

Bis(trimethyltin)bis-(η -toluene)-hafnium and -zirconium; X-Ray Crystal Structure of the Hafnium Compound

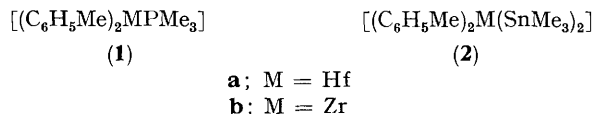
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Summary Treatment of the compound $[\text{Hf}(\eta\text{-C}_6\text{H}_5\text{Me})_2\text{-PMe}_3]$ with hexamethylditin gives the compound $[\text{Hf}(\eta\text{-C}_6\text{H}_5\text{Me})_2(\text{SnMe}_3)_2]$, a d^2 , bent bis-arene derivative, the crystal structure of which has been determined; the analogous zirconium compound is similarly prepared.

RECENT reports of the compounds $\{[\text{W}(\text{arene})_2\text{H}]\text{PF}_6\}^1$ and $[(\text{C}_6\text{H}_5\text{Me})_2\text{MPMe}_3]$ (**1**)² suggested that the chemistry of the bent bis-arene compounds of the transition metals might parallel the extensive and interesting chemistry of their bent bis-(η -cyclopentadienyl) metal analogues. Hence, we have further investigated the bis-arene derivatives.



Treatment of the compounds (**1**) with hexamethylditin at 45 °C gave a smooth reaction and, from the resulting deep red-purple solutions, black crystals of the compounds $[\text{M}(\text{C}_6\text{H}_5\text{Me})_2(\text{SnMe}_3)_2]$ (**2**), were isolated; ¹H n.m.r. (C_6H_6):

(**2a**) τ 4.47, 5.27, and 6.02 {[2H, t, J (H-H) 6.9 Hz], [4H, d, J (H-H) 6.0 Hz], and [4H, t, J (H-H) 6.9 Hz], respectively, all $2 \times \text{Ph}$ }, 8.49 [6H, t, J (Sn-H) 10 Hz, $2 \times \text{CMe}$], and 9.42 [18H, t, J (Sn-H) 29 Hz, $6 \times \text{SnMe}$]; (**2b**) 4.46, 5.29, and 6.03 {[2H, t, J (H-H) 6.9 Hz], [4H, d, J (H-H) 6.0 Hz], and [4H, t, J (H-H) 6.9 Hz], respectively, all $2 \times \text{Ph}$ }, 8.74 [6H, t, J (Sn-H) 8 Hz, $2 \times \text{CMe}$], and 9.44 [18H, t, J (Sn-H) 29 Hz, $6 \times \text{Me}$].

Solutions of the compounds (**2**) are very sensitive to oxygen and are slowly hydrolysed. Crystals of the compounds (**2**) are only slowly decomposed in air (hours). The mass spectrum of (**2a**)[†] shows a parent-ion centred at m/e 690, with the expected isotope-distribution pattern.

The crystal structure of (**2a**) has been determined.

Crystal structure: $\text{C}_{20}\text{H}_{34}\text{HfSn}_2$, M 690.09, monoclinic, space group $C_{2/c}$, $a = 14.027(3)$, $b = 9.714(3)$, $c = 17.946(8)$ Å, $\beta = 111.11(4)^\circ$, $U = 2281$ Å³, $Z = 4$, $F(000) = 1304$, $D_c = 2.01$ g cm⁻³. Intensities of 3326 independent reflections were measured ($2\theta_{\text{max}} = 52^\circ$) on a CAD-4 diffractometer using graphite-monochromated Mo- K_α radiation. 1737 Reflections with $I > 3\sigma(I)$, corrected for absorption [$\mu(\text{Mo-}K_\alpha) = 66.8$ cm⁻¹], were used in the refinement

[†] Satisfactory microanalyses have been obtained.

procedure. The structure was solved by heavy-atom and difference-Fourier methods and refined by full-matrix least-squares methods, using anisotropic temperature factors. The current R value is 0.031.[‡] Each hafnium atom is located on a two-fold axis (Figure). The molecular configuration adopted is analogous to that of the d^2 , 18-electron $\{[(\eta\text{-C}_5\text{H}_5)_2\text{MX}_2]\}$ compounds; the Sn(1)–Hf–Sn(1B) angle is less than 90° and the angle between the normal and the least-squares best-plane of the arene rings is 138.9° {*c.f.* the corresponding angles for $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Br}(\text{SnBr}_3)]$ which are 80.2 and 128.3° , respectively³}.

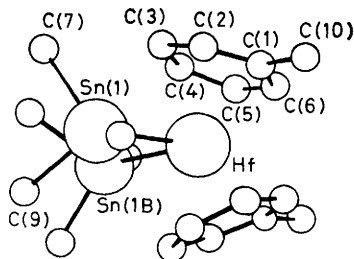


FIGURE. Molecular structure of (2a). Bond distances to the Hf atom are Sn(1) 2.953(1), C(1) 2.496(9), C(2) 2.491(9), C(3) 2.517(9), C(4) 2.523(9), C(5) 2.43(1), and C(6) 2.43(1) Å. The angle Sn(1)–Hf–Sn(1B) is $81.14(3)^\circ$.

The trimethyltin ligand was chosen because of its bulk which would give a sterically saturated molecule, which normally leads to thermal stability. In fact, compound (2a) has a slight curvature of the normally planar C_6 -ring which may reflect steric strain. Further, the trimethyltin group is electropositive relative to other common ligands. We wished to avoid a build-up of positive charge on the transition metal centres and thereby encourage back-donation from the d^2 metal electrons. Hexamethylditin may be regarded as 'bulky dihydrogen.'

The compounds (1) are clearly analogues of the d^4 compounds $[(\eta\text{-C}_5\text{H}_5)_2\text{ML}]$, $\text{M} = \text{Mo}$ or W and $\text{L} = \text{R}_3\text{P}$ or CO .⁴ Correspondingly, the compounds (2) are the first bis- η -arene analogues of the d^2 compounds $[(\eta\text{-C}_5\text{H}_5)_2\text{MR}_2]$, $\text{M} = \text{Mo}$ or W and $\text{R} = \text{alkyl}$.⁵

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[‡] Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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