

Electron-deficient Group IV Metal Alkyl Cations, and the Synthesis of $\text{Zr}(\text{CH}_2\text{Ph})_3(\eta^6\text{-C}_6\text{H}_5)\text{BPh}_3$: a Fluxional Arene π -Complex of a d^0 Metal

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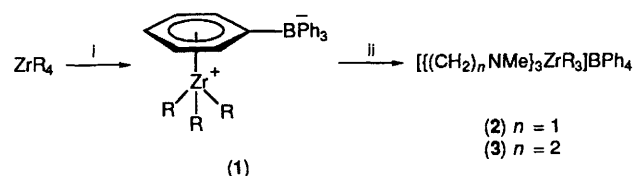
Mild protolysis of titanium and zirconium alkyls provides a general route to solvent or anion stabilised 6- and 10-electron cationic group IV alkyl complexes, including the first halide-free arene complex of a d^0 metal.

Cationic alkyl complexes of tetravalent d^0 metals represent a new class of organometallic Lewis acids where co-ordinative unsaturation is combined with the inability to stabilise π -ligands through back-donation. The only compounds of this kind known so far are the 14- and 16-electron bis(cyclopentadienyl) complexes $[\text{Cp}_2\text{MR}(\text{L})]^+$;^{1,2} complexes of this type have now been recognised as the catalytically active species in the homogeneous polymerisation of alkenes.² In an attempt to explore the stability and structures of more highly electron-deficient systems we have extended our studies to mono-Cp and Cp-free alkyl complexes and report here the synthesis of some solvated and solvent-free cationic alkyls of titanium and zirconium.

Treatment of a toluene solution of $\text{Zr}(\text{CH}_2\text{Ph})_4$ with dimethylanilinium tetraphenylborate at room temperature results in protolysis and the precipitation of $[\text{Zr}(\text{CH}_2\text{Ph})_3][\text{BPh}_4]$ (1). The orange microcrystalline compound can also be prepared in dichloromethane at 0 °C; it is

thermally stable as a solid and may be stored at room temperature but slowly decomposes in solution.

Variable-temperature high-field NMR reveals that the 6-electron cation $[\text{Zr}(\text{CH}_2\text{Ph})_3]^+$ is stabilised by η^6 -co-ordination to a phenyl ring of the anion, to give a zwitterionic



Scheme 1. Reagents and conditions: i, $[\text{PhNMe}_2\text{H}]\text{BPh}_4$ (1 equiv.), toluene, room temp., 1.5 h; ii, trimethylhexahydrotriazine ($n = 1$) or trimethyltriazacyclononane ($n = 2$), 1 equiv., CH_2Cl_2 , 0 °C.

structure.† The complex is non-fluxional at -40°C , with a clearly resolved doublet–triplet–triplet pattern for the *ortho*-, *meta*-, and *para*-hydrogens, respectively, for the co-ordinated phenyl ring, while the remaining boron phenyl groups give rise to a sharp singlet. The zirconium-bound benzyl ligands exhibit a pattern similar to that of tetrabenzylzirconium, with the *ortho*-hydrogens high-field shifted and well separated from the *meta*- and *para*-hydrogens. At higher temperatures the signals due to the η^6 -phenyl ring broaden and reach coalescence at *ca.* 25°C , whereas the other phenyl and benzyl signals show little change and do not participate in exchange processes. We assume that at higher temperatures the Zr-phenyl interaction is weakened, possibly involving a change from η^6 to η^2 co-ordination of the phenyl ring which would allow the $[\text{Zr}(\text{CH}_2\text{Ph})_3]^+$ cation to fluctuate between different ring sites. Site exchange of all four phenyl groups of the BPh_4^- anion would be expected to take place at higher temperature but was not observed because of instability of (1) in dichloromethane under such conditions.

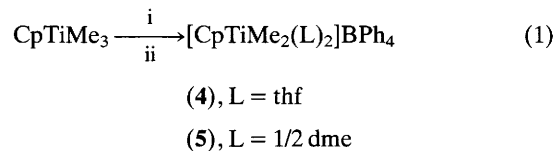
Few arene complexes are known for metals of the titanium triad, particularly in the higher oxidation states, and examples usually include Lewis-acidic halides, as in the recently isolated $[(\text{C}_6\text{Me}_6)\text{TiCl}_3][\text{Ti}_2\text{Cl}_3]_3^+$ and the cationic complexes of di- and tri-valent titanium and zirconium, *e.g.* $[\text{C}_6\text{Me}_6\text{TiCl}_2][\text{AlCl}_4]^-$ and $[\text{M}_3(\mu\text{-Cl})_6(\text{C}_6\text{Me}_6)_3]^{n+}$ ($\text{M} = \text{Ti}, \text{Zr}, n = 1, 2$);⁵ a number of bis(arene) complexes of the zerovalent metals also exist.⁶

The η^6 -co-ordination of BPh_4^- in (1) has precedent in several complexes of electron-rich metals, *e.g.* ruthenium(II)⁷ and rhodium(I);⁸ as far as is known, none of these complexes shows the fluxional behaviour of (1). The formation of the π -complex (1) is in interesting contrast to the analogous reaction of $[\text{Bu}_3\text{NH}]\text{BPh}_4$ with $(\text{C}_5\text{Me}_5)_2\text{ZrMe}_2$ which results in the metallation of BPh_4^- in *meta*-position to give the zwitterionic aryl compound $(\text{C}_5\text{Me}_5)_2\text{Zr}-\text{C}_6\text{H}_4\text{BPh}_3$.^{2d}

Electrostatic interactions contribute to the stability of (1), and the co-ordinated tetraphenylborate cannot be displaced by neutral arenes, such as toluene, hexamethylbenzene, or 1,3,5-tri-*t*-butylbenzene. However, (1) reacts readily with *O*- and *N*-donor ligands. For example, the addition of tetrahydrofuran (thf) to dichloromethane solutions of the complex leads to the formation of free BPh_4^- , indicated in the ^{13}C NMR spectrum by the replacement of the two B–C signals at δ 178.5 and 157.8 by one quartet at δ 164.7. While well-defined thf complexes cannot be isolated, the addition of cyclic amines such as 1,3,5-trimethylhexahydro-1,3,5-triazine and 1,4,7-trimethyl-1,4,7-triazacyclononane gives the corresponding

complexes (2) and (3) as yellow microcrystalline solids. No reaction takes place between dimethylanilinium tetraphenylborate and sterically more hindered complexes, such as $\text{Zr}(\text{CH}_2\text{Me}_2\text{Ph})_4$ or $\text{Zr}(\text{CH}_2\text{Ph})_2(\text{OC}_6\text{H}_3\text{Bu}^t_2)_2$.

The reaction of $\text{Ti}(\text{CH}_2\text{Ph})_4$ with dimethylanilinium tetraphenylborate in analogy to the formation of (1) fails to give isolable products. However, the monocyclopentadienyl complex CpTiMe_3 reacts readily at low temperature in thf or dimethoxyethane (dme) to give the 14-electron complexes $[\text{CpTiMe}_2(\text{thf})_2]\text{BPh}_4$ (4) and $[\text{CpTiMe}_2(\text{dme})]\text{BPh}_4$ (5), respectively, as sparingly soluble, thermally stable orange solids in high yields (equation 1). The co-ordination of two donor atoms in place of just one methyl ligand in the neutral starting material gives an indication of the increase in Lewis acidity of the metal centre on forming a cationic complex.



Reagents and conditions: i, $[\text{PhNMe}_2\text{H}]\text{BPh}_4$, 1 equiv.; ii, thf or dme solvent, -50°C to room temp.

Efforts to generate and characterise cationic alkyl complexes free of stabilising solvent ligands are continuing.

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† Selected spectroscopic data: (1): ^1H NMR (400 MHz, CD_2Cl_2 , rel. SiMe_4 , -40°C): Zr–benzyl: 1.56 (s, 6 H, Zr– CH_2), 6.29 (m, 6 H, *ortho*-H), 7.22 (overlapping with BPh_3 , *meta*-H), 7.10 (m, 3 H, *para*-H); $\eta^6\text{-C}_6\text{H}_5\text{-B}$: 8.25 (d, 2 H, *ortho*-H, 3J 7.3 Hz), 6.59 (t, 2 H, *meta*-H, 3J 7.3 Hz), 6.22 (t, 1 H, *para*-H, 3J 7.3 Hz); $-\text{BPh}_3$: 7.22 (m, overlapping with 6 benzyl-Hs, 21 H). ^{13}C NMR (100.5 MHz, CD_2Cl_2 , rel. SiMe_4 , -40°C): Zr–benzyl: 73.69 (Zr– CH_2 , J_{CH} 134 Hz), 137.5 (*ipso*-C), 130.1 (*ortho*-C), 129.8 (*meta*-C), 123.89 (*para*-C); $\eta^6\text{-C}_6\text{H}_5\text{-B}$: 178.5 (B–C), 127.27 (*ortho*-C), 136.3 (*meta*-C), 138.8 (*para*-C); $-\text{B}(\text{C}_6\text{H}_5)_3$: 157.8 (B–C), 135.8 (*ortho*-C), 126.65 (*meta*-C), 126.39 (*para*-C). (2): ^1H NMR (90 MHz, $\text{C}_5\text{D}_5\text{N}$): 2.11 (s, 9 H, N–Me), 2.71 (s, 12 H, N– CH_2CH_2), 2.71 (s, 6 H, Zr CH_2), 6.6–7.5 (m, 35 H, phenyl). (3): ^1H NMR (60 MHz, CD_2Cl_2): 2.33 (s, 9 H, N–Me), 2.43 (s, 12 H, N– CH_2CH_2), 2.71 (s, 6 H, Zr CH_2), 6.6–7.5 (m, 35 H, phenyl). (4): ^1H NMR (60 MHz, $\text{C}_5\text{D}_5\text{N}$): 1.48 (s, 6 H, Ti–Me), 1.61 (m, 8 H, thf), 3.66 (m, 8 H, thf), 6.89 (s, 5 H, Cp), 7.2, 8.0 (m, br, phenyl); ^{13}C NMR (22.5 MHz, $\text{C}_5\text{D}_5\text{N}$): 79.97 (Ti–Me), 25.58, 67.63 (thf), 120.12 (Cp), 125.97, 122.21, 136.94, 164.74 (BPh_4^-). (5): ^1H NMR (90 MHz, CD_2Cl_2 , -40°C): 1.08 (s, 6 H, Ti–Me), 3.1 (s, 6 H, OMe), 3.3 (s, 4 H, OCH_2), 6.5 (s, 5 H, Cp), 6.7–7.8 (m, br, 20 H); ^{13}C NMR (22.5 MHz, $\text{C}_5\text{D}_5\text{N}$): 80.1 (Ti–Me), 58.3, 71.8 (dme), 120.1 (Cp), 122.2, 126.0, 137.0, 164.7 (BPh_4^-).