Synthesis of Zerovalent Bis-(η-arene)(trimethylphosphine)-hafnium and -zirconium Compounds Using Metal Vapours

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Summary Co-condensation of hafnium or zirconium atoms from an electron-gun furnace with arenes and trimethylphosphine gives good yields of the compounds $[\mathrm{M}(\eta\text{-arene})_2(\mathrm{PMe}_3)]$, M = Hf or Zr.

In a continuing survey of the chemistry of atoms of the most refractory elements,[1] we have found that both hafnium and zirconium may be readily evaporated from a suitable electron-gun furnace with a water-cooled positive hearth, operating at *ca.* 3000 and 2800 °C, respectively (10^{-6} Torr). Co-condensation of the hafnium vapour with an excess of toluene and trimethylphosphine (molar ratio PhMe : PMe_3 *ca.* 20 : 1) at −196 °C gives, on warm-up, a dark green solution from which green-black crystalline $[\mathrm{Hf}(\eta\text{-PhMe})_2(\mathrm{PMe}_3)]$ (**1**)† may be isolated. In a typical experiment 1·5 g of hafnium were co-condensed with 80 cm^3 of toluene and 3 cm^3 of trimethylphosphine during 3 h giving *ca.* 1·2 g of the pure compound after recrystallisation from light petroleum (yield *ca.* 30% based on hafnium). The compound $[\mathrm{Hf}(\eta\text{-C}_6\mathrm{H}_6)_2(\mathrm{PMe}_3)]$, (**2**), could also be obtained in an identical manner by co-condensation of the hafnium vapour with an excess of benzene and trimethylphosphine at −196 °C.

The compounds (**1**) and (**2**) are readily soluble in benzene and toluene and moderately soluble in light petroleum. Solutions under argon appear to be indefinitely stable, but show signs of decomposition after a few minutes under a dinitrogen atmosphere. The compounds (**1**) and (**2**) are immediately decomposed upon exposure to air or water. Attempts to sublime (**1**) at 70 °C and 10^{-5} Torr led mainly to decomposition, although a slight green coloration of the liquid-nitrogen-cooled probe was observed. The mass spectrum of (**1**) shows only a very weak, highest band at *m/e* 440 corresponding to the ion $[\mathrm{Hf}\,(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})_2(\mathrm{PMe}_3)]^+$ containing ^{180}Hf the most abundant hafnium isotope. However, there is a strong series of bands (*m/e* 360—364) of appropriate intensity pattern corresponding to the (hafnium) isotopes of the ion $[\mathrm{Hf}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})_2]^+$. The only ion of high (>200) *m/e* in the mass spectrum of (**2**) is a weak band at *m/e* 412 corresponding to the ion $[^{180}\mathrm{Hf}(\eta\text{-C}_6\mathrm{H}_6)_2(\mathrm{PMe}_3)]^+$.

Similarly, co-condensation of zirconium vapour with an excess of toluene and trimethylphosphine gives the dark green crystalline compound $[\mathrm{Zr}(\eta\text{-C}_6\mathrm{H}_5\mathrm{Me})_2(\mathrm{PMe}_3)]$ (**3**) in *ca.* 40% yield after work-up.

The ^{1}H n.m.r. spectra of (**1**), (**2**), and (**3**) in $\mathrm{C}_6\mathrm{D}_6$ show the presence of co-ordinated trimethylphosphine and two co-ordinated arene groups: $[\mathrm{Hf}(\eta\text{-PhMe})_2(\mathrm{PMe}_3)]$ (**1**) δ 5·30 (2H, m, ArH), 4·00 (8H, m, ArH), 2·00 (6H, s, Me), and 0·90 (9H, d, J_{PH} 5 Hz, PMe_3); $[\mathrm{Hf}(\eta\text{-C}_6\mathrm{H}_6)_2(\mathrm{PMe}_3)]$ (**2**) δ 4·35 (12H, d, J_{PH} 0·8 Hz, ArH) and 0·95 (9H, d, J_{PH} 4 Hz, PMe_3); and $[\mathrm{Zr}(\eta\text{-PhMe})_2(\mathrm{PMe}_3)]$ (**3**) δ 5·55 (2H, m, ArH), 4·13 (8H, m, ArH), 2·20 (6H, m, Me), and 0·85 (9H, d, J_{PH} 4 Hz, PMe_3).

The compounds (**1**), (**2**), and (**3**) thus represent the first examples of zerovalent hafnium and zirconium and we suggest that they have the bent sandwich structures analogous to that shown for the cation $[(\eta\text{-C}_6\mathrm{H}_5\mathrm{F})_2\mathrm{WH}]^+$.[2]

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† Satisfactory microanalysis has been obtained.

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[2] P. R. Brown, F. G. N. Cloke, M. L. H. Green, B. Meunier, G. E. Morris, and C. K. Prout, to be published.