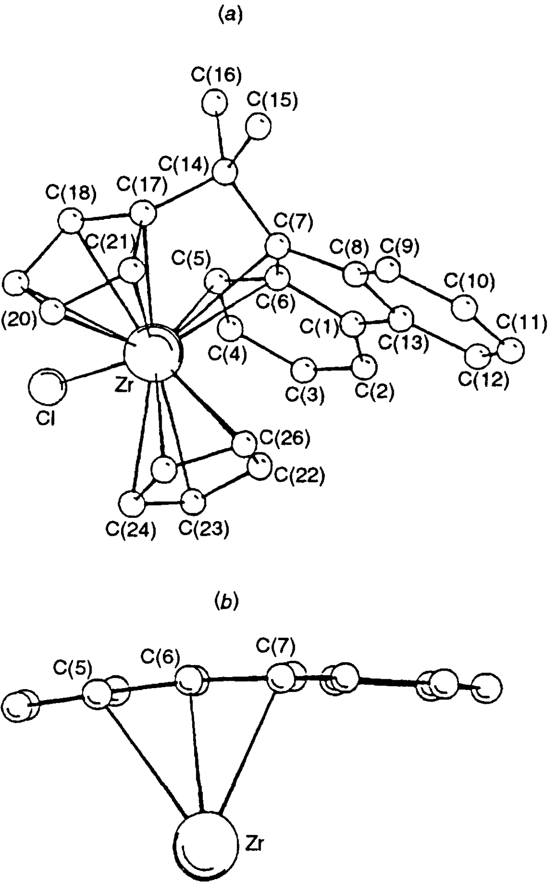


Fig. 4 (*a*) Molecular structure of complex **5**. (*b*) The curvature of the fluorenyl ligand

Table 4 Selected interatomic distances (Å) and angles (°) for compound **5**

Zr–C(5)	2.692(5)	Zr–Cl	2.560(1)
Zr–C(6)	2.633(5)	Zr–C (C_5H_5)	2.49 (mean)
Zr–C(7)	2.649(5)	Zr–C (C_5H_4)	2.49 (mean)
Zr–Cp	2.20	C(7)–C(8)	1.489(7)
Zr–Cp′	2.18	C(1)–C(6)	1.460(6)
C(5)–C(6)	1.406(7)	C(1)–C(13)	1.440(7)
C(6)–C(7)	1.445(7)		
C(17)–C(14)–C(7)	103.1(4)	C(14)–C(7)–C(8)	126.3(4)
C(14)–C(7)–C(6)	124.6(4)		

The ^1H NMR spectrum of complex **5** at room temperature was assigned on the basis of selective decoupling, COSY and NOESY experiments.[25] The spectrum shows an unusually low-field chemical shift for the C_5H_5 ligand (δ 4.84) probably a result of the shielding effect of the induced aromatic ring currents in the fluorenyl group. The spectrum is consistent with a stereorigid molecular structure with no facile rotation about the bridging C–C bonds of the *ansa* ligand. The ^{13}C NMR spectra were assigned with assistance from ^{13}C–^1H shift correlation experiments. The quaternary signal p was assigned to the *ipso*-carbon of the C_5H_4 ring by comparison with those of many other *ansa*-bridged complexes, that at δ 70.4 assigned to the bridgehead carbon of the fluorenyl group (C_r), whilst the signals of the other quaternary carbons of the fluorenyl group (s–v)[10] lie between δ 120 and 140. The low chemical shift of C_r is not consistent with η^5 co-ordination of the fluorenyl group to the metal,[32] nor with η^3 co-ordination of the C_5 ring of the fluorenyl group with C_r as the central carbon of a π-allylic fragment.[34] The chemical shift of C_a is also rather low (δ 105), which would be consistent with η^3 co-ordination of the fluorenyl ligand across the C_5–C_6 ring junction, with C_r and C_a as the terminal carbon atoms of a π-allyl system co-ordinated to the metal.

The η^3-fluorenyl co-ordination observed in compound **5**, across a C_5–C_6 ring junction, is rare. Another recent example is the compound $[Zr(C_5H_4CMe_2C_{13}H_8)H(Cl)]$.[35] A different η^3-fluorenyl co-ordination mode has been reported for $[Zr(\eta^3\text{-}C_{13}H_8)(\eta\text{-}C_{13}H_8)Cl_2]$.[34] An η^3-fluorenyl mode was originally proposed for the *ansa*-metallocenes $[M\{Me_2C(\eta\text{-}C_5H_4)(\eta\text{-}C_{13}H_8)\}Cl_2]$ (M = Zr or Hf) on the basis of the crystal structure of the hafnium compound, which showed a progressive increase in the Hf–C bond lengths from the bridgehead carbon (2.40 Å) and the neighbouring α-carbons (2.49, 2.57 Å) to the β-carbons (both 2.64 Å). However, in a following paper, which reported the crystal structure of the zirconium analogue with similar Zr–C distances (2.40; 2.50, 2.53; 2.65, 2.67 Å), it was proposed that the increase in M–C distance was not large enough for η^3 co-ordination and an η^5-fluorenyl co-ordination was proposed for both the zirconium and hafnium compounds.[32] The η^3 co-ordination of the fluorenyl group to the metal in compound **5** shows some resemblance to the η^3-benzyl co-ordination mode.[26,36–38]

Treatment of a mixture of $Li_2[Me_2C(C_5H_4)_2]$ and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot dme$ or $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot 2thf$ with toluene gave the mononuclear *ansa*-bridged complexes $[M\{Me_2C(\eta\text{-}C_5H_4)_2\}(\eta\text{-}C_5H_5)Cl]$ (M = Zr **6** or Hf **7**) respectively.

These compounds, both pale yellow, air- and moisture-sensitive crystalline solids, were characterised by elemental analysis, ^1H and ^{13}C NMR studies and single-crystal X-ray analyses. They are isostructural and crystallise in the space group $P2_1$. The molecular structure of **6** is shown in Fig. 5. Selected interatomic distances and angles for **6** and **7** are listed in Table 5. For both, all three C_5-rings show η^5 co-ordination to the metal centre. Only three tris(η^5-cyclopentadienyl) transition-metal compounds have been reported previously. They are all zirconium compounds.[39–42] In contrast, the hafnium analogues do not have tris(η^5-cyclopentadienyl) co-ordination.[43,44] The first crystallographically characterised tris(η^5-cyclopentadienyl) transition-metal compound was $[Zr(\eta\text{-}C_5H_5)_3(\eta^1\text{-}C_5H_5)]$.[39] Recently $[Zr(\eta\text{-}C_5H_5)_3]$[40] and $[Zr(\eta\text{-}C_5H_5)_3(\mu\text{-}H)AlEt_3]$[41] have been reported. The

Table 5 Selected interatomic distances (Å) and angles (°) for compounds **6** and **7***

	M = Zr	M = Hf		M = Zr	M = Hf
M–Cl	2.5363(7)	2.510(1)	R1′–M–R2′	119.6	120.2
M–R1	2.59 (mean)	2.59	R1′–M–R3′	119.1	118.5
M–R2	2.59 (mean)	2.57	R2′–M–R3′	110.6	111.2
M–R3	2.57 (mean)	2.58	Cl–M–R1′	100.7	100.5
M–R1′	2.301	2.297	Cl–M–R2′	100.2	98.7
M–R2′	2.306	2.270	Cl–M–R3′	102.0	103.0
M–R3′	2.277	2.287	C(10)–C(11)–C(14)	99.4(2)	97.7(5)
M–C(1)	2.55(1)	2.49(2)	M–C(6)	2.55(1)	2.62(2)
M–C(2)	2.61(1)	2.57(1)	M–C(7)	2.70(1)	2.64(2)
M–C(3)	2.635(3)	2.632(6)	M–C(8)	2.67(1)	2.58(1)
M–C(4)	2.61(1)	2.67(2)	M–C(9)	2.51(1)	2.52(2)
M–C(5)	2.56(1)	2.60(2)	M–C(17)	2.61(1)	2.69(1)
C(1)–C(2)	1.33(2)	1.41(2)	M–C(18)	2.517(9)	2.48(2)
C(1)–C(5)	1.417(5)	1.42(1)	C(6)–C(10)	1.33(2)	1.51(2)
C(2)–C(3)	1.35(2)	1.41(3)	C(8)–C(9)	1.49(2)	1.31(3)
C(3)–C(4)	1.45(2)	1.39(4)	C(14)–C(15)	1.49(1)	1.33(2)
C(4)–C(5)	1.48(2)	1.46(3)	C(17)–C(18)	1.33(2)	1.52(2)

* M–R1 is the M–C distance for the ring R1, and R1′ denotes the centroid of ring R1, where R1 is C(1)–C(5), R2 is C(6)–C(10) and R3 is C(14)–C(18).

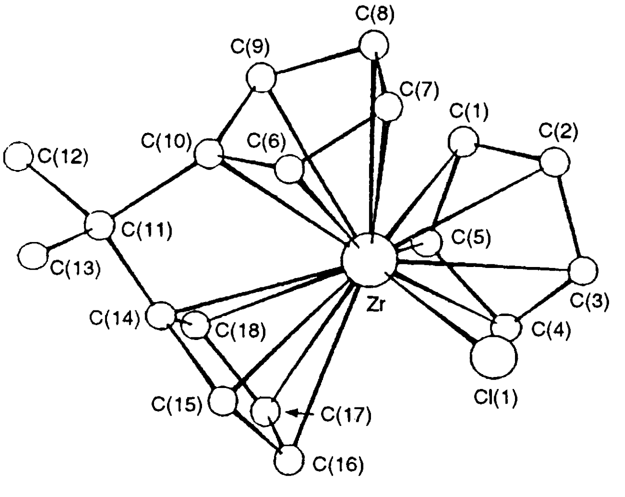


Fig. 5 Molecular structure of complex **6**

molecular structures of **6** and **7** are probably best compared with the structures of the non-bridged tris(cyclopentadienyl) derivatives [Zr(η^5-C_5H_5)$_3$Cl] and [Hf(η-C_5H_5)$_2$(η^1-C_5H_5)Cl].[42] The C_5H_4 rings of **6** and **7** are close to being eclipsed and the C–C distances of both the rings show large variations. The range of M–C distances in **6** and **7** is similar to those of [Zr(η-C_5H_5)$_3$(η^1-C_5H_5)] and [Zr(η-C_5H_5)$_3$Cl]. The unsymmetrical metal–ring bonding in **6** and **7** can be compared with that in the series of compounds [Mo(η-C_5H_5)$_2$(NO)X] (X = I, Me or η^1-C_5H_5).[45,46]

The molecular structures of complexes **6** and **7** and the other tris(η-cyclopentadienyl)zirconium complexes present similar problems of bonding description. Lauher and Hoffmann[18] have discussed transition-metal complexes of the type [M(η-C_5H_5)$_3$X] with C_{3v} symmetry. They noted there is a molecular orbital of symmetry arising from the three cyclopentadienyl rings but there is no corresponding orbital on the metal therefore the ligand-based a_2 orbital cannot donate to the metal orbital. Thus the Group 4 complexes [M(η-C_5H_5)$_3$X][47] have, in effect, 18- rather than 20-electron configurations. Although the *ansa* bridge in **6** and **7** lowers the symmetry from C_{3v}, it seems likely that a similar argument applies. This may account for the significantly longer M–C bond lengths in **6** and **7** and the other tris(η- cyclopentadienyl)zirconium derivatives (all average 2.58 Å) compared with [Zr(η-C_5H_5)$_2$Cl$_2$] (2.49 Å)[15] and [Hf(η-C_5H_5)$_2$ Cl$_2$] (2.47 Å).[13] Even the very sterically crowded zirconocene derivative [Zr(η- C_5H_5)$_2${CH(SiMe$_3$)$_2$}Ph] has a mean Zr–C (C_5H_5) bond length of only 2.54 Å.[39] The reduced steric crowding experienced by the C_5H_5 ligand in **7**, as a result of the short *ansa* bridge between the other two rings, may allow it to adopt η^5 co-ordination, and the complex thus attains a favoured 18-electron configuration.

The room-temperature ^{1}H and ^{13}C NMR spectra of complex **7** are consistent with a molecular structure in which the two C_5H_4 groups are equivalent and in which there is fast reorientation of the C_5H_5 ligand. Low-temperature NMR studies (500 MHz ^{1}H, [$^2H_8$]thf, 304–173 K) for **7** show no evidence of lowering of symmetry or freezing out of any fluxionality. The variable-temperature ^{13}C cross polarisation magic angle spinning (CP MAS) solid-state NMR spectra of **6** and **7** show that as the temperature is lowered exchange broadening is observed, with eventual splitting of the C_5H_5 signal into three which sharpen at low temperature with relative intensities 1:2:2. The data give estimated activation barriers (E_a) for the C_5H_5 ring reorientation of 74.0 ± 3.0 kJ mol^{-1} for **7** and 69 ± 3.0 kJ mol^{-1} for **6**. These large barriers to C-ring rotation probably reflect crystal-packing effects reinforcing intramolecular steric effects.

Addition of toluene to a mixture of Li$_2$[Me$_2$C(C_5H_4)(C_9H_6)]·0.75EtO$_2$ and [Zr(η-C_5H_5)Cl$_3$]·dme gives bright yellow crystals of the *ansa*-bridged binuclear compound [Cl$_2$(η-C_5H_5)Zr{C_5H_4(CMe$_2$)C_9H_6}Zr(η-C_5H_5)Cl$_2$] **8**. This compound is moderately air- and moisture-sensitive. It is soluble in benzene and toluene and very soluble in dichloromethane and thf. On the basis of NMR studies we propose the chiral structure shown in Scheme 2. The methyl groups on the bridging carbon atom are diastereotopic and have different chemical shifts, as observed. Selective ^{1}H decoupling revealed two overlapping doublets for the indenyl protons f and c, two overlapping multiplets for the indenyl protons e and d, and two doublets for the indenyl C_5-ring protons a and b (for labelling see Table 1). Selective ^{1}H decoupling also revealed two multiplets each of integrated intensity 1 H and one multiplet of intensity 2 H for the C_5H_4 protons; the 2 H multiplet overlaps the C_5H_5 signal at δ 6.13. Comparison with the NMR spectra of other compounds described later indicates that the band at δ 6.43 may be assigned to the C_5H_5 group which is co-ordinated to the zirconium attached also to the C_5H_4 ring, whilst the resonance at δ 6.13 may be assigned to the other zirconium which is co-ordinated to the indenyl group.

In the synthesis of compound **1** only 1 equivalent of [Zr(η-C_5H_5)Cl$_3$]·dme was used and the deep red compound was obtained in good yield. In the synthesis of **8** 2 equivalents were used, and when the initial deep red reaction mixture was refluxed overnight the yellow binuclear compound was obtained. These observations are consistent with the proposal that in the synthesis of **8**, the compound $Li_2[Me_2C(C_5H_4)(C_9H_6)]$ initially reacts with 1 equivalent of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme to form compound **1**, which then reacts with the second equivalent on heating to give the binuclear compound **8**.

Addition of toluene to a mixture of $Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot 0.6Et_2O$ and 2 equivalents of $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$dme gave yellow crystals of $[Cl_2(\eta\text{-}C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta\text{-}C_5H_5)Cl_2]$ **9**. Compound **9** is moderately air- and moisture-sensitive and is soluble in benzene and toluene and very soluble in dichloromethane. The ^1H and ^{13}C NMR spectra are very similar to those of compound **8**, suggesting an analogous molecular structure. The NOESY spectrum of **9** in CD_2Cl_2 at room temperature shows that one of the methyl groups of the *ansa* bridge is correlated to one of the indenyl C_5-ring protons a, whilst the other methyl group is correlated to one of the indenyl C_6-ring protons f and one of the C_5H_4 protons. These correlations are consistent with the proposed assignments of the indenyl signals, and also suggest that there is a preferred molecular conformation of **9** in solution in which proton a is close to one of the methyl groups and f is close to the other methyl group.

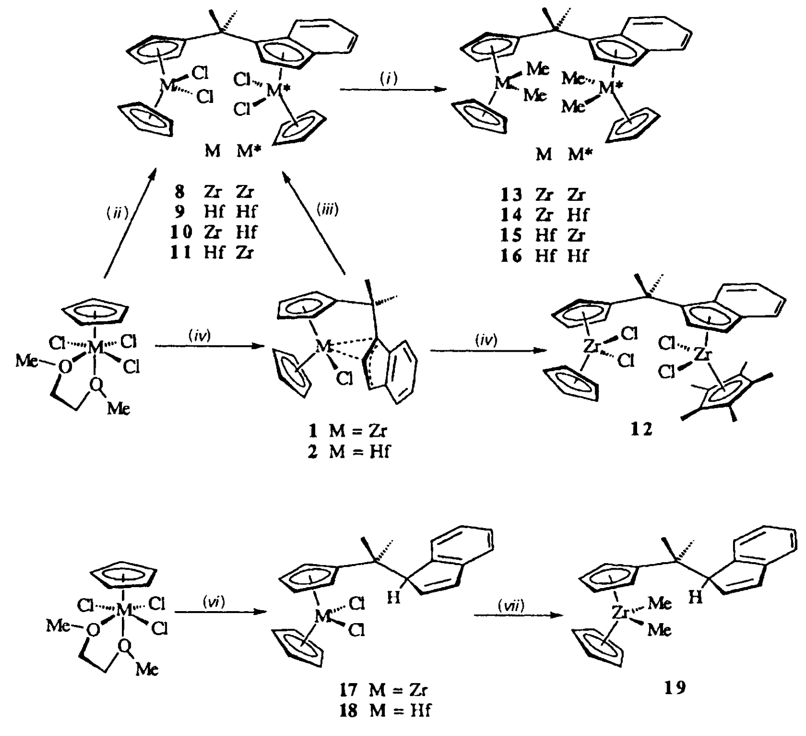
Addition of toluene to a mixture of complex **1** and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$dme gave yellow crystals of the desired *ansa*-bridged heterobinuclear compound $[Cl_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta\text{-}C_5H_5)Cl_2]$ **10**. The NMR spectra show no evidence for exchange of the metals between the C_5H_4 and indenyl sites.

The reaction between complex **2** and 1 equivalent of $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme in thf gave the expected heterobinuclear product $[Cl_2(\eta\text{-}C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta\text{-}C_5H_5)Cl_2]$ **11**, in a yield of *ca.* 80%. The chemical shifts of the C_5H_4 signals are almost identical to those of the dihafnium compound **9**, while the shifts of the indenyl proton signals are almost identical to those of the dizirconium compound **8**. The chemical shifts of the C_5H_5 signals are also consistent with the proposed molecular structure, closely matching the higher shift signal of **9** (δ 6.33) and the lower shift signal of **8** (δ 6.12). The ^1H and ^{13}C NMR chemical shifts of C_5H_5 ligands of compounds **8**–**11** are shown in Table 6. It can be seen that they are dependent on which metal the C_5H_5 ligand is co-ordinated to, and also on the 'site' occupied by the metal, *i.e.* whether the metal is co-ordinated to the C_5H_4 ring or the indenyl group of the *ansa* ligand. However, whilst the ^1H chemical shift appears to be primarily determined by the 'site', with the nature of the metal having a lesser effect on the shift, the opposite is true for the ^{13}C chemical shift. It also appears that the 'site effect' on the chemical shifts is opposite for ^{13}C and ^1H nuclei. The data in Table 6 provide strong evidence that compounds **8**–**11** are indeed a series of homo- and hetero-bimetallic compounds with analogous molecular structures.

Addition of toluene to a mixture of complex **1** and $[Zr(\eta\text{-}C_5Me_5)Cl_3]\cdot 2$thf gave yellow-orange $[Cl_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta\text{-}C_5Me_5)Cl_2]$ **12**, in a yield of 52%.

Table 6 Proton and ^{13}C NMR chemical shifts (in CD_2Cl_2) of C_5H_5 ligands of compounds $[Cl_2(\eta\text{-}C_5H_5)M\{C_5H_4(CMe_2)C_9H_6\}M^*(\eta\text{-}C_5H_5)Cl_2]$, where M, M* = Zr, Zr **8**, Hf, Hf **9**, Zr, Hf **10** and Hf, Zr **11**

Compound	M	$\delta[M(C_5H_5)]$	M*	$\delta[M^*(C_5H_5)]$
(*a*) ^1H				
8	Zr	6.43	Zr	6.13
9	Hf	6.33	Hf	6.00
10	Zr	6.43	Hf	6.01
11	Hf	6.33	Zr	6.12
(*b*) ^{13}C				
8	Zr	116.4	Zr	116.6
9	Hf	115.0	Hf	115.3
10	Zr	116.4	Hf	115.3
11	Hf	115.0	Zr	116.6



Scheme 2 (*i*) In toluene at −78 °C, LiMe, then r.t., yield 75 (**13**), 64 (**14**), 67 (**15**), 44% (**16**); (*ii*) typically, in toluene at −78 °C, then r.t. for 2 h, then 105 °C for 20 h, yield 52 (**8**), 68% (**9**); (*iii*) typically, in toluene, add $[M(\eta\text{-}C_5H_5)Cl_3]$, then at 80–105 °C for 15 h, yield M = Zr, 74 (**10**), Hf, 78% (**11**); (*iv*) in toluene at −78 °C, then at r.t. for 16 h, yield 75 (**1**) or 81% (**2**); (*v*) in toluene, $[Zr(\eta\text{-}C_5Me_5)Cl_3]\cdot 2$thf at r.t. for 2 d, then 95 °C for 18 h, yield 52%; (*vi*) in thf, $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme at r.t. for 13 h, yield 58 (**17**), 56% (**18**); (*vii*) in Et_2O at −78 °C, then LiMe and warm to r.t. for 5 h, yield 61%

The tetramethyl derivatives of the binuclear compounds **8**–**11** have been prepared. Thus addition of 4 equivalents of methyllithium to **8** gave air- and moisture-sensitive, pale orange crystals of $[Me_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta\text{-}C_5H_5)Me_2]$ **13** in 75% yield. The ^1H NMR spectrum of the cyclopentadienyl and indenyl region of **13** resembles that of compound **8**, except that the bands assignable to the C_5H_4 and C_5H_5 groups of **13** have chemical shifts about 0.3 ppm lower than those of **8**, and for **13** the bands due to the protons a and b coincide and appear as a pseudo-singlet. The chemical shifts of the methyl groups of dimethyl-zirconocene and -hafnocene compounds typically lie between δ 0.5 and −1.5.[48,49] For compound **13** there are four sharp singlets each of integrated intensity 3 H in this region. The presence of four bands reflects the presence of two diastereotopic pairs of methyl groups in the chiral structure. The chemical shift difference of the resonances assigned to the $ZrMe_2$ group co-ordinated to the indenyl ligand is much greater than that for the methyl hydrogens of the other $ZrMe_2$ group, which is more distant from the chiral centre of the molecule. The ^{13}C NMR spectrum of **13** shows a similar trend.

Treatment of compound **10** in toluene with 4 equivalents of methyllithium gives $[Me_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta\text{-}C_5H_5)Me_2]$ **14**. The NMR spectra are very similar to that of compound **13**, and are consistent with the presence of hafnium at the indenyl site in **14**. The compounds $[Me_2(\eta\text{-}C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta\text{-}C_5H_5)Me_2]$ **15** and $[Me_2(\eta\text{-}C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta\text{-}C_5H_5)Me_2]$ **16** have also been prepared (see Scheme 2). The ^1H and ^{13}C NMR data for the C_5H_5 and MMe_2 groups of compounds **13**–**16** are given in Table 7 and clearly show site dependency similar to that observed for **8**–**11**.

Table 7 Selected ^1H and ^{13}C NMR data (in C_6D_6) for the compounds $[Me_2(\eta\text{-}C_5H_5)M\{C_5H_4(CMe_2)C_9H_6\}Me^*(\eta\text{-}C_5H_5)Me_2]$, where M, M* = Zr, Zr **13**, Zr, Hf **14**, Hf, Zr **15** and Hf, Hf **16**

Compound	M	$\delta[M(C_5H_5)]$	M*	$\delta[M^*(C_5H_5)]$
(*a*) ^1H for the C_5H_5 hydrogens				
13	Zr	5.75	Zr	5.48
14	Zr	5.75	Hf	5.39
15	Hf	5.68	Zr	5.47
16	Hf	5.67	Hf	5.39
(*b*) ^{13}C for the C_5H_5 groups				
13	Zr	110.8	Zr	112.4
14	Zr	110.8	Hf	111.6
15	Hf	110.3	Zr	112.4
16	Hf	110.3	Hf	111.6
(*c*) ^1H for $M(CH_3)_2$ and $M^*(CH_3)_2$ groups				
		$\delta[M(CH_3)_2]$		$\delta[M^*(CH_3)_2]$
13	Zr	0.00, −0.01	Zr	0.05, −0.22
14	Zr	0.00, −0.01	Hf	−0.11, −0.39
15	Hf	−0.18, −0.19	Zr	0.05, −0.22
16	Hf	−0.18, −0.19	Hf	−0.11, −0.39
(*d*) ^{13}C for the CH_3 groups				
13	Zr	31.6, 31.4	Zr	35.3, 32.9
14	Zr	31.5, 31.4	Hf	41.1, 38.5
15	Hf	37.7, 37.5	Zr	35.2, 32.8
16	Hf	37.7, 37.5	Hf	41.1, 38.4

The lithium cyclopentadienide derivative $Li[C_5H_4CMe_2(C_9H_7)]$ was prepared from 6,6-dimethylfulvene with lithium indenide as air- and moisture-sensitive pale orange crystals. The ^1H and ^{13}C NMR spectra were consistent with the proposed molecular structure and indicated a high level of purity. Addition of $Li[C_5H_4CMe_2(C_9H_7)]$ to 1 equivalent of $[M(\eta\text{-}C_5H_5)Cl_3]\cdot dme$ (M = Zr or Hf) gave $[Zr(\eta\text{-}C_5H_5)\{C_5H_4CMe_2(C_9H_7)\}Cl_2]$ **17** or $[Hf\{C_5H_4CMe_2(C_9H_7)\}(\eta\text{-}C_5H_5)Cl_2]$ **18**, respectively. Treatment of **17** with methyllithium gave white crystals of the dimethyl derivative $[Zr\{C_5H_4CMe_2(C_9H_7)\}(\eta\text{-}C_5H_5)Me_2]$ **19**. The ^1H NMR spectrum of **19** (Table 1) shows two close singlets at δ −0.03 and −0.05 assignable to the $ZrMe_2$ hydrogens.

Polymerisation studies

In 1992 Kaminsky *et al.*[50] reported the polymerisation of ethene and propene by eleven different zirconocene and hafnocene catalysts with methylaluminoxane (MAO) cocatalyst, using a standard set of polymerisation conditions. In order to enable comparison with our new catalysts the same conditions were used. The ethene polymerisation experiments using the metallocene–MAO catalyst systems were repeated twice and were found to be reproducible. The data for the binuclear compounds **8**–**11** and $[Cl_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Rh(CO)_2]$[5] **20** and for the mononuclear compounds **17** and **18** are given in Table 8. When comparing the activities of the bi-with the mononuclear compounds one should bear in mind that the activities are quoted per mol of compound so that compared with the mononuclear compounds the binuclear ones have twice the number of transition-metal sites and thus half the aluminium/transition metal ratio (415 : 1). It has been shown that doubling this ratio for mononuclear Group 4 metallocene–MAO catalyst systems typically causes an increase in activity of between 5 and 30%.[51,52]

In Table 8 the activity is given as kg of polyethylene produced per mol of compound per hour. All of the catalyst systems remained active for the 1 h duration of the experiment. A 'relative activity' is also quoted; this is the activity divided by the monomer concentration, calculated from the monomer solubility in toluene (0.235 mol dm^{-3} for ethene in toluene at 30 °C and 2 bar ethene pressure).[50,53] The relative activities of the most active compounds are much lower than that reported by Kaminsky *et al.*[50] for $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$–MAO under similar conditions but are similar to that of the *ansa* metallocene $[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ (1550 kg mol^{-1} h^{-1} c_{mon}^{-1}). The binuclear zirconium compound **8** and the mononuclear zirconium compound **17** are both considerably more active than their hafnium analogues **9** and **18**. This trend is well established[50,54–60] and is associated with the observation that the metal–methyl bond enthalpy for the compounds $[M(\eta\text{-}C_5Me_5)_2Me_2]$ is 306 kJ mol^{-1} for M = Hf compared with 284 kJ mol^{-1} for M = Zr.[61,62] The activity of the heterobinuclear compound **10** is closer to the activity of the dizirconium analogue **8** and is significantly higher than that of the dihafnium analogue **9**. Correspondingly, the activity of **11** is much closer to that of **9** and is much lower than that of **8**. These observations

Table 8 Polymerisation of ethene using metallocene–MAO catalyst systems *

Compound	M	M*	Yield/g	Activity/ kg mol^{-1} h^{-1}	Relative activity/ kg mol^{-1} h^{-1} c_{mon}^{-1}
8	Zr	Zr	2.14	342	1460
9	Hf	Hf	0.59	94	400
10	Zr	Hf	1.69	270	1150
11	Hf	Zr	0.45	72	310
17	Zr	H	4.94	790	3360
18	Hf	H	1.71	274	1170
20	Zr	$Rh(CO)_2$	0.85	136	580

* At 2 bar absolute monomer pressure, 30 °C, 210 cm^3 toluene solvent, 1 h, 6.25×10^{-6} mol compound, 0.300 g MAO, c_{mon} = 0.235 mol dm^{-3}.

Table 9 Polymerisation of propene using metallocene–MAO catalyst systems[a]

Compound	M	M*	Yield/g	Activity/ kg mol^{-1} h^{-1}	Relative activity[b]/ kg mol^{-1} h^{-1} c_{mon}^{-1}
8	Zr	Zr	2.22	11.1	8.8
9	Hf	Hf	1.33	6.7	5.3
10	Zr	Hf	0.42	2.1	1.7
11	Hf	Zr	0.32	1.6	1.3
17	Zr	H	0.36[c]	7.2	5.7
20	Zr	Rh(CO)$_2$	0.22	1.1	0.9

[a] At 2 bar monomer pressure, 30 °C, 210 cm^3 toluene solvent, 4 h. [b] c_{mon} = 1.26 mol dm^{-3} for propene in toluene at 2 bar monomer pressure at 30 °C. [c] One hour for compound **17**, 5.0×10^{-5} mol compound, 2.40 g MAO.

suggest that the ethene polymerisation activity of the binuclear compounds has a greater dependence on the metal at the C_5H_4 site than on the metal at the indenyl site. Comparison of the activities of **8**–**11** suggests that for the homobimetallic compounds **8** and **9** the metal centre at the less sterically crowded C_5H_4 site of the bridging ligand has a higher activity than that at the indenyl site.

The ethene polymerisation activity of the zirconium–rhodium compound **20** is about half that of the dizirconium compound **8** and the zirconium–hafnium binuclear compound **10**. The activities of all of these binuclear compounds with zirconium at the C_5H_4 site are significantly lower than that of the mononuclear compound **17**.

So far as polyethylene productivity is concerned, there would appear to be no advantage in incorporating a second metal centre in these molecules. In fact the second metal centre, whether $MCl_2(C_5H_5)$ (M = Zr or Hf) or $Rh(CO)_2$, has a negative effect on polyethylene productivity.

The binuclear compounds **8**–**11** and **20**, and the mononuclear zirconocene compound **17**, were also tested as catalysts for the polymerisation of propene under conditions similar to those used for ethene. When the same amount of catalyst (6.25×10^{-6} mol) and MAO (0.300 g) were used, the activities were found to be very low, yielding less than 0.02 g of viscous liquid. Therefore, eight times the amount of compound and cocatalyst were used, compared with the ethene experiments. The data are given in Table 9. All of the metallocene–MAO systems have only very low propene polymerisation activities. Kaminsky *et al.*[50] have reported relative activities for propene polymerisation of 140 kg mol^{-1} h^{-1} c_{mon}^{-1} for $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ and 400 kg mol^{-1} h^{-1} c_{mon}^{-1} for *rac*-$[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta\text{-}C_9H_6)\}Cl_2]$ under similar conditions, and activities of over 1000 for some highly stereospecific *ansa*-zirconocene–MAO systems.

The propene polymerisation activities of complexes **8** and **11** are not only much lower than for ethene, but also show a different order. For ethene polymerisation the metal at the C_5H_4 site had a larger effect than that at the indenyl site on the activity of the binuclear compound, but this does not appear to be the case for propene polymerisation. The dizirconium compound **8** is more active than the dihafnium compound **9**, but **9** is considerably more active than both of the heterobimetallic zirconium–hafnium analogues **10** and **11**. This would not be predicted from the typical behaviour of mononuclear metallocene–MAO systems. Mononuclear zirconocene–MAO catalysts typically have higher propene polymerisation activities than those of hafnium analogues.[8,50,56,58–60]

The stereoregularity of the polypropylene formed in the polymerisation reactions has been investigated using standard NMR methods.[8,50,56,58–60] The polypropylene samples were highly viscous liquids and soluble in toluene. The polypropylene ^1H and ^{13}C NMR spectra were recorded at 120 °C in a solvent mixture of 1,2,4-trichlorobenzene and C_6D_6. The ^{13}C NMR spectrum of the polymer obtained from complex **8** and MAO is that expected for atactic, low-molecular-weight polypropylene[63–67] and the methyl region of the spectrum shows the pattern of signals typical of atactic polypropylene.[63–65] The intensities of bands assigned to chain-end structures indicate low average molecular weight.[65–67] The spectra show no detectable signals corresponding to regioirregular (head-to-head or tail-to-tail) structures, suggesting that the polymerisation proceeds in a regioregular fashion, probably by primary (1–2) insertion.[67,68]

The bands at δ 40.5, 30.8 and 14.3 can be attributed to the presence of *n*-propyl at the chain end, and the resonances at δ 144.2, 111.5 and 22.4 to the presence of chain-end vinylidene groups.[65–67] The bands at δ 22.4 and 14.3, corresponding to the methyl groups of the vinylidene and *n*-propyl chain-ends respectively, have approximately equal intensity, suggesting that the *n*-propyl and vinylidene chain-ends occur in approximately equal amounts. This observation, together with the absence of signals corresponding to other types of chain-end structure, suggests that the main chain-transfer process involves β-hydrogen elimination from a regioirregular (1–2) monomer unit, followed by initiation of a new polymer chain at a metal–hydrogen bond *via* primary (1–2) insertion. The ^1H and ^{13}C NMR spectra of the polypropylene obtained using compounds **9**–**11**, **17** and **20** are very similar to those of that produced by **8** except that for **9** and **11** the chain-end signals are considerably weaker, suggesting higher molecular weights, and the methyl regions of the ^{13}C NMR spectra suggest that the polymers are slightly more isotactic than the polymer obtained using **8**.

Table 10 shows the triad and dyad fractions for each set of polypropylene ^{13}C NMR data. The fractions of *meso* and racemic dyads are given by [m] = [mm] + 0.5[mr], [r] = [rr] + 0.5[mr] and the data show that although the compounds are all chiral, the metallocene–MAO catalyst systems give very low stereospecificities and all of the polymers are atactic. The $Hf(\eta\text{-}C_5H_4)$ compounds **9** and **11** produce slightly more isotactic polymer. Data for the triad mechanistic tests, to distinguish between enantiomorphic-site control ($2[\eta^2]/[mr] = 1$) or chain-end control ($4[mm][\eta^2]/[mr]^2 = 1$) of stereospecificity,[64] are also given in Table 10. Only the polymer from compound **17** gives a good agreement and suggests enantiomorphic-site control. These triad tests do not apply if two or more different active catalytic centres were present.[69] This might explain why most of the binuclear compounds give poor agreement with the tests. Also, there may be 'double stereodifferentiation', arising from both mechanisms of stereochemical control.[69]

The sum of the methyl pentad signal intensities, divided by the intensity of the methyl group at the vinylidene chain end, should give the approximate number of monomer units per polymer chain. Multiplying this number by the molecular mass of the monomer gives an approximate value for the number-average polymer molecular weight, M_n. The relevant methyl signal integrated intensities were measured, and the results are shown in Table 10 together with the [m] and [r] dyad fractions for comparison of polymer molecular weight and tacticity. The

Table 10 Triad and dyad fractions and triad mechanistic model tests for the methyl pentad region of the ^{13}C NMR spectra

Compound (metals)	Triad fractions			Dyad fractions		Triad tests		Average chain-length molecular weight from ^{13}C NMR	
	[mm]	[mr]	$[\eta^2]$	[m]	[r]	$4[mm][\eta^2]/[mr]^2$ chain-end	$2[\eta^2]/[mr]$ site	Chain length (monomer units)	M_n
8 (Zr,Zr)	0.26	0.47	0.27	0.49	0.51	1.26	1.16	21	870
9 (Hf,Hf)	0.42	0.47	0.11	0.65	0.35	0.82	0.46	115	4860
10 (Zr,Hf)	0.32	0.48	0.21	0.55	0.45	1.16	0.87	26	1090
11 (Hf,Zr)	0.39	0.44	0.17	0.61	0.39	1.40	0.78	76	3180
17 (Zr)	0.28	0.48	0.24	0.52	0.48	1.14	0.98	34	1430
20 (Zr,Rh)	0.22	0.48	0.29	0.47	0.53	1.15	1.23	22	920

Table 11 Polymerisation of ethene using binuclear metallocene dimethyl derivatives with $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $B(C_6F_5)_3$ cocatalysts[a]

Compound (metals)	Cocatalyst	Equivalents of cocatalyst	t/min	Yield/g	Activity/kg mol^{-1} h^{-1}	Relative activity[b]/kg mol^{-1} h^{-1} c_{mon}^{-1}
13 (Zr, Zr)	$[Ph_3C]^+$-$[B(C_6F_5)_4]^-$	2	2	0.85	4 100	17 000
15 (Hf, Zr)	$[Ph_3C]^+$-$[B(C_6F_5)_4]^-$	2	2	0.46	2 200	9 400
	$B(C_6F_5)_3$	1	60	0.10	16	68
	$B(C_6F_5)_3$	2	60	0.33	53	220
	$B(C_6F_5)_3$	16	60	0.25	40	170

[a] Conditions: 2 bar absolute monomer pressure, 30 °C, 40 cm^3 toluene solvent, 6.25×10^{-6} mol of compound. [b] c_{mon} = 0.235 mol dm^{-3}.

data show that the polypropylene produced by all of the systems is of low molecular weight.

Recently the strong Lewis acid $B(C_6F_5)_3$ was shown to be capable of abstracting a methide (CH_3^-) group from a variety of $[ZrL_2Me_2]$ complexes (L = η-C_5H_5, η-1,2-$Me_2C_5H_3$ or η-C_5Me_5) to provide isolable, crystallographically characterised, highly active 'cation-like' zirconocene polymerisation catalysts, $[ZrL_2Me]^+[BMe(C_6F_5)_3]^-$.[70,71] The Lewis acid triphenylcarbenium cation $[Ph_3C]^+$ can act similarly. Thus the chiral *ansa*-metallocene dimethyl derivative *rac*-$[\{C_2H_4(\eta\text{-}C_8H_6)_2\}ZrMe_2]$ and 1 equivalent of $[Ph_3C]^+[B(C_6F_5)_4]^-$ cocatalyst were shown to catalyse the isospecific polymerisation of propene. It was proposed that $[Ph_3C]^+$ abstracted a CH_3^- group from the metallocene to form Ph_3CCH_3 and the cationic zirconocene complex $[\{C_2H_4(\eta\text{-}C_8H_6)_2\}ZrMe]^+[B(C_6F_5)_4]^-$.[72]

We have examined the catalytic activities of the binuclear tetramethyl compounds **13** and **15** using $B(C_6F_5)_3$ or $[Ph_3C]^+$-$[B(C_6F_5)_4]^-$ as cocatalyst. The polymerisations were carried out under similar conditions to those employed for the metallocene–MAO experiments except the total solvent (toluene) volume was 40 cm^3, compared with 210 cm^3 for the former, and the reaction mixture was stirred for 1 h when using $B(C_6F_5)_3$ cocatalyst, or 2 min when using $[Ph_3C]^+$-$[B(C_6F_5)_4]^-$ cocatalyst. A 2 min reaction time was required for the $[Ph_3C]^+[B(C_6F_5)_4]^-$ cocatalysed reactions because the very high activity caused stirring problems with longer times. The data for these experiments are given in Table 11.

The dizirconium compound **13** with 2 equivalents of $[Ph_3C]^+[B(C_6F_5)_4]^-$ as cocatalyst was the most active system, with a relative activity more than ten times that of the analogous **8**–MAO system. The turnover rate (41 insertions per second) was similar to that reported for the polymerisation of ethene by $[Zr(\eta\text{-}C_5H_5)_2Me]^+[BMe(C_6F_5)_3]^-$ at 25 °C (45 insertions per second).[70]

The hafnium–zirconium heterobimetallic compound **15** was tested with 2 equivalents of $[Ph_3C]^+[B(C_6F_5)_4]^-$ cocatalyst, and also with 1, 2 or 16 equivalents of $B(C_6F_5)_3$. The activity with 2 equivalents of $[Ph_3C]^+[B(C_6F_5)_4]^-$ was very high, producing 0.42 g of polyethylene in only 2 min, corresponding to a relative activity of 9400 kg mol^{-1} h^{-1} c_{mon}^{-1}. However, the relative activity with 2 equivalents of $B(C_6F_5)_3$ cocatalyst was much lower (220 kg mol^{-1} h^{-1} c_{mon}^{-1}), and was similar to the activity of the analogous **11**–MAO system. When compound **15** was used with 2 equivalents of $B(C_6F_5)_3$ cocatalyst the system remained active during the 1 h experiment and 0.33 g of polyethylene was obtained. When 1 equivalent (6.25×10^{-6} mol) of $B(C_6F_5)_3$ cocatalyst was used the system was again active for the whole hour of the experiment but only 0.10 g of polyethylene was obtained. When 16 equivalents (1.0×10^{-4} mol) of $B(C_6F_5)_3$ were used the system was more active initially but after 10 min the activity was very low, and after 1 h only 0.25 g of polyethylene was obtained. These observations suggest some reaction occurs with $B(C_6F_5)_3$ causing deactivation.

The binuclear zirconium compound **13** was tested as a propene polymerisation catalyst with $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $B(C_6F_5)_3$ cocatalysts. The experiments were performed under conditions similar to those employed for the ethene polymerisations, except a solution of 5.0×10^{-5} mol **13** in 10 cm^3 of toluene was presaturated with propene at 2 bar pressure and 30 °C and 1.0×10^{-4} mol of cocatalyst in 10 cm^3 of toluene was then added. The reaction mixture was stirred at 30 °C under 2 bar propene pressure for 4 h. The results given in Table 12 show low activity and the resulting polypropylene produced is an atactic, low-molecular-weight polymer.

Table 12 Polymerisation of propene using the binuclear metallocene dimethyl derivative **13** with $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $B(C_6F_5)_3$ cocatalysts (2 equivalents)[a]

Cocatalyst	Yield/g	Activity/kg $mol^{-1}\ h^{-1}$	Relative activity[b]/kg $mol^{-1}\ h^{-1}\ c_{mon}^{-1}$
$[Ph_3C]^+$ $[B(C_6F_5)_4]^-$	0.15	0.75	0.60
$B(C_6F_5)_3$	trace	—	—

[a] Conditions: 2 bar absolute monomer pressure, 30 °C, 20 cm^3 toluene solvent, 5.0×10^{-5} mol compound. [b] $c_{mon} = 1.26\ mol\ dm^{-3}$.

Experimental

All manipulations of air- and/or moisture-sensitive materials 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 containing nitrogen. In each case the nitrogen was purified by passage over 4 Å molecular sieves, and either BASF catalyst for the dry-box or MnO for the Schlenk line. Solvents and solutions were transferred, using a positive pressure of nitrogen, through stainless-steel cannulae. Filtrations were generally performed using modified stainless-steel cannulae which could be fitted with glass-fibre filter discs. All glassware and cannulae were dried overnight at 200 °C before use.

Solvents were pre-dried by standing over 4 Å molecular sieves and refluxed and distilled under a nitrogen atmosphere from sodium–potassium alloy (1 : 3 w/w) [pentane, light petroleum (b.p. 40–60 °C), diethyl ether]; sodium (1,2-dimethoxyethane, toluene); potassium (tetrahydrofuran) or phosphorus pentaoxide (dichloromethane). All solvents were thoroughly deoxygenated before use by bubbling dinitrogen through the solvent for at least 30 min. Deuteriated solvents for NMR studies were stored in Young's ampoules over 4 Å molecular sieves under a nitrogen atmosphere (C_6D_6, CD_2Cl_2), or refluxed with potassium metal and stored over a potassium film in a Young's ampoule under a nitrogen atmosphere ($[^2H_8]$thf).

Solution NMR spectra were recorded on a Bruker AM 300 spectrometer (^1H, 300; ^{13}C, 75.5 MHz) and referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ 0). All chemical shifts are quoted in ppm. The ^{13}C NMR spectra of polypropylene were recorded at 120 °C in 1,2,4-trichlorobenzene–C_6D_6 (80 : 20 v/v). Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory, University of Oxford. The mass spectrum (electron impact) of compound **1** was recorded on an AEI MS902 spectrometer updated by a data-handling system supplied by Mass Spectroscopy Services Ltd. The cocatalysts $B(C_6F_5)_3$[73] and $[Ph_3C]^+[B(C_6F_5)_4]^-$[72] were prepared as described. The compounds $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$dme were prepared by the literature method.[9] The former was purified by washing with light petroleum and the latter by recrystallisation from thf giving $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$2thf.

Syntheses

$Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot 0.6Et_2O$. A modification of the reported method[8] was used. A solution of 6,6-dimethylfulvene (12.4 g, 0.117 mol) in diethyl ether (50 cm^3) was added dropwise, over 1 h, to a stirred solution of lithium indenide (15 g, 0.123 mol) in diethyl ether (300 cm^3) at 0 °C. The ice-bath was removed and the solution stirred for 22 h at r.t. The reaction mixture was cooled to 0 °C and $LiBu^n$ (0.117 mol, 68 cm^3 of 1.7 mol dm^{-3} hexane solution) was added dropwise. After stirring for 20 h at r.t., the pale yellow solid product was filtered off, washed with diethyl ether ($4 \times 50\ cm^3$) and dried *in vacuo*. Yield 29 g (89%). The amount of solvating diethyl ether, as determined by ^1H NMR spectroscopy, varied between 0.6 and 0.8 equivalent in subsequent preparations.

6,6-Pentamethylenefulvene. A modification of a literature preparation[9] was used. Cyclopentadiene monomer (19.8 g, 0.30 mol) and cyclohexanone (29.4 g, 0.30 mol) were added to methanol (100 cm^3). The solution was cooled to 0 °C and pyrrolidine (32 g, 0.45 mol) added. The resulting bright yellow solution was stirred for 1 h at r.t., cooled to 0 °C, and neutralised with acetic acid (27 g, 0.45 mol). The mixture was diluted with diethyl ether (100 cm^3) and deionised water (100 cm^3) and transferred to a separating funnel. The aqueous layer was separated and washed with diethyl ether ($2 \times 50\ cm^3$). The combined organic fractions were washed with water ($4 \times 50\ cm^3$) and saturated NaCl solution ($3 \times 50\ cm^3$) and dried over $MgSO_4$. The mixture was filtered and the bright yellow filtrate concentrated under reduced pressure at 0 °C until all the diethyl ether was removed, leaving the pure product as an orange oil. Yield 41.2 g (94%).

$Li_2[(CH_2)_5C(C_5H_4)(C_9H_6)]\cdot 0.8Et_2O$. A modification of the published method[32] was used. A solution of 6,6-pentamethylenefulvene (2.68 g, 18.3 mmol) in diethyl ether (20 cm^3) was added dropwise over 1 h to a stirred solution of lithium indenide (2.24 g, 18.3 mmol) in diethyl ether (180 cm^3) at 0 °C. The ice-bath was removed and the solution was stirred for 22 h at r.t. The reaction mixture was cooled to 0 °C and $LiBu^n$ (22 mmol, 13 cm^3 of 1.7 mol dm^{-3} hexane solution) was added dropwise over 20 min. After stirring for 20 h at r.t. the pale yellow solid product was filtered off, washed with diethyl ether ($2 \times 30\ cm^3$) and dried *in vacuo*. Yield 5.6 g (92%).

$Li[C_5H_4CMe_2(C_9H_7)]$. A solution of 6,6-dimethylfulvene (4.43 g, 41.7 mmol) in diethyl ether (30 cm^3) was added dropwise over 40 min to a stirred solution of lithium indenide (4.9 g, 40.1 mmol) in diethyl ether (300 cm^3) at 0 °C. The ice-bath was removed and the solution stirred for 15 h at r.t. Light petroleum (60 cm^3) was added and the reaction mixture allowed to stand for 30 min, during which time a small amount of dark oil settled to the bottom of the Schlenk tube. The desired clear orange solution was carefully decanted from the oil and cooled to −80 °C, giving the product as pale orange crystals. Yield 5.65 g (63%).

$[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ 1. The compounds $Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot 0.6Et_2O$ (3.95 g, 14.2 mmol) and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (5.0 g, 14.2 mmol) were treated with toluene (300 cm^3) at r.t. The resulting deep red reaction mixture was stirred for 16 h at r.t. Filtration, followed by concentration of the solution under reduced pressure and cooling to −20 °C, afforded red crystals of complex **1**. Yield 3.75 g (64%).

In a modified procedure, toluene (300 cm^3) at −78 °C was added to a stirred mixture of $Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot 0.75Et_2O$ (4.11 g, 14.2 mmol) and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (4.95 g, 14.0 mmol) also at −78 °C. The resulting orange mixture was allowed to warm to r.t. over 1 h, during which time it slowly darkened to deep red, and was stirred at r.t. for 16 h. Filtration, followed by concentration of the solution under reduced pressure and cooling to −20 °C, afforded red crystals of complex **1**. Yield 4.35 g (75%).

$[Hf\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ 2. Toluene (250 cm^3) was added to a stirred mixture of $Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot 0.75Et_2O$ (3.2 g, 11.3 mmol) and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$2thf (5.6 g, 11.3 mmol) at r.t. The resulting orange-red mixture was stirred for 16 h. Filtration, followed by concentration of the solution under reduced pressure and cooling to −20 °C, afforded dark orange crystals of complex **2**. Yield 4.0 g (71%).

In a modified procedure, toluene (300 cm^3) at −78 °C was added to a stirred mixture of $Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot0.75Et_2O$ (4.11 g, 14.2 mmol) and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (6.13 g, 13.9 mmol) at −78 °C. The resulting yellow mixture was allowed to warm to r.t. over 1 h, during which time it slowly darkened to orange, and was stirred for 18 h at r.t. Filtration, followed by concentration of the solution under reduced pressure and cooling to −20 °C, afforded orange crystals of complex **2**. Yield 5.65 g (81%).

$[Zr\{(CH_2)_5C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]\cdot0.5C_6H_5Me$ 3. Toluene (90 cm^3) was added to a stirred dry mixture of $Li_2[(CH_2)_5C(C_5H_4)(C_9H_6)]\cdot0.8Et_2O$ (0.50 g, 1.5 mmol) and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (0.53 g, 1.5 mmol) at r.t. The resulting red solution was stirred for 16 h. Filtration, followed by concentration of the filtrate under reduced pressure and cooling to −20 °C, afforded red crystals of complex **3**. Yield 0.59 g (79%).

$[Hf\{(CH_2)_5C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]\cdot0.5C_6H_5Me$ 4. Toluene (90 cm^3) was added to a stirred mixture of $Li_2[(CH_2)_5C(C_5H_4)(C_9H_6)]\cdot0.8Et_2O$ (0.50 g, 1.5 mmol) and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$2thf (0.74 g, 1.5 mmol) at r.t. The resulting orange-red mixture was stirred for 16 h. Filtration followed by concentration of the filtrate under reduced pressure and cooling to −20 °C afforded dark orange crystals of complex **4**. Yield 0.51 g (58%).

$Li_2[Me_2C(C_5H_4)(C_{13}H_8)]\cdot0.75Et_2O$. A modification of the published[32] method was used. A solution of 6,6-dimethylfulvene (2.16 g, 2.45 cm^3, 20.3 mmol) in diethyl ether (60 cm^3) was added dropwise, over 40 min, to a stirred solution of lithium fluorenide [$Li(C_{13}H_9)\cdot Et_2O$; 5.0 g, 20.3 mmol] in diethyl ether (200 cm^3) at 0 °C. The ice-bath was removed and the solution was stirred for 22 h at r.t. The reaction mixture was cooled to 0 °C and $LiBu^n$ (21.6 mmol, 12 cm^3 of 1.8 mol dm^{-3} hexane solution) was added dropwise over 40 min. After stirring for 4 h at r.t. the bright yellow solid product was filtered off, washed with 50 cm^3 of diethyl ether and dried *in vacuo*. Yield 6.2 g (90%).

$[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)\}(\eta\text{-}C_5H_5)Cl]$ 5. Toluene (90 cm^3) was added to a stirred mixture of $Li_2[Me_2C(C_5H_4)(C_{13}H_8)]\cdot0.75Et_2O$ (0.96 g, 2.8 mmol) and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (1.0 g, 2.8 mmol) at r.t. The resulting red mixture was stirred for 16 h. Filtration followed by removal of volatiles under reduced pressure gave crude product (*ca.* 80% compound **5** according to NMR spectroscopy). This red solid was washed with light petroleum and extracted into toluene (110 cm^3). The toluene solution was concentrated under reduced pressure and cooled to −20 °C giving red crystals of **5**. Yield 0.75 g (57%).

$[Zr\{Me_2C(\eta\text{-}C_5H_4)_2\}(\eta\text{-}C_5H_5)Cl]$ 6. Toluene (400 cm^3) was added to a stirred mixture of $Li_2[Me_2C(C_5H_4)_2]$ (1.0 g, 5.4 mmol)[24] and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (1.9 g, 5.4 mmol) at r.t. The resulting pale yellow mixture was stirred for 60 h at r.t. Filtration, followed by concentration of the filtrate under reduced pressure and cooling to −20 °C, afforded pale yellow crystals of complex **6** (0.43 g). The residue was extracted with toluene (300 cm^3), which yielded 0.38 g of **6**. Total yield 0.81 g (41%).

$[Hf\{Me_2C(\eta\text{-}C_5H_4)_2\}(\eta\text{-}C_5H_5)Cl]$ 7. Toluene (200 cm^3) was added to a stirred mixture of $Li_2[Me_2C(C_5H_4)_2]$ (0.5 g, 2.7 mmol) and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$2thf (1.34 g, 2.7 mmol) at r.t. The resulting yellow mixture was stirred for 60 h at r.t. The solution was filtered from the solid residue, which was extracted with toluene (80 cm^3). The combined toluene solutions, when concentrated under reduced pressure and cooled to −20 °C, gave pale yellow crystals of complex **7**. Yield 0.52 g (43%).

$[Cl_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta\text{-}C_5H_5)Cl_2]$ 8. Toluene (200 cm^3) at −78 °C was added to a stirred mixture of $Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot0.6Et_2O$ (2.0 g, 7.18 mmol) and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (5.05 g, 1.43 mmol) at −78 °C in a thick-walled Rotaflo ampoule. The resulting orange mixture was allowed to warm to r.t., becoming deep red. After stirring at r.t. for 2 h the ampoule was partially evacuated and placed in an oil-bath at 105 °C for 20 h. The resulting mixture was filtered to give a clear, yellow-orange solution which was concentrated under reduced pressure and cooled to −20 °C giving large yellow-orange crystals of complex **8**. Yield 3.87 g (80%).

$[Cl_2(\eta\text{-}C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta\text{-}C_5H_5)Cl_2]$ 9. Toluene (200 cm^3) at −78 °C was added to a stirred mixture of $Li_2[Me_2C(C_5H_4)(C_9H_6)]\cdot0.6Et_2O$ (2.0 g, 7.18 mmol) and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (6.32 g, 14.3 mmol) also at −78 °C, in a thick-walled Rotaflo ampoule. The resulting yellow mixture was allowed to warm to r.t., becoming orange. After stirring at r.t. for 1 h the ampoule was partially evacuated and placed in an oil-bath at 105 °C for 18 h. The resulting suspension was allowed to settle and the clear yellow solution decanted into a Schlenk tube, concentrated under reduced pressure and cooled to −20 °C, giving yellow crystals of complex **9**. Yield 4.09 g (68%).

$[Cl_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta\text{-}C_5H_5)Cl_2]$ 10. Compound **1** (0.50 g, 1.21 mmol) and $[Hf(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (0.53 g, 1.20 mmol) were weighed into a thick-walled Rotaflo ampoule. Toluene (90 cm^3) was added and the red reaction mixture was stirred at r.t. for 1 h. The ampoule was partially evacuated and placed in an oil-bath at 105 °C for 16 h. The resulting clear, orange solution was transferred to a Schlenk vessel, concentrated under reduced pressure and cooled to −20 °C, affording yellow crystals of complex **10**. Yield 0.68 g (74%).

$[Cl_2(\eta\text{-}C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta\text{-}C_5H_5)Cl_2]$ 11. Compound **2** (1.50 g, 3.00 mmol) and $[Zr(\eta\text{-}C_5H_5)Cl_3]\cdot$dme (1.00 g, 2.83 mmol) were weighed into a thick-walled Rotaflo ampoule. Tetrahydrofuran (130 cm^3) was added and the orange-red solution was stirred at r.t. for 1 h. The ampoule was partially evacuated and placed in an oil-bath at 80 °C for 15 h. The resulting clear, yellow solution was transferred to a Schlenk tube and volatiles were removed, leaving the crude product as a slightly oily yellow solid (*ca.* 90% compound **11** according to ^1H NMR spectroscopy). Washing with diethyl ether (140 cm^3) left the pure product **11** as a fine yellow powder. Yield 1.69 g (78%).

$[Cl_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta\text{-}C_5Me_5)Cl_2]$ 12. Compound **1** (0.70 g, 1.70 mmol) and $[Zr(\eta\text{-}C_5Me_5)Cl_3]\cdot$2thf (0.81 g, 1.70 mmol)[4] were weighed into a thick-walled Rotaflo ampoule. Toluene (100 cm^3) was added and the red reaction mixture was stirred at r.t. for 2 d. The ampoule was partially evacuated and placed in an oil-bath at 95 °C for 18 h. The resulting orange suspension was filtered to give a clear orange solution, which was concentrated under reduced pressure and cooled to −20 °C, affording compound **12** as a yellow crystalline solid. Yield 0.66 g (52%).

$[Me_2(\eta\text{-}C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Zr(\eta\text{-}C_5H_5)Me_2]$ 13. Toluene (50 cm^3) was added to complex **8** (0.50 g, 0.74 mmol) and the yellow suspension was stirred and cooled to −78 °C. Four equivalents of methyllithium (1.8 cm^3 of a 1.7 mol dm^{-3} diethyl ether solution) were added, the reaction mixture was allowed to warm to r.t. over *ca.* 30 min, giving a pale orange cloudy solution. This was stirred at r.t. for 90 min. Filtration and removal of volatiles under reduced pressure, at r.t., gave an orange oil. Light petroleum (160 cm^3) was added and the mixture stirred vigorously at r.t. for 4 h. The resulting pale yellow solution was filtered from the residues, concentrated under reduced pressure and cooled to −80 °C, affording very pale orange crystals of complex **13**. Yield 0.33 g (75%).

[$Me_2(\eta$-$C_5H_5)Zr\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta$-$C_5H_5)Me_2$] 14. Toluene (30 cm^3) was added to complex **10** (0.25 g, 0.33 mmol) and the pale yellow suspension stirred and cooled to −78 °C. Four equivalents of methyllithium (0.8 cm^3 of a 1.7 mol dm^{-3} diethyl ether solution) were added, the reaction mixture was allowed to warm to r.t. and stirred for 2 h. Filtration, and removal of volatiles from the filtrate under reduced pressure gave a pale yellow oil. Light petroleum (100 cm^3) was added and the mixture stirred vigorously at r.t. for 1 h. The resulting colourless solution was filtered from the residues, concentrated under reduced pressure and cooled to −80 °C, affording the product **14** as a very pale yellow crystalline solid. Yield 0.15 g (64%).

[$Me_2(\eta$-$C_5H_5)Hf\{\eta$-$C_5H_4(CMe_2)C_9H_6\}Zr(\eta$-$C_5H_5)Me_2$] 15. Toluene (70 cm^3) was added to complex **11** (1.00 g, 1.31 mmol) and the bright yellow suspension stirred and cooled to −78 °C. Four equivalents of methyllithium (3.2 cm^3 of a 1.7 mol dm^{-3} diethyl ether solution) were added, the reaction mixture was allowed to warm to r.t. and stirred for 4 h. Filtration and removal of volatiles from the filtrate under reduced pressure gave a yellow oil. Light petroleum (170 cm^3) was added and the mixture stirred vigorously at r.t. for 2 h. The resulting yellow solution was filtered from the residues, concentrated under reduced pressure and cooled to −80 °C, giving the product **15** as a pale yellow crystalline solid. Yield 0.595 g (67%).

[$Me_2(\eta$-$C_5H_5)Hf\{C_5H_4(CMe_2)C_9H_6\}Hf(\eta$-$C_5H_5)Me_2$] 16. Toluene (35 cm^3) was added to complex **9** (0.50 g, 0.59 mmol) and the pale yellow suspension stirred and cooled to −78 °C. Four equivalents of methyllithium (1.5 cm^3 of a 1.7 mol dm^{-3} diethyl ether solution) were added, the reaction mixture was allowed to warm to r.t. and stirred for 3 h. Filtration and removal of volatiles from the filtrate under reduced pressure gave a yellow oil. Light petroleum (140 cm^3) was added and the mixture stirred vigorously at r.t. for 1 h. The solution was filtered from the residues, concentrated under reduced pressure and cooled to −80 °C, giving the product **16** as a very pale yellow crystalline solid. Yield 0.20 g (44%).

[$Zr\{C_5H_4CMe_2(C_9H_7)\}(\eta$-$C_5H_5)Cl_2$] 17. A solution of $Li[C_5H_4CMe_2(C_9H_7)]$ (0.73 g, 3.20 mmol) in thf (30 cm^3) was added dropwise to a stirred solution of [$Zr(\eta$-$C_5H_5)Cl_3$]·dme (1.07 g, 3.04 mmol) in thf (70 cm^3) at r.t. The resulting yellow solution was stirred for 13 h at r.t. Removal of volatiles under reduced pressure, followed by extraction into toluene (150 cm^3), concentration of the filtrate under reduced pressure and cooling to −20 °C, afforded the product **17** as a white microcrystalline solid. Yield 0.79 g (58%).

[$Hf\{C_5H_4CMe_2(C_9H_7)\}(\eta$-$C_5H_5)Cl_2$] 18. A solution of $Li[C_5H_4CMe_2(C_9H_7)]$ (0.30 g, 1.31 mmol) in thf (15 cm^3) was added dropwise to a stirred solution of [$Hf(\eta$-$C_5H_5)Cl_3$]·dme (0.578 g, 1.31 mmol) in thf (35 cm^3) at r.t. The resulting yellow solution was stirred for 13 h at r.t. Removal of volatiles under reduced pressure, followed by extraction into toluene (70 cm^3), concentration of the filtrate under reduced pressure and cooling to −20 °C, afforded the product **18** as a white microcrystalline solid. Yield 0.39 g (56%).

[$Zr\{C_5H_4CMe_2(C_9H_7)\}(\eta$-$C_5H_5)Me_2$] 19. Diethyl ether (60 cm^3) was added to complex **17** (0.68 g, 1.52 mmol) and the suspension stirred and cooled to −78 °C. Two equivalents of methyllithium (1.8 cm^3 of a 1.7 mol dm^{-3} diethyl ether solution) were added, the reaction mixture was allowed to warm to r.t. and stirred for 5 h. Filtration and removal of volatiles under reduced pressure gave a white solid. Light petroleum (120 cm^3) was added and the mixture stirred vigorously at r.t. for 1 h. The colourless solution was filtered from the residues, concentrated under reduced pressure and cooled to −80 °C, giving the product **19** as white crystals. Yield 0.38 g (61%).

Methylaluminoxane (MAO). Methylaluminoxane was prepared by partial hydrolysis of trimethylaluminium using $CuSO_4$·$5H_2O$, following the procedures of Kaminsky *et al.*[54] and Giannetti *et al.*[55] as modified by Green and Ishihara.[56] Finely pulverised $CuSO_4$·$5H_2O$ (76.9 g, 0.31 mol; 1.54 mol H_2O) and toluene (550 cm^3) were added to a nitrogen-filled three-necked round-bottomed flask (1 l) fitted with a thermometer. The flask was placed in a cold-water bath and the contents were stirred. Trimethylaluminium (74.0 g, 1.03 mol) was added very slowly, dropwise, whilst the temperature of the reaction mixture was maintained at approximately 20 °C by adjusting the rate of addition, and adding ice to the water bath when necessary. The mixture was stirred for 24 h at r.t., and the solution was filtered from the solid residues. The filtrate was concentrated under reduced pressure and dried *in vacuo* at 50 °C to give the product as a white glassy solid. Yield 22 g (37%).

Polymerisation experiments

All manipulations of catalysts and cocatalysts were carried out in an inert atmosphere using either a dual vacuum/nitrogen line and standard Schlenk techniques or in an inert-atmosphere drybox containing nitrogen. Ethene and propylene (pure grade) were further purified by passage through columns of 4 Å molecular sieves and over finely divided potassium metal supported on glass-wool. Polymerisations were carried out in a Fischer–Porter reactor placed in a thermostatically heated bath and equipped with a magnetic stirrer.

Of ethene using metallocene–MAO catalysts. The polymerisations were carried out under conditions as close as possible to those employed by Kaminsky *et al.*[50] Methylaluminoxane (250 mg) was weighed into a Fischer–Porter bottle, which was connected to the ethene supply. The bottle was evacuated and filled with ethene. Toluene (200 cm^3) was added, the ethene pressure increased to 2 bar (absolute pressure) and the mixture stirred at 30 °C for 20 min. The metallocene catalyst (6.25×10^{-6} mol) in toluene (10 cm^3) was added to MAO (50 mg) and stirred for 15 min as a pre-activation event. The metallocene–MAO mixture was added quickly, *via* a cannula, to the reactor vessel. The ethene pressure was increased to 2 bar again. The reaction mixture was stirred vigorously at 30 °C under a 2 bar pressure of ethene for 1 h. 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 a 20% (by volume) solution of concentrated HCl in ethanol (300 cm^3) was added and the mixture stirred overnight. The polymer was separated from the solution using a sintered glass funnel (on a Buchner flask, connected to a water aspirator for suction) and was washed with water, ethanol and finally diethyl ether and dried to constant weight *in vacuo* at 50 °C

Of propylene using metallocene–MAO catalysts. These experiments were performed under the same conditions (2 bar monomer pressure, 30 °C) using essentially the same procedure as for ethene, except: (*i*) MAO (2.00 g) and toluene (130 cm^3) were presaturated with propylene at 2 bar and 30 °C; (*ii*) metallocene (5.0×10^{-5} mol) in toluene (80 cm^3) was added to MAO (400 mg) for 15 min pre-activation; (*iii*) the reaction mixture was stirred under 2 bar propylene pressure at 30 °C for 4 h. After 4 h the polymerisation was quenched by venting the propylene and adding a small amount of ethanol. The reactor contents were transferred to a conical flask and a 20% (by volume) solution of concentrated HCl in ethanol (300 cm^3) was added and the mixture stirred overnight. The polypropylene was soluble in toluene, so the toluene layer was separated, washed well with water (5 × 100 cm^3) and stirred with $MgSO_4$ drying agent. After filtration, the toluene was removed under reduced pressure leaving the polypropylene, typically a highly viscous liquid, which was dried to constant weight *in vacuo* at 50 °C.

Of ethene and propene using methylated metallocenes and $B(C_6F_5)_3$ or $[Ph_3C]^+[B(C_6F_5)_4]^-$ cocatalysts. A Fischer-Porter reactor was filled with ethene (2 bar) and toluene (36 cm^3) and the catalyst solution (6.25×10^{-6} mol of the metallocene in 2 cm^3 toluene) and the cocatalyst solution (2 cm^3) were added quickly, *via* cannulae. The ethene pressure was made up to 2 bar and the mixture stirred vigorously at 30 °C, for 1 h with $B(C_6F_5)_3$ cocatalyst, or for 2 min with $[Ph_3C]^+[B(C_6F_5)_4]^-$ cocatalyst. The polymerisation was quenched by venting the ethene and adding ethanol. The polymer was separated and purified as described earlier.

The procedure for propene polymerisation was the same as for ethene using a solution of the binuclear metallocene (5×10^{-5} mol) in toluene (10 cm^3) and a propylene pressure of 2 bar. The cocatalyst solution (1.0×10^{-4} mol in 10 cm^3 toluene) was added and the reaction mixture stirred vigorously at 30 °C under 2 bar of propylene for 4 h. The resulting polymer was isolated as described above.

Crystal structure determinations

The crystal data and methods for complexes **1**,[5] **3**,[10] **5**,[10] **6**[11] and **7**[11] are given in the references indicated.

Complete atom coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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