Synthesis of Bis(η-1,3,5-tri-t-butylbenzene) Sandwich Complexes of Titanium, Zirconium, and Hafnium, and of the Hafnium(0) Carbonyl Complex [Hf(η-$Bu^{t}{}_{3}C_{6}H_{3})_{2}(CO)$]

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Cocondensation of 1,3,5-tri-t-butylbenzene with atoms of Ti, Zr, or Hf yields the diamagnetic sandwich compounds [M(η-$Bu^{t}{}_{3}C_{6}H_{3})_{2}$], M = Ti, Zr, or Hf; the hafnium complex reacts with carbon monoxide to afford [Hf(η-$Bu^{t}{}_{3}C_{6}H_{3})_{2}(CO)$].

Of the homoleptic bis(η-arene) complexes of the group IV elements, only bis(η-arene)titanium compounds have thus far been prepared (*via* metal vapour synthesis).[1,2] In the case of zirconium and hafnium, the simple 16-electron sandwich complexes appeared to be highly unstable; however, the 18-electron trimethylphosphine adducts [M(η-arene)$_{2}$(PMe$_{3}$)], M = Zr or Hf, have been prepared by cocondensation of the metal vapours with a mixture of the appropriate arene (benzene or toluene) and trimethylphosphine.[3]

We report the use of the bulky arene ligand 1,3,5-tri-t-butylbenzene to stabilise the homoleptic bis(η-arene) complexes of all three of the group IV elements. This ligand promises to have a useful role in transition metal chemistry; it has already been employed to prepare the stable neutral Rh^{I} complex [Rh(η-$Bu^{t}{}_{3}C_{6}H_{3}$)(η-$C_{8}H_{14}$){Sn(NR$_{2}$)$_{2}$Cl}] ($C_{8}H_{14}$ = cyclo-octene, R = SiMe$_{3}$).[4]

In a typical experiment, electron-beam vapourised titanium (*ca.* 1.0 g) was cocondensed with an excess of 1,3,5-tri-t-butylbenzene over a period of 2 h at 77 K, using an apparatus of a type previously described.[5] After extraction of the solid product from the apparatus with hexane and removal of excess of ligand by sublimation, low-temperature recrystallisation of the residue from pentane afforded deep red crystals of [Ti(η-$Bu^{t}{}_{3}C_{6}H_{3})_{2}$] (**1**),[†] in *ca.* 40% yield (based on titanium). The analogous reactions with zirconium and hafnium vapours gave similar yields of deep green [Zr(η-$Bu^{t}{}_{3}C_{6}H_{3})_{2}$] (**2**)[†] and deep purple [Hf(η-$Bu^{t}{}_{3}C_{6}H_{3})_{2}$] (**3**),[†] respectively.

The compounds (**1**), (**2**), and (**3**) dissolve readily in hydrocarbon solvents and may be sublimed with slight decomposition at 80—100 °C and 10^{-4} mbar; they are highly air sensitive both in solution and in the solid state. Their ^{1}H and ^{13}C n.m.r. spectra[‡] show the expected shifts to low

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[†] Satisfactory microanalysis has been obtained.

[‡] ^{1}H and ^{13}C n.m.r. data: recorded at probe temperature on Brucker WH360 or WP80 instruments in $C_{6}D_{6}$ Coupling constants are in Hz; δ is relative to internal solvent (**1**) ^{1}H: 5.04 (3H, s, $Bu^{t}{}_{3}C_{6}\mathit{H}_{3}$) and 1.48 (27H, s, $\mathit{Bu}^{t}{}_{3}C_{6}H_{3}$); $^{13}C\{^{1}H\}$: 111.14 (ring C), 79.76 (ring *C*H), 36.27 [$\mathit{C}(CH_{3})_{3}$], and 33.07 [$C(\mathit{C}H_{3})_{3}$]. (**2**) ^{1}H: 5.34 (3H, s, $Bu^{t}{}_{3}C_{6}\mathit{H}_{3}$) and 1.33 (27H, s, $\mathit{Bu}^{t}{}_{3}C_{6}H_{3}$); $^{13}C\{^{1}H\}$: 111.19 (ring C), 80.28 (ring *C*H), 35.16 [$\mathit{C}(CH_{3})_{3}$], and 32.79 [$C(\mathit{C}H_{3})_{3}$]. (**3**) ^{1}H: 5.15 (3H, s, $Bu^{t}{}_{3}C_{6}\mathit{H}_{3}$) and 1.34 (27H, s, $\mathit{Bu}^{t}{}_{3}C_{6}H_{3}$); $^{13}C\{^{1}H\}$: 107.49 (ring *C*), 76.80 (ring *C*H) 35.57 [$\mathit{C}(CH_{3})_{3}$], and 33.39 [$C(\mathit{C}H_{3})_{3}$]. (**4**) ^{1}H: 5.25 (3H, d, $Bu^{t}{}_{3}C_{6}\mathit{H}_{3}$, J_{CH} 0.98) and 1.47 (27H, s, $\mathit{Bu}^{t}{}_{3}C_{6}H_{3}$); $^{13}C\{^{1}H\}$: 239.91 (*C*D), 118.62 (ring *C*), 82.90 (ring *C*H), 35.46 [$\mathit{C}(CH_{3})_{3}$], and 31.89 [$C(\mathit{C}H_{3})_{3}$]. ^{13}C(gated decoupled}: 239.9 (m, *C*O, J_{CH} 0.98).

frequency (compared with the free ligand) for the ring protons and carbons characteristic of η-arene transition metal complexes.[6] Low temperature ^{13}C n.m.r. studies gave no evidence for agostic interactions.

The deep green colour of the zirconium complex appears somewhat anomalous when compared with that of the titanium and hafnium analogues, but may be due to a slight structural change affecting the energy of the metal-to-ligand charge transfer band. A striking example of another Ti, Zr, Hf discontinuity has previously been observed in the *X*-ray structures of the tetracyclopentadienylmetal(IV) complexes: $[M(\eta\text{-}C_5H_5)_2(\sigma\text{-}C_5H_5)_2]$ for M = Ti or Hf, but $[M(\eta\text{-}C_5H_5)_3(\sigma\text{-}C_5H_5)]$ for M = Zr;[7] the M–C(σ) bond lengths (Å) decrease in the order Zr [2.447(6)] > Hf [2.38(2)] > Ti [2.332(2)].[8] We await *X*-ray data on complexes (**1**)—(**3**).§

A pentane solution of the hafnium complex (**3**) reacted irreversibly with carbon monoxide (1 atm), resulting in an immediate colour change from purple to green. From this solution were isolated green crystals of the 18-electron carbonyl adduct, $[Hf(\eta\text{-}Bu^t{}_3C_6H_3)_2(CO)]$ (**4**).† The carbonyl ligand in (**4**) is characterised by a strong i.r. stretch at 1870 cm^{-1} (Nujol mull) and, in a sample prepared using 90% ^{13}CO, a ^{13}C n.m.r. resonance‡ at δ 239.91 which is a partially resolved septet in the gated decoupled spectrum owing to coupling with the ring protons of the two $\eta\text{-}Bu^t{}_3C_6H_3$ ligands.

Complex (**4**) is the first carbonyl of a heavy group IV metal in oxidation state zero, although $[Ti(CO)_6]$ has been identified in a matrix at 10—15 K,[9] and the phosphine-stabilised complexes $[Ti(CO)_{3-n}(PF_3)_n(Me_2PCH_2CH_2PMe_2)_2]$ (n = 0 or 1) have been structurally characterised.[10]

The ability of the tri-t-butylbenzene ligand to stabilise the 16-electron zirconium and hafnium complexes is presumably a reflection of its steric bulk, but may also be due to the increase in metal–arene bond strength arising from the electron donating t-butyl substituents on the arene rings.[6] We suggest that this ligand may have considerable potential in preparing novel η-arene complexes of other elements.

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§ *Note added in proof: X*-ray crystallography confirms the structure of (**1**).

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