Crystal and Molecular Structure of Monochlorotris(2,6-di-t-butylphenoxo)hafnium

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The compounds $MCl(OC_6H_3Bu^t_2\text{-}2,6)_3$ (M = Zr, Hf) have been synthesized and the hafnium compound has been structurally characterized to show a sterically congested, mononuclear molecule in which several distortions of the aryloxo-ligands have taken place.

Treatment of MCl_4 (M = Zr, Hf) with LiOAr′ (OAr′ = 2,6-di-t-butylphenoxo) in benzene or diethyl ether solvents gives good yields of $MCl(OAr')_3$ **(1a)** (M = Zr) and **(1b)** (M = Hf) which can be recrystallized from toluene at −20 °C as white crystals. Efforts to prepare $MCl_2(OAr')_2$ have so far proved unsuccessful. Treatment of MCl_4 with 2 equiv. of LiOAr′ gave only **(1a)** and **(1b)** in lower yields, while an attempted ligand redistribution between MCl_4 and **(1)** in refluxing toluene led to decomposition.

$MCl(OC_6H_3Bu^t_2\text{-}2,6)_3$
(1)a; M = Zr
b; M = Hf

In the mass spectrum, **(1)** showed a mass parent molecular ion as well as fragments due to loss of Cl and OAr′. The i.r. spectrum of **(1)** between 50 and 4 000 cm^{-1} (Nujol mull) shows a strong band at 354 cm^{-1} **(1a)** or 372 cm^{-1} **(1b)** which we assign to the M–Cl stretch. A somewhat weaker band at 460 cm^{-1} **(1a)** or 465 cm^{-1} **(1b)** can be assigned to the anti-symmetric MO_3 stretching vibration.[1] Satisfactory analytical data were obtained for both new compounds.

Neither **(1a)** nor **(1b)** undergo ready substitution with alkylating agents. They can be recovered unchanged after being treated with $LiCH_2SiMe_3$ for weeks in either benzene or diethyl ether solvents at 30 °C. However, use of the smaller LiMe in diethyl ether does lead to reaction.† A similar reactivity pattern has been reported for the compounds $MCl[N(SiMe_3)_2]_3$.[2] A crystal structure determination of the hafnium compound **(1b)** revealed the reason for this lack of reactivity to be the blocking of potential sites of nucleophilic attack by the Bu^t-groups of the aryloxo-ligands.‡

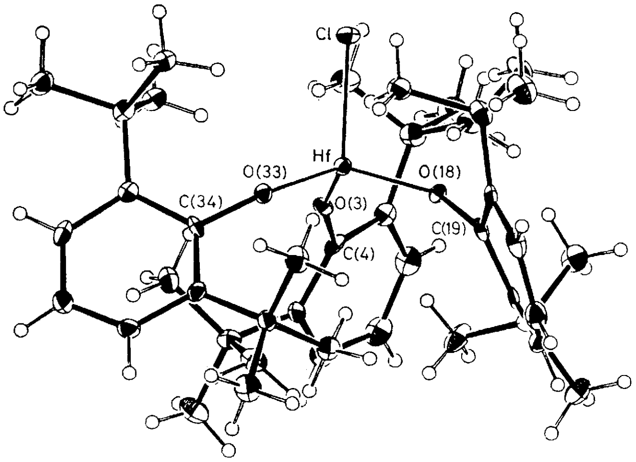

Figure 1. A view of the $HfCl(OC_{14}H_{21})_3$ molecule giving the atom numbering scheme used. Some pertinent bond distances and angles are: Hf(1)–Cl(2) = 2.365(1), Hf(1)–O(3) = 1.938(3), Hf(1)–O(18) = 1.925(2), Hf(1)–O(33) = 1.917(3) Å, Cl(2)–Hf(1)–O(3) = 109.5, Cl(2)–Hf(1)–O(18) = 103.9, Cl(2)–Hf(1)–O(33) = 108.8, O(3)–Hf(1)–O(18) = 114.9, O(3)–Hf(1)–O(33) = 109.9, O(18)–Hf(1)–O(33) = 109.7, Hf(1)–O(3)–C(4) = 159.4, Hf(1)–O(18)–C(19) = 152.0, Hf(1)–O(33)–C(34) = 155.9°.

The *X*-ray diffraction studies show the compound to have a slightly distorted tetrahedral geometry. The molecule is shown in Figure 1 with some of the pertinent bond distances and angles. Despite the bulky nature of the aryloxo-groups, there is little distortion of the co-ordination geometry from tetrahedral. Only one of the bonds to the substituents, to O(3), is distorted, being bent towards the Cl atom, and away from one of the other substituents, O(18). The other four angles between donor atoms are 109.5 ± 1°. To relieve the obvious steric crowding in the molecule, the ligand itself undergoes a number of distortions. The aryl groups are aligned so that there are two types of CMe_3 groups, one proximal to the Hf–Cl bond and the other distal. The mean value of the angle between these aryl planes and the Hf–Cl vector is 24. This type of distortion is a typical feature in the coordination chemistry of the bulky $N(SiMe_3)_2$ ligand.[3] The arene rings show considerable distortion from planarity, resulting in the oxygen and two CMe_3 carbons being puckered out of the plane by between 0.2 and 0.3 Å, allowing the CMe_3 groups to move away from the congested metal centre. Furthermore, the Hf–O–C bond angles are opened up to between 152 and 159° allowing further relief of steric strain. This angle increase is much more pronounced than seen in other compounds containing this ligand, *e.g.* 142.3° in $(C_5H_5)Ti(OAr')$.[4] This probably reflects the greater steric crowding in the title compound, and is not necessarily indicative of a large amount of π-bonding between Hf and the oxygen atoms of the OAr′ groups.

Space filling models show that in **(2a)** attack at the metal atom *trans* to Cl is strongly inhibited by the distal Bu^t groups and a similar problem is encountered for attack on the other side of the molecule, resulting in substitution being both slow, and limited to small incoming groups.

Both **(1a)** and **(1b)** give temperature-dependent ^1H n.m.r.

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† Addition of an excess (2 equiv.) of LiMe to a diethyl ether solution of **(1b)** gave a dark solution after 2 h. Removal of solvent and extraction with pentane gave a colourless solution from which $Hf(Me)(OAr')_3$ could be isolated.

‡ *Crystal data* (at −165 °C) for $HfCl(OC_{14}H_{21})_3$: triclinic, space group = $P\bar{1}$, a = 17.521(5), b = 11.155(2), c = 10.686(2) Å, α = 104.71(1), β = 99.51(1), γ = 83.82(1)°, D_c = 1.387 g cm^{-3}, Z = 2. The structure was solved by Patterson and Fourier techniques using 5213 unique intensities collected on an automated diffractometer using Mo-K_α radiation for $5 \leqslant 2\theta \leqslant 50°$. All hydrogen atoms were located and refined. Final refinement utilized anisotropic thermal parameters for all nonhydrogen atoms and converged to $R(F)$ = 0.0235 and $R_w(F)$ = 0.025.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

spectra.§ At 35 °C only one type of CMe_3 signal is observed, indicating that at this temperature exchange of the proximal and distal groups by rotation about the M–O–Ar′ bonds is rapid on the n.m.r. time scale. On cooling this signal broadens and at −60 °C (90 MHz) splits into two broad, equal-intensity peaks. However, further cooling of the sample sharpens only one of these signals, the other remains broad and at −90 °C begins to show further splitting, indicating that two exchange processes are taking place. The first involves restricted rotation about the M–O–Ar′ bond while the second involves a restricted rotation of one of the types of CMe_3 groups [probably that proximal to the Hf–Cl bond (Figure 1)] causing a non-equivalence of the methyl groups. Interestingly, the compound $Hf(Me)(OAr')_3$ shows only one CMe_3 signal even at temperatures as low as −90 °C, although some broadening of the signal is seen at this temperature. This may indicate a more facile rotation about the Hf–O–Ar bonds in this compound compared to (**1**), or may be due to the proximal and distal CMe_3 groups having closer chemical shifts.

We have also isolated the blue, monomeric $[Ti(OAr')_3]$;¶ an extensive monomeric aryoxo-chemistry for these Group 4B metals in their lower oxidation states is thus possible.

Received, 7th April 1982; Com. 397

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§ ^{1}H N.m.r. spectra (recorded in $C_6D_5CD_3$) of the CMe_3 groups at 90 MHz; (**1a**): 35 °C, 1.40 (s); −90 °C, 1.74 (v.br.), 1.30 (br.), (**1b**): 35 °C, 1.42 (s); −90 °C, 1.75 (br.), 1.35 (br.).

¶ Reaction of an excess of LiOAr′ with $TiCl_3(NMe_2)_2$ in benzene gave a deep blue mixture after 2 days. Extraction with hexane gave a blue extract from which $[Ti(OAr')_3]$ could be crystallized as blue plates on cooling. The product shows a sharp e.s.r. signal at room temperature in toluene with g_0 = 1.9102. In the mass spectrometer a strong peak due to $[Ti(OAr')_3]^+$ can be seen.