New Metallocene Compounds of Zirconium and Hafnium showing Unusual *ansa*-Ligand Coordination: X-Ray Crystal Structures of [{$(CH_2)_5C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)$}$Zr(\eta^5\text{-}C_5H_5)Cl$] and [{$Me_2C(\eta^5\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)$}$Zr(\eta^5\text{-}C_5H_5)Cl$]

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The new *ansa*-bridged compounds [{$Me_2C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)$}$M(\eta^5\text{-}C_5H_5)Cl$], [{$(CH_2)_5C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)$}$M(\eta^5\text{-}C_5H_5)Cl$] (M = Zr, Hf) and [{[$Me_2C(\eta^5\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)$}$Zr(\eta^5\text{-}C_5H_5)Cl$] show unusual modes of coordination of the indenyl or fluorenyl groups.

In recent years *ansa*-bridged metallocene compounds of titanium, zirconium and hafnium have been recognised as an important class of compounds for stoichiometric and catalytic asymmetric induction,[1] especially for the catalytic stereoregular polymerization of prochiral olefins.[2,3] Here we report a series of zirconium and hafnium compounds containing the *ansa*-bridging ligands [$Me_2C(C_5H_4)(C_9H_6)$], [$(CH_2)_5C(C_5H_4)(C_9H_6)$] and [$Me_2C(C_5H_4)(C_{13}H_8)$] for which unprecedented modes of coordination are observed.

In a typical reaction, a mixture of [{$Me_2C(C_5H_4)(C_9H_6)$}Li_2{$0.6(Et_2O)$}] (3.95 g, 14.2 mmol) and [$(\eta^5\text{-}C_5H_5)ZrCl_3\cdot$dme] (5.0 g, 14.2 mmol; dme = 1,2-dimethoxyethane) in toluene was stirred at room temperature for 16 h. The resulting red solution, when filtered from the solid residues, reduced in volume and cooled to −20 °C, afforded air- and moisture-sensitive red crystals of [{$Me_2C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)$}$Zr(\eta^5\text{-}C_5H_5)Cl$] **1** (yield 3.75 g, 64%). [$(\eta^5\text{-}C_5H_5)HfCl_3\cdot 2$thf] reacts similarly to give orange crystals of [{$Me_2C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)$}$Hf(\eta^5\text{-}C_5H_5)Cl$] **2** (yield 71%). Similar reactions using [{$(CH_2)_5C(C_5H_4)(C_9H_6)$}$Li_2$}$0.8(Et_2O)$}] yield red crystals of [{$(CH_2)_5C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)$}$Zr(\eta^5\text{-}C_5H_5)Cl$] **3** (79%) and orange crystals of [{$(CH_2)_5C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)$}$Hf(\eta^5\text{-}C_5H_5)Cl$] **4** (58%). Similarly, the reaction between [$(\eta^5\text{-}C_5H_5)ZrCl_3\cdot$dme] and [{$Me_2C(C_5H_4)(C_{13}H_8)$}$Li_2${$0.75(Et_2O)$}] gave the compound [{$Me_2C(\eta^5\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)$}$Zr(\eta^5\text{-}C_5H_5)Cl$] **5** as red crystals from toluene in 57% yield.

Compounds **1** to **5** have been characterised by elemental analysis, ^1H and ^{13}C NMR spectroscopy.† The NMR spectra show that in each case only one diastereoisomer (pair of enantiomers) is present. With the exception of the signals arising from the bridging groups, the NMR spectra of **1**, **2**, **3** and **4** are very similar. Most interestingly, the ^{13}C chemical shifts of the C_p, C_a and C_b carbons of the indenyl groups are *ca.* δ 85, 110 and 130 respectively, in all four cases. The substantial difference in these values suggest that the indenyl group is not bonded in the η^3 mode expected for an 18-electron compound.

An unusual mode of coordination of the indenyl fragment to the metal in **3** was confirmed by a single crystal X-ray diffraction study.‡ The molecular structure of **3** is shown in Fig. 1, together with selected data. Compound **3** adopts a bent-metallocene type structure with a centroid–Zr–centroid angle of 130.4°. The Zr, Cl, C(17) and C(18) atoms are approximately coplanar (deviations from best least-squares plane less than 0.12 Å) and lie in the equatorial plane between the cyclopentadienyl rings. The indenyl group is planar (to within 0.02 Å) and is bonded in an η^2 fashion to the metal. The C(17)–C(18) and C(18)–C(19) bond lengths are consistent with a σ,π-type coordination to the metal, through the π interaction is highly unsymmetrical. The Zr–C(17) bond is longer than expected for a Zr–C σ-bond, and about 0.06 Å longer than the Zr–C(18) distance. This may be as a result of the strained *ansa* bridge [the angle C(10)–C(11)–C(17) is 101.5°]. The NMR studies indicate that this unusual coordination mode is also present in **1**, **2** and **4**, and is maintained

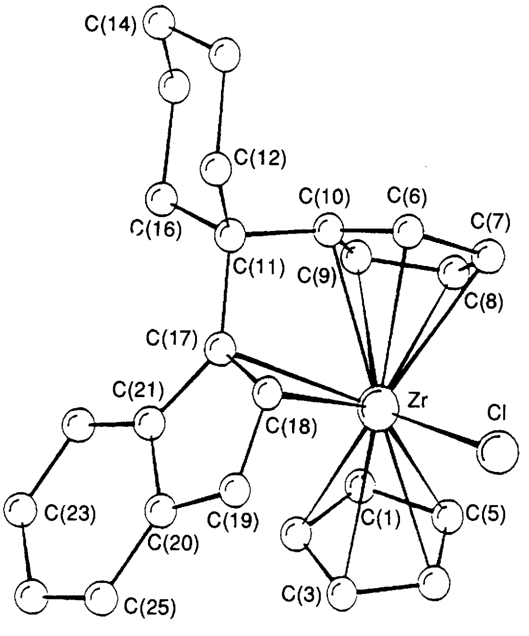


Fig. 1. Molecular structure of **3**. Selected interatomic distances (Å) and angles (°): Zr–Cl 2.500(1), Zr–C(17) 2.564(4), Zr–C(18) 2.508(5), Zr–C(19) 3.170(5), Zr–C(21) 3.335(4), Zr–C(C_5H_5)$_{(mean)}$ 2.51, Zr–C(C_5H_4)$_{(mean)}$ 2.49, Zr–Cp 2.214, Zr–Cp′ 2.174, C(17)–C(18) 1.439(7), C(18)–C(19) 1.376(7); C(11)–C(17)–C(21) 130.7(5), C(10)–C(11)–C(17) 101.5(3), Zr–C(17)–C(18) 71.4(2), Cl–Zr–C(17) 117.5(1), Cp–Zr–Cp′ 130.4°. Cp and Cp′ denote centroids of (C_5H_5) and (C_5H_4) rings respectively.

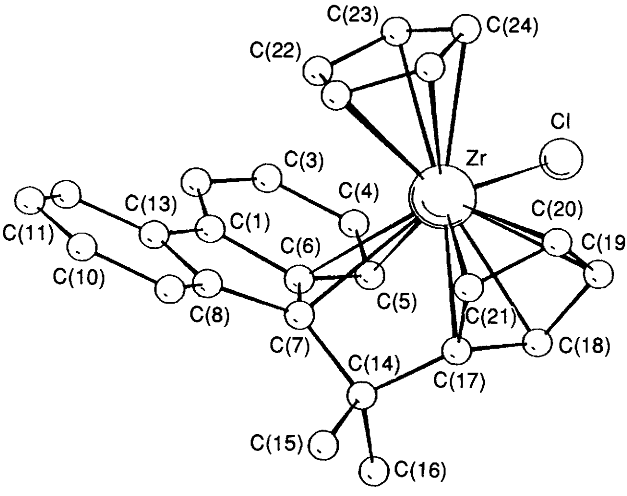
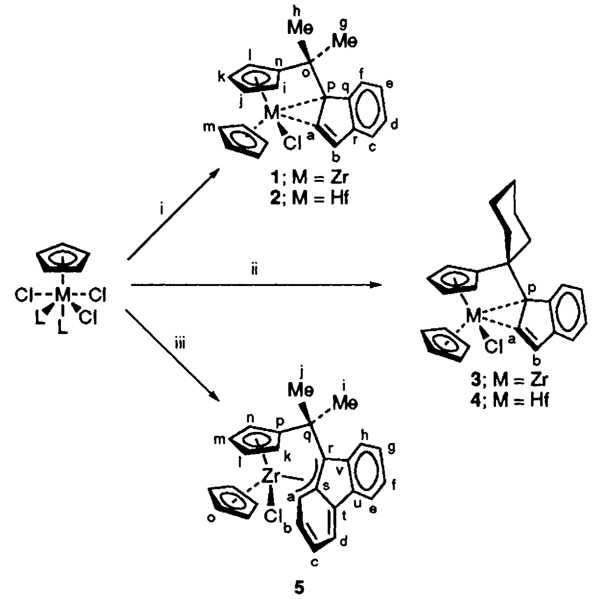


Fig. 2 Molecular structure of **5**. Selected interatomic distances (Å) and angles (°): Zr–Cl 2.560(1), Zr–C(5) 2.692(5), Zr–C(6) 2.633(5), Zr–C(7) 2.649(5), Zr—C(C_5H_5)$_{(mean)}$ 2.49, Zr–C(C_5H_4)$_{(mean)}$ 2.49, Zr–Cp 2.20, Zr–Cp′ 2.18, C(5)–C(6) 1.406(7), C(6)–C(7) 1.445(7), C(7)–C(8) 1.489(7), C(1)–C(13) 1.440(7); C(14)–C(7)–C(8) 126.3(4), C(14)–C(7)–C(6) 124.6(4), C(17)–C(14)–C(7) 103.1(4), Cp and Cp′ denote centroids of (C_5H_5) and (C_5H_4) rings respectively.



Scheme 1 *Reagents and conditions*: i, $[Me_2C(C_5H_4)(C_9H_6)]Li_2[0.6(Et_2O)]$, toluene, room temp., 16 h; ii, $[(CH_2)_5C(C_5H_4)(C_9H_6)]Li_2[0.8(Et_2O)]$, toluene, room temp., 16 h; iii, $[Me_2C(C_5H_4)(C_{13}H_8)]Li_2[0.75(Et_2O)]$, toluene, room temp., 16 h. For M = Zr, 2L = dme, for M = Hf, L = thf. Yields 57–79%.

in solution. The recently reported butadiene(zirconocene) derivative $[(\eta^5\text{-}C_5H_5)_2Zr\{\mu\text{-}(1,2\text{-}\eta^2\text{-}Zr):(4\text{-}\eta^1\text{-}Al)\text{-}C_4H_6\}(\mu\text{-}Cl)AlCl_2]$ shows a similar η^2 σ,π-type coordination of the butadiene ligand to zirconium.[4]

This is the first report of η^2 coordination of an indenyl moiety to a transition metal centre, although η^2 coordination of C_5H_5 has been observed in the crystal structure of $[(\eta^5\text{-}C_5H_5)_2Ti(\eta^2\text{-}C_5H_5)]$.[5] It is likely that the indenyl group is constrained by the *ansa* bridge from adopting a π-η^3 coordination mode.

The molecular structure of **5** has been determined by a single crystal X-ray diffraction study and is shown in Fig. 2. The molecule adopts a bent-metallocene type structure, with η^3 coordination of the fluorenyl moiety close to the equatorial plane which also contains the chlorine atom. The mode of coordination of the fluorenyl group to the metal resembles that seen in η^3-benzyl complexes, for example $[(\eta^3\text{-}p\text{-}MeC_6H_4CH_2)(\eta^5\text{-}C_5H_5)Mo(CO)_2]$,[6] and contrasts with a different η^3 coordination (of the C_5 ring) reported for one of the fluorenyl ligands in $[(\eta^3\text{-}C_{13}H_8)(\eta^5\text{-}C_{13}H_8)ZrCl_2]$.[7] In compound **5** the fluorenyl group is not planar but curves 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 bond lengths of the C(8) to C(13) ring appear to be largely unperturbed by the coordination of the fluorenyl group to the metal centre.

The Zr–Cl distance in **5** (which has an 18-electron configuration) is significantly longer (2.56 Å) than the mean distance of 2.44 Å observed in the 16-electron complex $[(\eta^5\text{-}C_5H_5)_2ZrCl_2]$.[8] The Zr-Cl distance in **3** is about halfway between these two values (2.50 Å), which we believe reflects the extent of electronic rather than steric saturation of the metal centre, since the mean Zr–Cl distance in $[(\eta^5\text{-}C_9Me_7)_2ZrCl_2]$ is 2.43 Å despite the large steric bulk of the permethylindene ligands.[9]

In conclusion, we have prepared the series of compounds **1**–**5** shown in Scheme 1 in which the bridging ligands $[Me_2C(C_5H_4)(C_9H_6)]$, $[(CH_2)_5C(C_5H_4)(C_9H_6)]$ and $[Me_2C(C_5H_4)(C_{13}H_8)]$ adopt unusual modes of coordination, reflecting not only competition between indenyl (or fluorenyl) and cyclopentadienyl ligands for coordination of the metal centre, but also constraints imposed by the short *ansa*-bridges.

We thank Imperial Chemical Industries plc for a CASE award (to G. M. D.).

Received, 1st June 1993; Com. 3/03099G

Footnotes

† *Selected NMR data*, (J/Hz, δ/ppm): **1**; δ_H (300 MHz, $[^2H_8]$THF) 7.59 (1 H, d, $J_{H_fH_e}$ 8, H_f), 7.47 (1 H, d, $J_{H_cH_d}$ 8, H_c), 7.29 (1 H, d, $J_{H_bH_a}$ 4, H_b), 7.03 (1 H, pseudo t, $J_{H_eH_{d,f}}$ 8, H_e), 6.81 (1 H, pseudo t, $J_{H_dH_{c,e}}$ 8, H_d), 6.43 (1 H, d, $J_{H_aH_b}$ 4, H_a), 6.28 (1 H, pseudo q, $J_{H_kH_{i,j,l}}$ 3, H_k), 6.24 (1 H, pseudo q, $J_{H_iH_{j,k,l}}$ 3, H_i], 5.97 (1 H, pseudo q, $J_{H_jH_{i,k,l}}$ 3, H_j), 5.74 (1 H, pseudo q, $J_{H_lH_{i,j,k}}$ 3, H_l), 5.41 (5 H, s, H_m), 2.08 (3 H, s, H_g), 1.70 (3 H, s, H_h); δ_C (75.5 MHz, $[^2H_8]$THF) 142.4 (s, C_n), 137.6 (s, $C_{q\text{ or }r}$), 129.8 [d, J_{CH} 170, C_b), 127.9 (s, $C_{q\text{ or }r}$), 123.9 (d, J_{CH} 157, C_e), 123.3 (d, J_{CH} 156, C_c), 121.4 (d, J_{CH} 175, C_j), 120.4 (d, J_{CH} 159, C_d), 119.7 (d, J_{CH} 157, C_f), 114.6 (d, J_{CH} 174, C_m), 112.0 (d, J_{CH} 174, C_k), 111.7 (d, J_{CH} 156, C_a), 107.8 (d, J_{CH} 173, C_i), 99.4 (d, J_{CH} 173, C_l), 84.4 (s, C_p), 39.2 (s, C_o), 31.2 (s, C_h), 26.7 (s, C_g).

For **2**; $\delta_C\{^1H\}$(75.5 MHz, $[^2H_8]$THF) 129.4 (s, C_b), 108.6 (s, C_a), 85.1 (s, C_p).

For **3**; δ_C(75.5 MHz, C_6D_6) 128.9 (coupling obscured by solvent, C_b), 111.0 (d, J_{CH} 152, C_a), 85.7 (s, C_p).

For **4**; δ_C(75.5 MHz C_6D_6) 129.5 (coupling obscured by solvent, C_b), 108.0 (d, J_{CH} 156, C_a), 84.9 (s, C_p).

For **5**; $\delta_H(CD_2Cl_2)$ 8.26 (1 H, m, H_d), 8.11 (1 H, d, $J_{H_eH_f}$ 8, H_e), 7.91 (1 H, d, $J_{H_hH_g}$ 8, H_h), 7.42 (2 H, m, H_b and H_c), 7.41 (1 H, m, H_g), 7.31 (1 H, m, H_a), 7.20 (1 H, pseudo t, $J_{H_fH_{e,g}}$ 8, H_f), 6.31 (1 H, pseudo q, $J_{H_lH_{k,m,n}}$ 3, H_l), 6.28 (1 H, pseudo q, $J_{H_mH_{k,l,n}}$ 3, H_m), 6.06 (1H, pseudo q, $J_{H_kH_{l,m,n}}$ 3, H_k), 5.59 (1 H, pseudo q, $J_{H_nH_{k,l,m}}$ 3, H_n), 4.84 (5 H, s, H_o), 2.20 (3 H, s, H_i), 1.35 (3 H, s, H_j). δ_C(75.5 MHz, CD_2Cl_2) 145.3 (s, C_p), 137.6 (s, $C_{s,t,u\text{ or }v}$), 133.4 (s, $C_{s,t,u\text{ or }v}$), 133.0 (d, J_{CH} 162, $C_{b\text{ or }c}$), 126.3 (d, J_{CH} 158, C_g), 125.4 (s, $C_{s,t,u\text{ or }v}$), 123.1 (d, J_{CH} 178, C_l), 121.8 (d, J_{CH} 161, $C_{b\text{ or }c}$), 121.6 (d, J_{CH} 155, C_d), 121.4 (d, J_{CH} 158, C_h), 121.1 (d, J_{CH} 161, C_f), 120.1 (d, J_{CH} 157, C_e), 120.1 (s, $C_{s,t,u\text{ or }v}$), 113.6 (d, J_{CH} 175, C_o), 109.7 (d, J_{CH} 174, C_m), 107.3 (d, J_{CH} 180, C_k), 105.0 (d, J_{CH} 158, C_a), 97.1 (d, J_{CH} 178, C_n), 70.4 (s, C_r), 36.6 (s, C_q), 30.9 (q, J_{CH} 127, C_i), 24.2 (q, J_{CH} 127, C_j).

^1H assignments from NOESY experiments, ^{13}C assignments from ^{13}C–^1H shift correlation experiments.

‡ *Crystal data for* compound **3**: $C_{25}H_{25}ClZr(0.5C_7H_8)$, $M = 498.22$, monoclinic, space group $P2_1/n$, $a = 12.123(2)$, $b = 7.069(3)$, $c = 27.504(7)$ Å, $\beta = 101.76(2)$, $V = 2307.5$ Å^3, F(000) = 1028, $Z = 4$, $D_c = 1.43$ g cm^{-3}, $\mu = 5.98$ cm^{-1}, crystal size *ca.* 0.16 × 0.31 × 0.71 mm, 4539 total (3843 independent) reflections, $R = 0.033$ and $R_w = 0.035$ from 2086 reflections with $I > 4\sigma(I)$ (280 variables, observations/variables 7.5), maximum peak in final Fourier difference synthesis 0.28 e Å^{-3}.

For compound **5**; $C_{26}H_{23}ClZr$, $M = 462.1$, monoclinic, space group $P2_1/c$, $a = 15.249(3)$, $b = 8.588(2)$, $c = 16.185(6)$ Å, $\beta = 108.65(2)$, $V = 2008.4$ Å^3, $F(000)$ 944, $Z = 4$, $D_c = 1.53$ g cm^{-3}, $\mu = 6.81$ cm^{-1}, crystal size *ca.* 0.2 × 0.3 × 0.3 mm, 4335 total (3138 independent) reflections, $R = 0.038$ and $R_w = 0.037$ from 2037 reflections with $I > 3\sigma(I)$ (253 variables, observations/variables 8.1), maximum peak in final Fourier difference synthesis 0.41 e Å^{-3}. Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (ω/2θ scan mode, $\theta_{max} = 24.5°$ for **3**, $\theta_{max} = 24°$ for **5**). Corrections were made for Lorentz and polarization effects for both structures as well as empirical correction for absorption.[10] Both structures were solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation (Chebyshev weighting scheme, parameters 3.66, −2.49, 2.39 for **3** and 13.0, −19.3, 13.0, −5.50, 1.51 for **5**). For **3**, all hydrogen atoms were located in the difference Fourier maps, except the H atoms of the toluene solvate molecules whose positions were calculated geometrically. For **3**, the hydrogen atoms were located in the difference Fourier maps, except the H atoms of the toluene solvate molecules whose positions were calculated geometrically. For **5**, the hydrogen atoms were located in the difference Fourier maps except the η^5-C_5H_5 hydrogen atoms which were placed geometrically. In the final refinement of both structures all H atoms were included with fixed positional and thermal parameters. Crystallographic calculations were carried out using the CRYSTALS[11] program package on a MicroVAX 3800 computer. Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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