Electron-deficient Group IV Metal Alkyl Cations, and the Synthesis of Zr(CH₂Ph)₃(η⁶-C₆H₅)BPh₃: a Fluxional Arene π-Complex of a d⁰ 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 d⁰ metal.

Cationic alkyl complexes of tetravalent d⁰ 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 [Cp₂MR(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 Zr(CH₂Ph)₄ with dimethylanilinium tetraphenylborate at room temperature results in protolysis and the precipitation of [Zr(CH₂Ph)₃][BPh₄] (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 [Zr(CH₂Ph)₃]⁺ is stabilised by η⁶-co-ordination to a phenyl ring of the anion, to give a zwitterionic

$$ZrR_4 \xrightarrow{i} (1) \xrightarrow{ii} [\{(CH_2)_nNMe\}_3ZrR_3]BPh_4$$

(2) n = 1
(3) n = 2
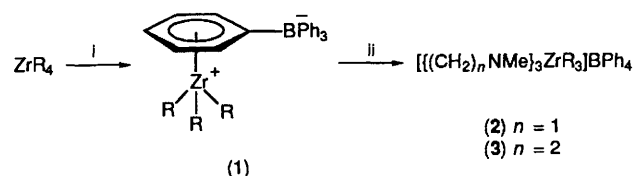
Scheme 1. *Reagents and conditions:* i, [PhNMe₂H]BPh₄ (1 equiv.), toluene, room temp., 1.5 h; ii, trimethylhexahydrotriazine (*n* = 1) or trimethyltriazacyclononane (*n* = 2), 1 equiv., CH₂Cl₂, 0 °C.

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 η⁶-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 [Zr(CH₂Ph)₃]⁺ cation to fluctuate between different ring sites. Site exchange of all four phenyl groups of the BPh₄⁻ 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 [(C₆Me₆)TiCl₃][Ti₂Cl₉]³ and the cationic complexes of di- and tri-valent titanium and zirconium, e.g. [C₆Me₆TiCl₂][AlCl₄]⁴ and [M₃(μ-Cl)₆(C₆Me₆)₃]ⁿ⁺ (M = Ti, Zr, n = 1, 2);⁵ a number of bis(arene) complexes of the zerovalent metals also exist.⁶

The η⁶-co-ordination of BPh₄⁻ 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 [Bu₃NH]BPh₄ with (C₅Me₅)₂ZrMe₂ which results in the metallation of BPh₄⁻ in meta-position to give the zwitterionic aryl compound (C₅Me₅)₂Zr–C₆H₄BPh₃.²ᵈ

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 BPh₄⁻, indicated in the ¹³C 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 Zr(CH₂Me₂Ph)₄ or Zr(CH₂Ph)₂(OC₆H₃Buᵗ₂-2,6)₂.

The reaction of Ti(CH₂Ph)₄ with dimethylanilinium tetraphenylborate in analogy to the formation of (1) fails to give isolable products. However, the monocyclopentadienyl complex CpTiMe₃ reacts readily at low temperature in thf or dimethoxyethane (dme) to give the 14-electron complexes [CpTiMe₂(thf)₂]BPh₄ (4) and [CpTiMe₂(dme)]BPh₄ (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.

$$CpTiMe_3 \xrightarrow[\text{ii}]{\text{i}} [CpTiMe_2(L)_2]BPh_4 \quad\quad (1)$$

$$(4), L = thf$$

$$(5), L = 1/2 \, dme$$
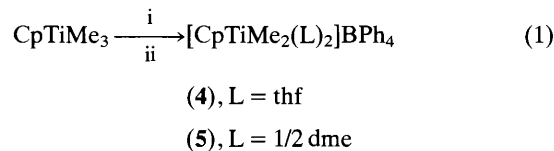
Reagents and conditions: i, [PhNMe₂H]BPh₄, 1 equiv.; ii, thf or dme solvent, −50 °C to room temp.

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, CD₂Cl₂, rel. SiMe₄, −40 °C): Zr–benzyl: 1.56 (s, 6 H, Zr–CH₂), 6.29 (m, 6 H, ortho-H), 7.22 (overlapping with BPh₃, meta-H), 7.10 (m, 3 H, para-H); η⁶-C₆H₅–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); −BPh₃: 7.22 (m, overlapping with 6 benzyl-Hs, 21 H). ¹³C NMR (100.5 MHz, CD₂Cl₂, rel. SiMe₄, −40 °C): Zr–benzyl: 73.69 (Zr–CH₂, J_CH 134 Hz), 137.5 (ipso-C), 130.1 (ortho-C), 129.8 (meta-C), 123.89 (para-C); η⁶-C₆H₅–B: 178.5 (B–C), 127.27 (ortho-C), 136.3 (meta-C), 138.8 (para-C); −B(C₆H₅)₃: 157.8 (B–C), 135.8 (ortho-C), 126.65 (meta-C), 126.39 (para-C). (2): ¹H NMR (90 MHz, C₅D₅N): 2.11 (s, 9 H, N–Me), 2.71 (s, 12 H, N–CH₂CH₂), 2.71 (s, 6 H, ZrCH₂), 6.6—7.5 (m, 35 H, phenyl). (3): ¹H NMR (60 MHz, CD₂Cl₂): 2.33 (s, 9 H, N–Me), 2.43 (s, 12 H, N–CH₂CH₂), 2.71 (s, 6 H, ZrCH₂), 6.6—7.5 (m, 35 H, phenyl). (4): ¹H NMR (60 MHz, C₅D₅N): 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); ¹³C NMR (22.5 MHz, C₅D₅N): 79.97 (Ti–Me), 25.58, 67.63 (thf), 120.12 (Cp), 125.97, 122.21, 136.94, 164.74 (BPh₄⁻). (5): ¹H NMR (90 MHz, CD₂Cl₂, −40 °C): 1.08 (s, 6 H, Ti–Me), 3.1 (s, 6 H, OMe), 3.3 (s, 4 H, OCH₂), 6.5 (s, 5 H, Cp), 6.7—7.8 (m, br, 20 H); ¹³C NMR (22.5 MHz, C₅D₅N): 80.1 (Ti–Me), 58.3, 71.8 (dme), 120.1 (Cp), 122.2, 126.0, 137.0, 164.7 (BPh₄⁻).