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$[Cp_2ZrMe(12\text{-}\mu\text{-}Me\text{-}1\text{-}\mathit{closo}\text{-}CB_{11}HMe_{10})]$: a transition metal complex of a highly-methylated carborane anion

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Received (in Cambridge, UK) 28th April 2003, Accepted 12th June 2003
First published as an Advance Article on the web 27th June 2003

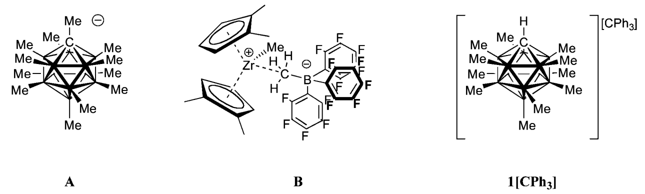
$[Cp_2ZrMe(12\text{-}\mu\text{-}Me\text{-}1\text{-}\mathit{closo}\text{-}CB_{11}HMe_{10})$, isolated by methide abstraction from Cp_2ZrMe_2 using $[CPh_3][\mathit{closo}\text{-}HCB_{11}Me_{11}]$ displays an intermolecular $Zr\cdots H_3C$ interaction in both the solid state and solution.

The permethylated icosahedral carborane monoanion, $[\mathit{closo}\text{-}CB_{11}Me_{12}]^-$, **A** (Scheme 1), first synthesised by Michl,[1] represents an important subclass of the "least coordinating anions",[2] which are best represented by the perfluoroarylborates[3] and halogenated carboranes such as $[\mathit{closo}\text{-}CB_{11}H_6Br_6]^-$.[4] $[\mathit{closo}\text{-}CB_{11}Me_{12}]^-$ is unique in that it presents an almost uniform methyl surface to an electrophile which means that, in addition to its potential use as an innocent lipophilic anion,[1b] given suitable conditions coordination with cationic metal fragments should give rise to single (or even multiple) intermolecular metal$\cdots H_3C$ interactions, which are of significant contemporary interest.[5] Given this, the coordination chemistry of **A** and its derivatives has been limited to two, *non-transition* metal, examples: $[{}^nBu_3Sn][\mathit{closo}\text{-}CB_{11}Me_{12}]$[6] and $[(PPh_3)Ag][\mathit{closo}\text{-}CB_{11}HMe_{11}]$.[7] In contrast, the coordination chemistry of borate anions such as $[MeB(C_6F_5)_3]^-$ with group 4 metallocenes (*e.g.* **B**)[3a,8,9] and more recently group 13[10] complexes has received considerable attention due to their ability to effectively partner cationic metal centres in single-site olefin polymerisation catalysis. A group 4 metallocene paired with an anion such as **A** would thus be of significant interest. We report here a preliminary account of such a complex, using the derivative anion $[\mathit{closo}\text{-}HCB_{11}Me_{11}]^-$, $[\mathbf{1}]^-$, in the synthesis of $[Cp_2ZrMe(12\text{-}\mu\text{-}Me\text{-}1\text{-}\mathit{closo}\text{-}CB_{11}HMe_{10})]$ (Cp = η^5–C_5H_5).

Addition of an equimolar quantity of $[CPh_3][\mathit{closo}\text{-}HCB_{11}Me_{11}]$, **1[CPh₃]**,[11] to Cp_2ZrMe_2 in fluorobenzene resulted in a colour change from orange/brown to pale yellow. Inspection of the resulting ^1H NMR spectrum (d_8-toluene) showed the clean formation of a single new product, identified by multinuclear NMR spectroscopy† and single crystal X-ray diffraction‡ to be $[Cp_2ZrMe(12\text{-}\mu\text{-}Me\text{-}1\text{-}\mathit{closo}\text{-}CB_{11}HMe_{10})]$, **2**. Fig. 1 shows the molecular structure determined in the solid state. Complex **2** crystallises with a single molecule of solvent (C_6H_5F) in the unit cell (not shown).

The solid-state structure of **2** reveals a closely associated ion-pair with a linking $Zr(\mu\text{–}CH_3)B$ motif. There are no other close intermolecular contacts in the lattice, unlike both $[{}^nBu_3Sn][\mathit{closo}\text{-}CB_{11}Me_{12}]$[6] and $[(PPh_3)Ag][\mathit{closo}\text{-}CB_{11}HMe_{11}]$[7] which also exhibit extended $M\cdots H_3C$ interactions, as does the related lithium tetramethylborate complex $Li[BMe_4]$.[12] Data collected were of sufficient quality to afford location and free refinement of hydrogen atoms associated with the bridging methyl group. The methylated anion is in relatively close contact with the metal centre through the unique antipodal vertex [C(12)–Zr(1) 2.516(2) Å], this distance being slightly shorter than those observed in analogous $[MeB(C_6F_5)_3]^-$ complexes.[8] Overall this gives the anion local C_{5v} symmetry in the solid state, as is also observed in solution at room temperature (*vide infra*). Calculations on related systems suggest that the bonding interaction between the $\{(C_6F_5)_3BCH_3\}^-$ and $\{Zr\}^+$ fragments is predominantly electrostatic in origin.[13] For **2**, the B(12)–C(12)–Zr(1) angle is almost linear [172.2(1)°] and the three Zr–H distances are not significantly different within experimental error. The arrangement of hydrogen atoms around C(12) is essentially tetrahedral with no significant C–H lengthening. Overall, this suggests that the interaction between the cage-methyl and the metal can also be described as predominantly ionic in **2**. That this is a relatively strong interaction is reflected by the associated longer Zr(1)–C(13) distance [2.261(2) Å] compared with equivalent $[MeB(C_6F_5)_3]^-$ complexes {for example 2.252(2) Å in $[(\eta^5\text{–}Me_2C_5H_3)_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$}.[8]

In solution (d_8-toluene) a single Cp peak is observed at δ 5.55 ppm in the ^1H NMR spectrum of **2** and the terminal [C(13)] Zr–*Me* at δ 0.29 ppm, both close to that observed for $[Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$,[8] while ^{11}B and ^1H NMR data demonstrate local C_{5v} symmetry for the cage anion. The $Zr\cdots H_3C$ interaction is maintained in solution, as shown by a change in chemical shift for the methyl groups that coordinate with the metal fragment relative to $[\mathbf{1}]^-$ when partnered with a non-coordinating cation.[14] ^1H-^{11}B HMQC and ^{11}B-^{11}B COSY NMR experiments were successfully used to unambiguously assign the methyl region in $[\mathbf{1}]^-$ and **2**, and follows the same order in both (low field to high field, Fig. 2): CH_3(2–6), CH_3(7–11) and CH_3(12). Compared with $[\mathbf{1}]^-$ in the same solvent (d^8-toluene),[14] CH_3(12) broadens (confirmed by comparison of the respective $^1H\{^{11}B\}$ NMR spectra) and shifts significantly upfield by −0.91 ppm to −0.59 ppm in **2**, CH_3(7–11) broadens slightly and shifts by −0.42 ppm, while CH_3(2–6) shows a smaller



Scheme 1

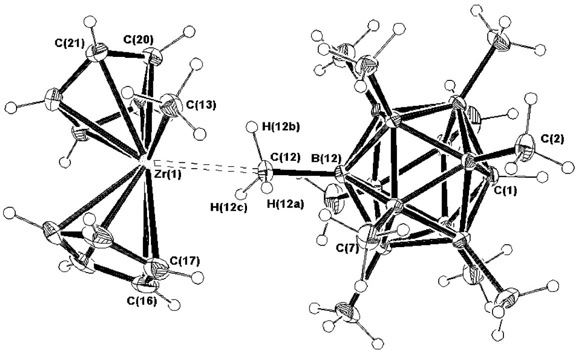


Fig. 1 Selected bond lengths (Å) and angles (°) for **2**: Zr(1)–C(13) 2.261(2), Zr(1)–C(12) 2.516(2), B(12)–C(12) 1.624(2), C(12)–H(12A) 0.84(2), C(12)–H(12B) 0.97(2) C(12)–H(12C) 0.99(2), Zr(1)–H(12A) 2.38(2), Zr(1)–H(12B) 2.34(2), Zr(1)–H(12C) 2.45(2); Zr(1)–B(12)–C(12) 172.2(1), C(12)–Zr(1)–C(13) 89.1(1), C(1)–B(12)–C(12) 177.34(9), B(12)–C(12)–H(12A) 103(1), B(12)–C(12)–H(12B) 109(1), B(12)–C(12)–H(12C) 113(2).

DOI: 10.1039/b304568d

(−0.23 ppm) upfield shift and does not broaden appreciably. These data suggest that the metal fragment interacts predominantly with both the $CH_3(7–11)$ and $CH_3(12)$ vertices at room temperature, fluxional between the unique and lower belt cage-methyls on the NMR timescale, consistent with the C_{5v} symmetry observed for the anion. Chemical shift changes of a similar magnitude have previously been observed on coordination of $\{Ag(PPh_3)\}^+$ to $[\mathbf{1}]^-$ (in CD_2Cl_2 solvent) but these are opposite in sign, moving *downfield*.[7] However, $[H_3CB(C_6F_5)_3]^-$ shows an *upfield* shift on interaction with $\{Cp_2ZrMe\}^+$ fragments,[15] consistent with that observed in this study for **2**. Progressive cooling (d_8-toluene) of **2** results in the signal due to $CH_3(12)$ becoming increasingly broader at first (273 K) and then sharper (223 K). At the same time, the $CH_3(12)$ peak shifts further upfield, being observed at δ −1.00 ppm at 223 K, while signals due to $CH_3(2–6)$ and $CH_3(7–11)$ become more like those observed for free $[\mathbf{1}]^-$ in both chemical shift and line-shape. The Cp resonance is now observed at δ 5.23 ppm. These observations suggest a structure at low temperature that is the same as observed in the solid state, *i.e.* $Zr\cdots H_3C(12)$. There is also evidence for another species in solution (*ca.* 10%) at 223 K, by an additional Cp resonance at δ 5.30 ppm and at least six broad, low intensity, $\{BCH_3\}$ resonances observed between δ 0.65 and −0.90 ppm, suggesting the C_{5v} symmetry seen for the 12-isomer is not present in this minor species. We assign these peaks to the isomer $[Cp_2ZrMe(7\text{-}\mu\text{-}Me\text{-}1\text{-}\mathit{closo}\text{-}CB_{11}HMe_{10})]$. Warming to room temperature restores the original spectrum, suggesting a dynamic equilibrium exists (Scheme 2) between 7- and 12-isomers. Interaction of the metal fragment with the lower surface of the cage is consistent with the charge distribution over the cage-*B*-methyl groups: $BCH_3(7–12)$ being negatively charged, while $BCH_3(2–6)$ are slightly positive.[6,7] All other spectroscopic and analytical data for **2** are in full accord with the formulation.

Dissolution of **2** in CD_2Cl_2 rapidly results in the formation of $Cp_2ZrMeCl$, while in MeCN the solvent adduct $[Cp_2ZrMe(NCMe)][\mathbf{1}]$ is formed (both by ^1H NMR spectroscopy). Heating a solution (d_8-toluene) of **2** to 60 °C resulted in decomposition after *ca.* 1 hour to afford as yet unidentified products, that showed cage degradation in both ^1H and ^{11}B NMR spectra.

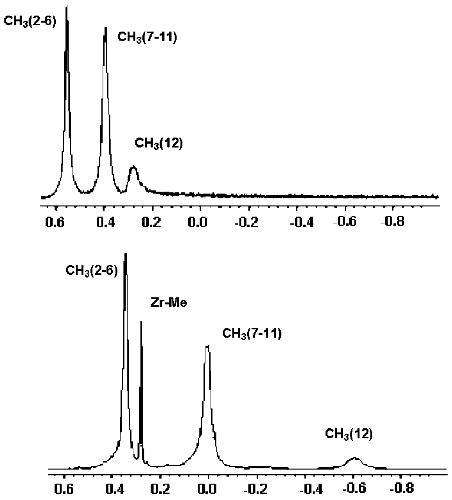
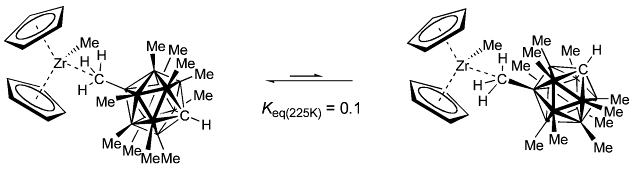


Fig. 2 Room temperature ^1H NMR spectra (δ/ppm, cage methyl region, d_8-toluene) of $[\mathbf{1}]^-$ (top)[14] and **2** (bottom).



Scheme 2

The synthesis of **2**, the first transition metal complex of a highly-methylated carborane and the relatively tight ion-pairing observed between cation and anion in both the solid state and solution, suggests that the chemistry of other, later, transition-metal coordination complexes of these anions should be accessible. We are currently actively pursing their synthesis and characterisation as well as further studies on the reactivity of **2**.

ASW thanks the Royal Society and MJI the EPSRC (GR/R36824) for financial support.

Notes and references

† *Experimental and spectroscopic data for* **2:** A Young's tube was charged with $[CPh_3][HCB_{11}Me_{11}]$ (0.041 g, 0.076 mmol) and Cp_2ZrMe_2 (0.019 g, 0.076 mmol). Fluorobenzene (5 cm^3) was cooled to 243 K and added by cannula to the solids, to give a yellow solution. The sample was then layered with *n*-pentane and stored at 243 K to yield large yellow crystals of $[Cp_2ZrMe][HCB_{11}Me_{11}]$ (0.020 g, 0.037 mmol, 48%). *NMR* (d_8-toluene, 293 K, assignments follow from $^1H–^{11}B$ and $^{11}B–^{11}B$ correlation experiments): $\delta^{11}B$: 3.6 (1H, s, B12), −3.6 (5H, s, B7–11), −5.9 (5H, s, B2–6); δ^1H: 5.55 (5H, s, Cp), 1.48 (1H, s, cage C–H), 0.36 [15H, s, BCH_3 (2–6)], 0.29 (3H, s, Zr–Me), 0.02 [15H, s, $BCH_3(7–11)$] and −0.59 (3H, s, $BCH_3(12)$. $\delta^{13}C\{^1H\}$: 119.9 (Cp), 68.0 (v br, CH_{cage}), 44.4 (Zr–Me, s), 3.9 (v br, B–CH_3). IR (fluorobenzene, $\nu(CH_3)$, cm^{-1}) 2962 vs, 2929 s, 2873 s. Satisfactory microanalytical data have been obtained for **2**.

‡ *Crystallographic data for* **2:** $C_{29}H_{52}B_{11}FZr$, M = 629.84, λ = 0.71073 Å, Monoclinic, space group $P2_1/c$, a = 10.3930(1), b = 23.4150(2), c = 14.4070(1) Å, β = 97.547(1)°, U = 3475.60(5) $Å^3$, Z = 4, T = 150(2) K, D_c = 1.204 g cm^{-3}, μ = 0.341 mm^{-1}, $F(000)$ = 1320, crystal 0.30 × 0.40 × 0.50 mm, 12960 [R(int) = 0.0660], $R1$ = 0.0361 $wR2$ = 0.0899 [$I > 2\sigma(I)$]. CCDC 209456. See http://www.rsc.org/suppdata/cc/b3/b304568d/ for crystallographic data in .cif format.

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