Methanolysis of tetraphenylborate (BPh_4^-) as a reaction unit in halotris(2,4-pentadianato) complexes of Zr(IV) and Hf(IV)†

Sibusiso N. Mlondo, Paul O'Brien,* P. John Thomas, Madeleine Helliwell, James Raftery and David J. Procter

Received (in Cambridge, UK) 16th January 2008, Accepted 4th March 2008
First published as an Advance Article on the web 31st March 2008
DOI: 10.1039/b800791h

The complexes $\{(C_5H_8O_2)_2Zr[(OCH_3)_2B(C_6H_5)_2]_2\cdot\frac{1}{2}C_{12}H_{10}\}$ (M = Zr (1) or Hf (2)) have been obtained from the reaction of $[M(acac)_3Cl]$ with sodium tetraphenylborate (BPh_4^-) in methanol. Crystal structures show 8-coordinate complexes with two 2,4-pentanedionato groups and two dimethoxydiphenylborate groups each coordinated through methoxy groups to the metal centre.

The tetraphenylborate anion (BPh_4^-) is often used as a weakly coordinating anion in coordination chemistry.[1,2] In some cases the phenyl rings of the BPh_4^- anion have been reported to interact with the metal centre, as in the case of group-f elements. The anion is often used to stabilise unsolvated cationic complexes that would normally not be isolable.[1–3] The tetraphenylborate anion has thus been widely used and is frequently regarded as a readily available and chemically inert anion, particularly in rare earth chemistry.[4]

However, there are a small number of examples of the tetraphenylborate anion reacting on the formation of complexes. Robson *et al.* reported the complete methanolysis of tetraphenylborate anion, over a period of several weeks.[5] The reaction of a cadmium complex tricyanomethamide led to an unexpected polymeric complex $[Cd(C(CN)_3)(B(OCH_3)_4)]$ as a methanol solvate. Ward *et al.* reported the reaction in which two phenyl units of BPh_4^- were substituted with the phenolate groups where 6-(2-hydroxyphenyl)-2,2′-pyridine (L) zinc acetate was reacted in methanol to form $[Zn(L)_2(BPh_2)][BPh_4]$.[6] In an earlier example of such reactivity, complete methanolysis of cyanotrihydroborate in the reaction with lanthanide nitrate, 2,6-diformyl-*p*-cresol and 3,6-dioxa-1,8-octanediamine to form $[Ln(B(OCH_3)_4)(NO_3)_2(CH_3OH)_2$ was reported by Kahwa *et al.*[7] In this communication we report the rapid methanolysis of the tetraphenylborate anion on the reaction with chlorotris(2,4-pentanedionato) complexes of Zr(IV) or Hf(IV) {[Zr(acac)$_3$Cl] and [Hf(acac)$_3$Cl]} to form **1** or **2**.

We have been interested in the use of coordination complexes to develop new routes to semiconductor thin films at the aqueous/organic interface.[8] This work has led to attempts to synthesise tetraphenylborate salts of the trisacetylacetanato complexes of Hf and Zr, as precursors. The sodium tetraphenylborate salt was reacted in a 1 : 1 ratio with [Zr(acac)$_3$Cl] or [Hf(acac)$_3$Cl] complexes in an attempt to replace the chloride ion.‡ This reaction resulted in the methanolysis of BPh_4^-, forming the complexes **1** or **2**. Both complexes **1** and **2** were stable. The structure for **1** is shown in Fig. 1 and the crystal data for both **1** and **2** is given in the caption.†§ The hafnium complex **2** (selected geometric parameters in Fig. 1 caption) is isomorphous with the zirconium analogue **1**. It is interesting to observe that the crystal structures not only give information about the formed complexes, but also the nature of a by-product; both structures have biphenyl in their crystal lattice. Biphenyl, the apparent by-product of the methanolysis of the tetraphenylborate, does not participate in coordination to the metal centre.

The isomorphous complexes crystallize in the monoclinic *C*2/*c* space group and pack as layers, bound by (200) planes, along *a*. The 8-coordinate metal centres, which are bonded to four unsaturated oxygen atoms of two acetylacetonate groups and two dimethoxydiphenylborate groups, each coordinated through two *cis* –OCH$_3$ groups to the $M(acac)_2^{2+}$ fragment (M = Hf, Zr), form dodecahedrons. Dephenylation of the BPh_4^- was unexpected. The BPh_4^- anion was expected to act as a non coordinating counter ion as previously reported.[9] The metal–oxygen bond lengths with the 2,4-pentanedionate groups are shorter than those of the dimethoxydiphenyl group.

The distance for M–O interaction with the 2,4-pentanedionate ligands are an average of 2.14 Å in both complexes **1** and **2**. This distance is relatively shorter compared to the mean bond length for zirconium(IV) tetrakisacetylacetonate complex,[10] which is *ca.* 2.20 Å, but slightly longer than that of chlorotris(acetylacetanato) zirconium(IV),[11] which is *ca.* 2.13 Å. This effect could be due to weak ligation of the $BPh_2(–OCH_3)_2$ through –OCH$_3$. The average M–O distance for the metal centre with the –OCH$_3$ groups are 2.21 Å and 2.20 Å for the complex **1** and **2**, respectively. The B–O bonds for the zirconium complex (**1**) are 1.503(8) Å, B(1)–O(5); 1.522(7) Å, B(1)–O(6); 1.511(8) Å, B(2)–O(7) and 1.542(8) Å, B(2)–O(8). These B(1)–O bond lengths are on average (1.51 Å) slightly shorter than those of structurally characterised $(BPh_2)^+$ bridged through phenolate[6] and oximate[12] oxygen atoms, which are 1.54 Å. The same observation was made for the hafnium complex (**2**). The M–O bond lengths to the –OCH$_3$ groups are longer than the B–O bonds. The B–O distances are longer than those in the bridged $[B(OCH_3)_4]^-$ anion (1.461 Å).[7]

Although BPh_4^- can be considered to be a stable counterion in many reactions, the B–C bonds in BPh_4^- can also be cleaved to liberate benzene under strongly acidic[13] and/or forcing conditions of temperature.[14] These reactions can result in the formation of diphenyl- and triphenylborates.

School of Chemistry, University of Manchester, Oxford Road, Manchester, UK M13 9PL. E-mail: paul.obrien@manchester.ac.uk

† CCDC 674752 & 677357. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b800791h

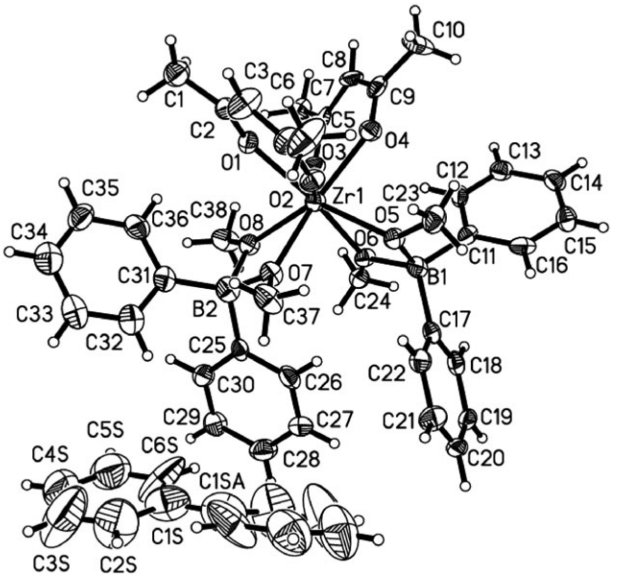
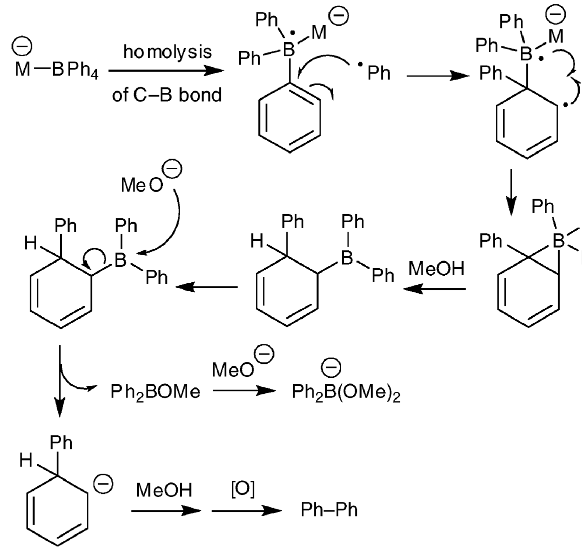


Fig. 1 The crystal structure for **1**. The thermal ellipsoids are contoured at 50% probability. The phenyl groups of the biphenyl are related by a crystallographic two fold. Selected geometric parameters for **1** (Å): Zr(1)–O(1) 2.138(4), Zr(1)–O(2) 2.160(4), Zr(1)–O(3) 2.129(4), Zr(1)–O(4) 2.147(4), Zr(1)–O(5) 2.228(4), Zr(1)–O(6) 2.183(4), Zr(1)–O(7) 2.195(4), Zr(1)–O(8) 2.223(4), O(5)–B(1) 1.503(8), O(6)–B(1) 1.522(7), O(7)–B(2) 1.511(8), O(8)–B(2) 1.542(8), B(1)–C(11) 1.628(9), B(1)–C(17) 1.629(9), B(2)–C(31) 1.588(10), B(2)–C(25) 1.629(9). Selected geometric parameters for **2**: Hf(1)–O(1) 2.129(3), Hf(1)–O(2) 2.147(3), Hf(1)–O(3) 2.132(3), Hf(1)–O(4) 2.131(3), Hf(1)–O(5) 2.215(3), Hf(1)–O(6) 2.175(3), Hf(1)–O(7) 2.179(3), Hf(1)–O(8) 2.216(3), O(5)–B(1) 1.514(6), O(6)–B(1) 1.535(5), O(7)–B(2) 1.527(5), O(8)–B(2) 1.520(6).†

There are several possible mechanisms for the observed methanolysis of tetraphenylborate and the formation of biphenyl. Whilst phenyl cleavage due to protic acids[15] can be discounted in this case, phenyl group transfer from BPh_4^- to metal centres is well known[2] and could initiate the formation of dimethoxydiphenylborate. Alternatively, the radical decomposition of tetraphenylborate to give biphenyl, after oxidation, and borate derivatives perhaps provides the most likely mechanistic pathway in this case.[16] A possible mechanism is outlined in Scheme 1. We propose that coordination of tetraphenylborate to the metal promotes the decomposition as biphenyl is not formed in the absence of the metals.[17]



Scheme 1 Possible mechanistic pathway for the radical decomposition of tetraphenylborate to form biphenyl and dimethoxydiphenylborate (see ref. 16) (M = Zr or Hf).

In conclusion, we have isolated and characterised complexes of Zr and Hf, in which the metal centres are bonded to dimethoxydiphenylborate through the two methoxy groups. The complexes result from *in situ* decomposition of tetraphenylborate. The crystals also contain the by-product of decomposition, biphenyl, within the lattice. The process is straight forward and the novel complexes are obtained in good yield.

We acknowledge RCUK for funding. SNM acknowledges CSIR and NRF (South Africa) for a scholarship.

Notes and references

‡ *Synthesis of* $M(acac)_3Cl$ (M = Hf, Zr): $M(acac)_3Cl$ complexes were prepared as reported previously.[18] Elemental Analysis for $Zr(acac)_3Cl$ Calc: C, 42.2; H, 5.7. Found: C, 41.8; H, 5.4. Elemental Analysis for $Hf(acac)_3Cl$ Calc: C, 35.0; H, 4.1. Found: C, 34.1; H, 3.8.

Synthesis of $\{(C_5H_8O_2)_2Zr[(OCH_3)_2B(C_6H_5)_2]_2\cdot\frac{1}{2}C_{12}H_{10}\}$: $Zr(acac)_3Cl$ (2.00 g) and $NaB(C_6H_5)_4$ (1.61 g) were each dissolved in 100 ml of methanol. $Zr(acac)_3Cl$ solution was added to $NaB(C_6H_5)_4$ in a 250 ml round bottom flask and refluxed for 6 h. After 6 h, the pale yellow solution was evaporated to 100 ml in a rotor evaporator and left for 24 h to form colourless crystals. The crystals were dried *in vacuo* at room temperature and analyzed. Yield: 48.13%. ^1H NMR δ_H (ppm) (300 MHz; CD_3OD) 2.24 (12H, s, Me of acac × 4), 3.38 (12H, s, MeO ×4), 5.95 (2H, s, CH of acac × 2), 7.05–7.70 (30H, m, ArCH of 2 × PhB and biphenyl). IR (Nujol, cm^{-1}): νC–H (Ar + Nujol, str), 2894; νC=C (Ar, str), 1556; νCH_3, 1365–1454; νC–H, 720–1032; νHf–O, 246–370; νHf–O (str), 430 cm^{-1}. Elemental Analysis: Calc. C, 64.4; H, 2.3; Zr, 11.1. Found. C, 64.2; H, 2.1; Zr, 11.1.

Synthesis of $\{(C_5H_8O_2)_2Hf[(OCH_3)_2B(C_6H_5)_2]_2\cdot\frac{1}{2}C_{12}H_{10}\}$: $Hf(acac)_3Cl$ (2.00 g) and $NaB(C_6H_5)_4$ (1.34 g) were each dissolved in 100 ml of methanol. $Hf(acac)_3Cl$ solution was added to $NaB(C_6H_5)_4$ in a 250 ml round bottom flask and refluxed for 10 h. After 10 h, the pale yellow solution was evaporated to 100 ml in a rotor evaporator and left for 24 h to form clear colorless crystals which were then dried *in vacuo* at room temperature and analyzed. Yield: 41.06%. ^1H NMR δ_H (ppm) (300 MHz; CD_3OD) 1.95–2.05 (12H, broad s, Me of acac × 4), 3.38 (12H, s, MeO × 4), 5.85 (2H, s, CH of acac × 2), 7.05–7.70 (30H, m, ArCH of 2 × PhB and biphenyl). IR (Nujol, cm^{-1}): νC–H (Ar + Nujol, str), 2900; νC=C (Ar, str), 1571; νCH_3, 1372–1453; νC–H, 718–1157; νHf–O, 274–381; νHf–O (str), 444 cm^{-1}. Elemental Analysis: Calc. C, 58.2; H, 5.7; Hf, 19.7. Found. C, 57.7; H, 5.5; Hf, 21.6.

§ *Crystal data for* $\{(C_5H_8O_2)_2Zr[(OCH_3)_2B(C_6H_5)_2]_2\cdot\frac{1}{2}C_{12}H_{10}\}$: $C_{44}H_{51}B_2O_8Zr$, $M = 820.69$, monoclinic, space group $C2/c$, $a = 35.793(5)$ Å, $b = 12.420(5)$ Å, $c = 20.562(5)$ Å, $\beta = 115.439(5)°$, $V = 8255$ Å^3, $T = 100$ (2) K, $\lambda = 0.71069$ Å, $Z = 8$, $D_c = 1.321$ g cm^{-3}, $\mu(MoK\alpha) = 0.318$ mm^{-1}, $F(000) = 3432$. 24979 reflections measured, 5921 unique data ($2\theta_{max} = 23.25$, $R_{int} = 0.1178$). $R = 0.0609$ for 3352 reflections with $I > 2\sigma(I)$, w$R2 = 0.112$ (all data).

Crystal data for $\{(C_5H_8O_2)_2Hf[(OCH_3)_2B(C_6H_5)_2]_2\cdot\frac{1}{2}C_{12}H_{10}\}$: $C_{44}H_{51}B_2O_8Hf$, M = 907.96, monoclinic, space group $C2/c$, $a = 35.841(3)$ Å, $b = 12.4200(9)$ Å, $c = 20.5810(9)$ Å, $\beta = 115.637(2)°$, $V = 8259.6(10)$ Å, $T = 100$ (2) K, $\lambda = 0.71073$ Å, $Z = 8$, $D_c = 1.460$ g cm^{-3}, $\mu(MoK\alpha) = 2.577$ mm^{-1}, $F(000) = 3688$. 34953 reflections measured, 9822 unique data ($2\theta_{max} = 28.32$, $R_{int} = 0.0641$). $R = 0.034$ for 6845 reflections with $I > 2\sigma(I)$, w$R2 = 0.088$ (all data).

1 G. B. Deacon, D. J. Evans, C. M. Forsyth and P. C. Junk, *Coord. Chem. Rev.*, 2007, **251**, 1699.
2 S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927.
3 G. B. Deacon and C. M. Forsyth, *Chem. Commun.*, 2002, **21**, 2252; G. B. Deacon, C. M. Forsyth and P. C. Junk, *Eur. J. Inorg. Chem.*,

2005, 817; W. J. Evans, C. A. Seibel and W. J. Ziller, *J. Am. Chem. Soc.*, 1998, **120**, 6745; W. J. Evans, S. A. Kozimor and J. W. Ziller, *Chem. Commun.*, 2005, **37**, 4681; G. A. Molander and R. M. Rzasa, *J. Org. Chem.*, 2000, **65**, 1215; W. J. Evans, D. S. Lee, M. A. Johnson and J. W. Ziller, *Organometallics*, 2005, **24**, 6393; W. J. Evans, J. M. Perotti and J. W. Ziller, *J. Am. Chem. Soc.*, 2005, **127**, 1068; W. J. Evans, J. M. Perotti and J. W. Ziller, *J. Am. Chem. Soc.*, 2005, **127**, 3894; D. A. Long, A. J. Blake, N. R. Champness, C. Wilson and M. Schroeder, *J. Am. Chem. Soc.*, 2001, **123**, 3401; C. J. Schaverien, *Organometallics*, 1992, **11**, 3476; W. J. Evans, M. A. Johnson and J. W. Ziller, *Inorg. Chem.*, 2000, **39**, 3421; W. J. Evans, T. M. Champagne and J. W. Ziller, *Organometallics*, 2007, **26**, 1204.

4 P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, *Chem. Rev.*, 2006, **106**, 2404; P. M. Zeimentz and J. Okuda, *Organometallics*, 2007, **26**, 6388.

5 S. R. Batten, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 636.

6 D. A. Bardwell, J. C. Jeffery and M. D. Ward, *Inorg. Chim. Acta*, 1996, **241**, 125.

7 K. D. Matthews, I. A. Kahwa, M. P. Johnson, J. T. Mague and G. L. McPherson, *Inorg. Chem.*, 1993, **32**, 1442.

8 D. Fan, M. Afzaal, M. A. Mallik, C. Q. Nguyen, P. O'Brien and P. J. Thomas, *Coord. Chem. Rev.*, 2007, **251**, 1878.

9 A. D. Horton and J. H. G. Frijns, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1152; A. J. Blake and V. Lippolis, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **61**, m207; G. R. Lewis and C. Wilson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **57**, 1159; Y. Fuma and M. Ebihara, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, **62**, m2808.

10 J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, 1963, **2**, 243.

11 R. B. VonDreele, J. Stezowski and R. C. Fay, *J. Am. Chem. Soc.*, 1971, **93**, 2887.

12 M. Verhage, D. A. Hoogwater and H. van Bekkun, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 351.

13 H. Raber and W. Likussar, *Microchim. Acta*, 1972, **60**, 92.

14 B. R. Currell, W. Gerrard and M. Khodabocus, *J. Organomet. Chem.*, 1967, **8**, 411.

15 J. Yan, M. Zhu and Z. Zhou, *Eur. J. Org. Chem.*, 2006, 2060.

16 P. J. Grisdale, J. L. R. Williams, M. E. Glogowski and B. E. Babb, *J. Org. Chem.*, 1971, **36**, 544.

17 Biphenyl is also formed during control experiments in which tetraphenylborate is heated with $ZrCl_4$ and $HfCl_4$ in MeOH.

18 T. J. Pinnavia and R. C. Fay, *Inorg. Chem.*, 1968, **7**, 502.