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ansa-Bridged Tris(cyclopentadienyl) Compounds of Zirconium and Hafnium: X-Ray Crystal Structures of [M{$Me_2C(\eta^5-C_5H_4)_2$}($\eta^5-C_5H_5$)Cl] (M = Zr or Hf)

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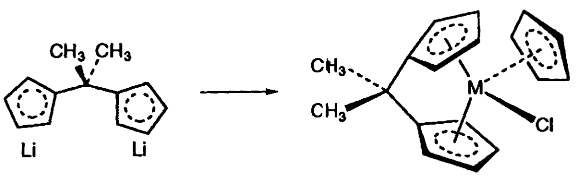
The new *ansa*-bridged compounds [M{$Me_2C(\eta^5-C_5H_4)_2$}($\eta^5-C_5H_5$)Cl] (M = Zr or Hf) have been synthesised and their molecular structures determined by X-ray crystallography. The latter is the first example of a tris(η^5-cyclopentadienyl) derivative of hafnium.

In recent years *ansa*-bridged metallocene derivatives 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 polymerisation of prochiral olefins.[2] Here we report the synthesis of new tris(η^5-cyclopentadienyl) compounds of zirconium and hafnium, in which a short CMe_2 *ansa* bridge links two of the rings. Only three authentic tris(η^5-cyclopentadienyl) transition-metal compounds have been reported previously and in each case the transition metal is zirconium.[3-5] Where the crystal structures of the hafnium analogues of the zirconium compounds have been determined they do *not* have tris(η^5-cyclopentadienyl) co-ordination.[5,6] However the new *ansa*-bridged η-cyclopentadienyl derivatives have the previously unattainable tris(η^5-cyclopentadienyl) co-ordination for hafnium, as described below.

In a typical reaction, a mixture of $Li_2[Me_2C(C_5H_4)_2]$ (1.0 g, 5.4 mmol) and [Zr($\eta^5-C_5H_5$)Cl_3]·dme (1.9 g, 5.4 mmol; dme = 1,2-dimethoxyethane) in toluene was stirred at room temperature for 60 h. The resulting yellow solution, when filtered from the solid residue, reduced in volume and cooled to −20 °C, afforded pale yellow air- and moisture-sensitive crystals of [Zr{$Me_2C(\eta^5-C_5H_4)_2$}($\eta^5-C_5H_5$)Cl] **1** (yield 0.81 g, 41%). The compound [Hf($\eta^5-C_5H_5$)Cl_3]·2thf (thf = tetrahydrofuran) reacts similarly (see Scheme 1) to give pale yellow crystals of [Hf{$Me_2C(\eta^5-C_5H_4)_2$}($\eta^5-C_5H_5$)Cl] **2** (yield 43%). Compounds **1** and **2** have been characterised by elemental analysis, ^1H and ^{13}C NMR spectroscopy* and single crystal X-ray diffraction studies.†

The molecular structure of **1** and **2** is shown in Fig. 1, together with selected data. The most important point is that compound **2** is essentially isostructural with compound **1**. This contrasts with the hafnium analogues of [Zr($\eta^5-C_5H_5$)$_3$Cl][5] and [Zr(η^5-



1 M = Zr
2 M = Hf

Scheme 1 [M(C_5H_5)Cl_3]·2L, toluene, room temperature, 60 h. For M = Zr, 2L = dme; for M = Hf, L = thf

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* Selected NMR data (*J* in Hz, δ in ppm). Compound **1**: δ_H(300 MHz, C_6D_6, 291 K), 6.00 [1 H, pseudo q, J_{HH} 3, C_5H_4], 5.83 [1 H, pseudo q, J_{HH} 3, C_5H_4], 5.70 (5 H, s, C_5H_5), 5.35 [1 H, pseudo q, J_{HH} 3, C_5H_4], 5.22 [1 H, pseudo q, J_{HH} 3, C_5H_4], 1.30 (3 H, s, CH_3), 1.24 (3 H, s, CH_3); δ_C{^1H}(75.5 MHz, CD_2Cl_2, 291 K), 146.7 [s, C_{ipso}(C_5H_4)], 122.9 [s, CH (C_5H_4)], 115.5 (s, C_5H_5), 112.5 [s, CH (C_5H_4)], 110.0 [s, CH (C_5H_4)], 93.1 [s, CH (C_5H_4)], 35.4 (s, *C*Me_2), 24.0 (s, CH_3). Compound **2**: δ_H(300 MHz, C_6D_6, 291 K), 5.99 (1 H, m, C_5H_4), 5.75 (1 H, m, C_5H_4), 5.58 (5 H, s, C_5H_5), 5.52 (1 H, m, C_5H_4), 5.18 (1 H, m, C_5H_4), 1.34 (3 H, s, CH_3), 1.30 (3 H, s, CH_3); δ_C(75.5 MHz, [$^2H_8$]thf, 291 K), 142.1 [s, C_{ipso}(C_5H_4)] 120.4 [d, J_{CH}, 172, CH (C_5H_4)], 117.0 [d, J_{CH} 178, CH (C_5H_4)], 114.6 [d, J_{CH} 174, C_5H_5], 105.5 [d, J_{CH} 173, CH (C_5H_4)], 96.9 [d, J_{CH} 173, CH (C_5H_4)], 35.9 (s, *C*Me_2), 27.3 (q, J_{CH} 130, CH_3), 25.0 (coupling obscured by solvent, CH_3).

† Crystallographic details. Compound **1**: $C_{18}H_{19}ClZr$, M = 362.0, monoclinic, space group $P2_1$, a = 7.139(1), b = 9.581(1), c = 10.876(1) Å, β = 92.30(1)°, U = 743.3 Å^3, $F(000)$ = 368, Z = 2, D_c = 1.62 g cm^{-3}, μ = 8.96 cm^{-1}, crystal size *ca.* 0.16 × 0.22 × 0.50 mm, 3999 total (2878 independent) reflections, R = 0.0241 and R' = 0.0243 from 2100 reflections with $I > 3\sigma(I)$ (181 variables, observations/variables 11.6), maximum peak in final Fourier difference synthesis 0.29 e Å^{-3}. Compound **2**: $C_{18}H_{19}ClHf$, M = 449.3, monoclinic, space group $P2_1$, a = 7.115(6), b = 9.572(6), c = 10.883(6) Å, β = 92.39(7)°, U = 740.5 Å^3, $F(000)$ = 432, Z = 2, D_c = 2.02 g cm^{-3}, μ = 71.5 cm^{-1}, crystal size *ca.* 0.19 × 0.22 × 0.50 mm, 3575 total (2881 independent) reflections, R = 0.0244 and R' = 0.0263 from 2453 reflections with $I > 3\sigma(I)$ (181 variables, observations/variables 13.5), maximum peak in final Fourier difference synthesis 0.86 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, ω/θ = 1.2, θ_{max} = 33°). Both structures were solved by direct methods and refined by full-matrix least-squares technique in the anisotropic approximation (Chebyshev weighting scheme, parameters 2.80, −1.94, 1.71 for **1** and 8.24, −6.88, 5.75 for **2**). All hydrogen atoms were located in the Fourier-difference maps and included in the final refinement with the fixed positional and thermal parameters. Corrections for Lorentz and polarisation effects for both structures, as well as empirical correction for absorption[7] for **2**, were applied. Polar axis direction was determined using an enantiopole parameter.[8] Crystallographic calculations were carried out using the CRYSTALS[9] program package on a Micro VAX 3800 computer. Atomic coordinates, thermal parameters and bond lengths and angles for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

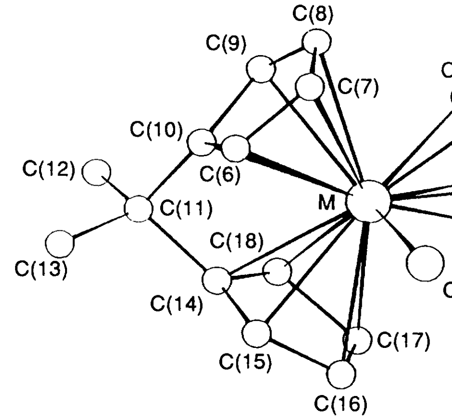

Fig. 1 Molecular structure of **1** (**2**). Important bond lengths (Å) and angles (°): M–Cl 2.5363(7) [2.510(1)], M–R_1 2.301 (2.297), M–R_2 2.306 (2.270), M–R_3 2.277 (2.287), R_1–M–R_2 119.6 (120.2), R_1–M–R_3 119.1 (118.5), R_2–M–R_3 110.6 (111.2), Cl–M–R_1 100.7 (100.5), Cl–M–R_2 100.2 (98.7), Cl–M–R_3 102.0 (103.0), C(10)–C(11)–C(14) 99.4(2) [97.7(5)]. R_1, R_2 and R_3 denote the centroids of the rings C(1)–C(5), C(6)–C(10) and C(14)–C(18) respectively

$C_5H_5)_3(\sigma\text{-}C_5H_5)]$[3] which have been shown crystallographically to adopt markedly different structures: $[Hf(\eta^5\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)Cl]$[5] and $[Hf(\eta^5\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)_2]$[6] respectively.

For both **1** and **2** all three rings show η^5-co-ordination to the metal centre and all the rings are planar to within 0.033 Å for **1** and 0.061 Å for **2**. In both molecules the mean M–C bond lengths of the three rings are similar. The overall mean M–C bond length is 2.58 Å for both **1** and **2**, which is identical to the values reported for the tris(η^5-cyclopentadienyl)zirconium derivatives $[Zr(\eta^5\text{-}C_5H_5)_3(\sigma\text{-}C_5H_5)]$,[3] $[Zr(\eta^5\text{-}C_5H_5)_3HAlEt_3]$[4] and $[Zr(\eta^5\text{-}C_5H_5)_3Cl]$.[5] It has been proposed that for transition-metal complexes of the type $[M(\eta^5\text{-}C_5H_5)_3X]$ there is a molecular orbital of a_2 symmetry which is localised on the cyclopentadienyl rings and is non-bonding with respect to the metal.[10] Thus d^0 transition-metal complexes of this type will have 18- rather than 20-electron configurations and each η^5-$C_5H_5^-$ ring donates fewer than the normal six electrons, hence the average M–C bond order is less than one. This may account for the significantly longer M–C bond lengths in these tris(η^5-cyclopentadienyl) derivatives compared with $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ (2.49 Å)[11] and $[Hf(\eta^5\text{-}C_5H_5)_2Cl_2]$ (2.47 Å).[12] Even the very sterically crowded zirconocene derivative $[Zr(\eta^5\text{-}C_5H_5)_2\{CH(SiMe_3)_2\}Ph]$ has a mean Zr–C(C_5H_5) bond length of only 2.54 Å.[3]

The Zr–Cl distance in **1** (2.54 Å) is similar to that observed in the 18-electron complex $[Zr\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)\}(\eta^5\text{-}C_5H_5)Cl]$ (2.56 Å)[13] and is significantly longer than the mean Zr–Cl distance of 2.44 Å observed in the 16-electron complex $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$. Similarly, the Hf–Cl bond length in **2** (2.51 Å) is significantly longer than those reported for the 16-electron complexes $[Hf(\eta^5\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)Cl]$ (2.41 Å) and $[Hf(\eta^5\text{-}C_5H_5)_2Cl_2]$ (2.42 Å).[14]

The molecular structure of **1** differs most significantly from that of the non-bridged analogue in the centroid–Zr–centroid angles. For **1**, the angle between the centroids of the bridged rings is only 110.6° compared with over 119° for the non-bridged angles. For $[Zr(\eta^5\text{-}C_5H_5)_3Cl]$ the three centroid–Zr–centroid angles are very similar and average 117.3°, compared with 127.0° for $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$. For compound **2**, the 111.2° angle between the centroids of the rings joined by the short CMe_2 bridge is much smaller than the centroid–Hf–centroid angles in $[Hf(\eta^5\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)Cl]$ (129°) and $[Hf(\eta^5\text{-}C_5H_5)_2Cl_2]$ (127.1°).

We propose that the structures adopted by tris(cyclopentadienyl) transition-metal complexes depend on a fine balance between steric and electronic factors. Although the atomic radius of hafnium is only about 0.01 Å less than that of zirconium, average M–C and M–Cl bond lengths are about 0.02 to 0.03 Å shorter in organometallic compounds of hafnium compared with zirconium.[12,14] We propose that the cumulative steric effects in the $[M(\eta^5\text{-}C_5H_5)_2Cl]$ fragment may be sufficient to disfavour η^5-co-ordination of the third C_5H_5 ligand when M = Hf. The reduced steric crowding experienced by the C_5H_5 ligand in **2**, as a result of the short *ansa* bridge between the other two rings, may allow it to adopt η^5-co-ordination. Complex **2** thus attains a favoured 18-electron configuration.

The ^1H and ^{13}C NMR spectra of compounds **1** and **2** are consistent with the tris(η^5-cyclopentadienyl) structures being maintained in solution, with fast reorientation of the C_5H_5 ligand on the NMR timescale. Low-temperature NMR studies (500 MHz, $[^2H_8]$thf, 304–173 K) show no evidence of lowering of symmetry or freezing out of any fluxionality.

The molecular structure of **2** compared with $[Hf(\eta^5\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)Cl]$ demonstrates the effect that an *ansa* bridge can have on the gross structure of a complex. The crystal structures of the related *ansa*-bridged complexes $[Zr\{(CH_2)_5C(\eta^5\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta^5\text{-}C_5H_5)Cl]$ and $[Zr\{Me_2C(\eta^5\text{-}C_5H_4)(\eta^3\text{-}C_{13}H_8)\}(\eta^5\text{-}C_5H_5)Cl]$ have recently been determined.[13] The observed η^2-indenyl and η^3-fluorenyl modes of bonding in these compounds are unprecedented and we assume they reflect constraints imposed by the short *ansa* bridges.

In conclusion, we have reported the synthesis and molecular structure of the first tris(cyclopentadienyl) derivative of hafnium in which all three rings show η^5-co-ordination to the metal centre. We have shown that by including a suitable bridging group, previously unattainable co-ordination modes may be achieved.

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