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$[(PPh_3)Ag(HCB_{11}Me_{11})]$: A Complex with Intermolecular Ag···H_3C Interactions[**]

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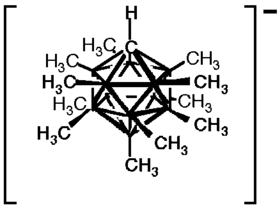
Nathan J. Patmore, Giuseppe D. Ruggiero, and
Andrew S. Weller[*]

Dedicated to Professor Thomas P. Fehlner
on the occasion of his 65th birthday

The "least-coordinating" peralkylated monoanionic carboranes based around $[1\text{-}closo\text{-}CB_{11}R_{12}]^-$ (R = alkyl)[1,2] are of significant technological interest. They can form stable, lipophilic, free radicals that are also strong oxidants,[3] novel electrolytes,[2] act as partners with lithium ions as catalysts for pericyclic rearrangements,[4] or can be used to isolate reactive cations such as $[nBu_3Sn]^+$[5] or Me^+.[6] They constitute some of weakest nucleophiles within the family of icosahedral monocarborane anions,[7] and also have the attractive properties of being relatively chemically robust[8] and available in gram quantities. Given that much of the interest in least-coordinating anions, such as the perfluorinated tetraaryl borates, is based around the generation of cationic Lewis acidic metal centers that show enhanced catalytic properties,[9] analogous complexes partnered with peralkylated carborane anions are of significant interest. The fact that peralkylated anions such as **1** can be considered as being negatively charged "alkane balls" is of particular relevance as there is considerable interest in the isolation and structure of metal–alkane complexes.[10] The structures of simple alkali-metal salts of $[1\text{-}closo\text{-}CB_{11}Me_{12}]^-$ have been reported,[11] while the main-group-metal complex $[nBu_3Sn][1\text{-}closo\text{-}CB_{11}Me_{12}]$ is a closely associated ion-pair in the solid state, a structure that is thought to be retained in solution.[5] However, no analogous transition-metal complexes have been described. We have a current interest in the chemistry of metal–ligand complexes partnered with monoanionic carborane anions[12] and report here the first example of a d-block-metal complex containing



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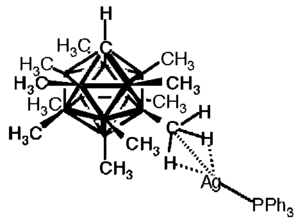

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a peralkylated carborane, $[PPh_3Ag][1\text{-}closo\text{-}HCB_{11}Me_{11}]$ (**2**), that displays unprecedented intermolecular $Ag\cdots H_3C$ interactions between the silver center and the carborane periphery in both the solid and solution state.

The addition of a solution of triphenylphosphane in CH_2Cl_2 to $Ag[1\text{-}closo\text{-}HCB_{11}Me_{11}]$ ([Ag]**1**)[13] affords a colorless solution from which crystalline $[PPh_3Ag][1\text{-}closo\text{-}HCB_{11}Me_{11}]$ (**2**) can be isolated in good yield. The solid-state structure of **2** is shown in Figure 1.

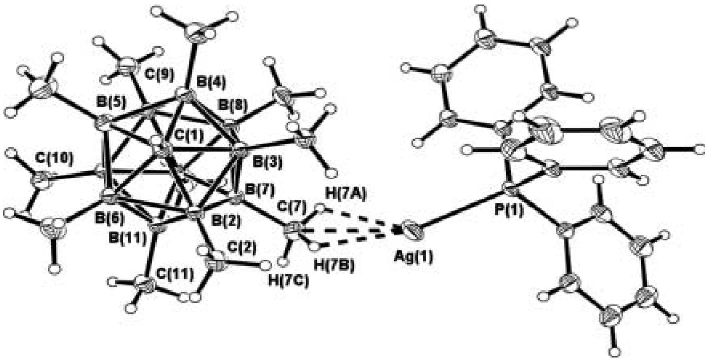

Figure 1. ORTEX diagram[27] of complex **2** showing thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ag(1)-H(7A) 2.19(3), Ag(1)-H(7B) 2.20(3), Ag(1)-H(7C) 3.033, C(7)-H(7A) 0.93(3), C(7)-H(7B) 0.93(3), C(7)-H(7C) 0.93(4), Ag(1)-C(7) 2.544(2), Ag(1)-P(1) 2.3871(5); C(7)-Ag(1)-P(1) 152.21(4), H(7A)-C(7)-B(7) 109(1), H(7B)-C(7)-B(7) 109(1), H(7C)-C(7)-B(7) 112(2).

In the solid state, the asymmetric unit shows that the silver–phosphane fragment is in close contact to one of the methyl groups (C(7)) on the lower pentagonal belt of the cage. The interactions between the $\{Ag(PPh_3)\}^+$ fragment and the C(7) methyl group are significant, as judged by the $Ag(1)\cdots C(7)$ separation (2.544(2) Å) being longer than that found for a Ag–C single bond (for example, 2.144(5) Å in $[(PPh_3)AgCH_2C_6F_5)]$)[14] but much shorter than the sum (3.29 Å) of the van der Waals radius of a methyl group (2.00 Å) and the ionic radius of an Ag^I ion (1.29 Å).[15] Moreover, the $Ag(1)\cdots C(7)$ separation is only slightly longer than those found in silver–arene complexes (2.47 Å) in which significant silver–carbon interactions are suggested to occur.[16] The hydrogen atoms on C(7) were located in the penultimate Fourier difference map and refined freely. There are two close $H\cdots Ag$ contacts ($Ag(1)\cdots H(7A)$ 2.19(3) and $Ag(1)\cdots H(7B)$ 2.20(3) Å) in the asymmetric unit; the separation from the third methyl hydrogen atom ($Ag(1)\cdots H(7C)$ 3.033 Å) is significantly longer resulting in a B(7)-C(7)-Ag(1) angle of 138.9(2)°. While acknowledging the limitations of X-ray diffraction in the accurate location of hydrogen atoms, it is reasonable to say that there is no lengthening of the C–H bonds for the hydrogen atoms in close proximity to Ag(1) in **2**. The structural motif in **2** is similar on first inspection to that reported for the zwitterionic complexes $[\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$ (**A**)[17] and $[(1,2\text{-}Me_2Cp)_2ZrCH_3(\mu\text{-}Me)B(C_6F_5)_3]$ (**B**)[18] in which $Zr\cdots H_3C$ agostic interactions are suggested to be present. In the extended lattice (Figure 2) there are two further, significantly longer, $Ag\cdots C$ contacts from permethylated cages proximate in the lattice: $Ag(1)\cdots C(9)'$ 3.154(2), $Ag(1)\cdots C(12)''$ 3.336(2) Å. The associated hydrogen atoms were located and refined; one methyl group (C(9)') is bidentate with respect to the $Ag\cdots H$ interactions, while the other (C(12)'') is monodentate. The overall structural motif is reminiscent of that found for $Li[B(CH_3)_4]$, in which extended tridentate and bidentate $CH_3\cdots Li$ interactions are observed in the solid state.[19]

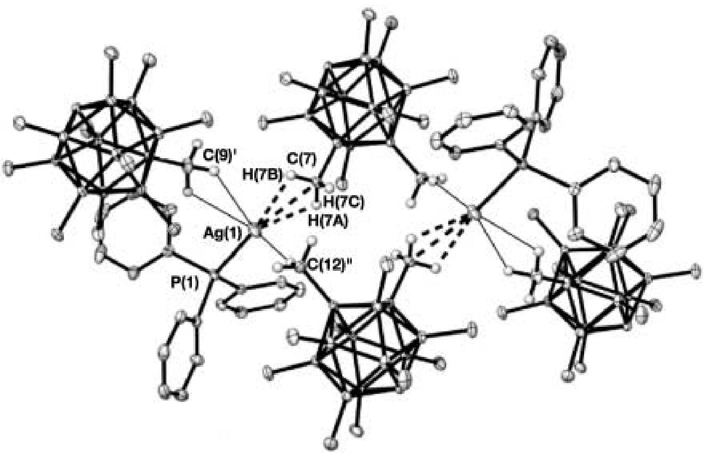

Figure 2. Packing diagram for **2** showing the extended $\{BCH_3\}\cdots\{Ag\}$ interactions in the solid state. Only the hydrogen atoms on C(7), C(9)', and C(12)'' are shown for clarity. Selected bond lengths [Å]: Ag(1)-C(9)' 3.154(2), Ag(1)-C(12)'' 3.336(2).

Energy minimization at the B3LYP/DZVP level for $[\mathbf{1}]^-$ and the three possible isomers of **2** shows that there is a small energy difference between the isomers (Table 1), with the metal fragment favoring interaction with the (7)–(11) vertices as observed experimentally, very closely followed by vertex (12). This observation is consistent with the distribution of charge on the three chemically different $\{B(CH_3)\}$ moieties in the free anion, $[\mathbf{1}]^-$ (Table 1) and is similar to that previously reported for $[nBu_3Sn][1\text{-}closo\text{-}CB_{11}Me_{12}]$.[5]

Table 1. Comparison of the charges (from natural bond orbital (NBO) analysis) on $[1\text{-}H\text{-}closo\text{-}1\text{-}CB_{11}Me_{11}]^-$, ($[\mathbf{1}]^-$), and the relative energies of the isomers of $[1\text{-}H\text{-}closo\text{-}1\text{-}CB_{11}Me_{11}][AgPPh_3]$ (**2**), all calculated at the B3LYP/DZVP level.

	$[HCB_{11}Me_{11}]^-$		$[HCB_{11}Me_{11}][AgPPh_3]$
Vertex/isomer	CH_3	$B(CH_3)$	energy [kJ mol^{-1}]
(12)	−0.28	−0.09	+6
(7)–(11)	−0.28	−0.13	0
(2)–(6)	−0.29	+0.07	+24

In solution the $Ag\cdots H_3C$ interactions are still present and significant, as shown by NMR spectroscopy. The $^1H\{^{11}B\}$ NMR spectrum of **2** shows a 5:1:5 pattern for the cage methyl groups. These signals are considerably broadened compared with those of $[Me_4N][1\text{-}closo\text{-}HCB_{11}Me_{11}]$ ($[Me_4N]\mathbf{1}$) (Figure 3), which is indicative of interaction with $\{Ag(PPh_3)\}$, while other peaks in the spectrum were sharp and well-resolved. $^1H\{^{11}B\text{-selective}\}$ NMR experiments were used to assign the methyl resonances, and demonstrate that the signal for the unique C(12) methyl carbon atom is shifted by

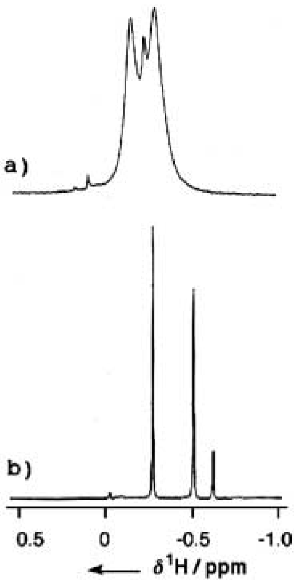

Figure 3. ^{1}H{^{11}B} NMR spectra of **2** (a) and **1**[NMe$_4$][13] (b). Peak assignments (downfield to upfield) for **2**: C(7)–C(11), C(12), C(2)–C(6) and for **1**[NMe$_4$]: C(2)–C(6), C(7)–C(11), C(12).

0.41 ppm downfield relative to that of **1**[NMe$_4$].[13,20] There is also a comparable downfield shift observed for the methyl groups on the lower pentagonal belt (0.37 ppm), while C(2)–C(6) are not shifted significantly. These results are consistent with the metal fragment interacting mostly with the C(7)–C(12) unit in solution. Similar downfield shifts have been reported for the BeCH$_3$ protons in [(η^5-C$_5$Me$_5$)$_2$Yb(μ-Me)Be(η^5-C$_5$Me$_5$)] (**C**) in which the Yb···{H$_3$CBe} interaction may be considered more electrostatic.[21] In contrast, in related complexes such as **A** and **B**, where agostic Zr···{H$_3$CB} interactions are proposed,[9] upfield shifts of the BCH$_3$ group are observed.[22] The ^{11}B{^{1}H} NMR spectrum of **2** confirms C_{5v} symmetry for the cage in solution (1:5:5 pattern), while in the ^{31}P{^{1}H} NMR spectrum a single phosphorus environment reveals coupling to both ^{109}Ag and ^{107}Ag nuclides (J(Ag$_{av}$P) 824 Hz). No significant change was observed in either the ^{1}H or the ^{31}P{^{1}H} NMR spectra on cooling the solution to −60 °C. Progressive heating of the sample (C$_2$D$_2$Cl$_4$, 20–70 °C) resulted in gradual decomposition to unidentified species.

The Ag···{H$_3$CB} interactions in **2** may be switched off by addition of one equivalent of [NBu$_4$][1-*closo*-CB$_{11}$H$_6$Br$_6$][23] to a solution of **2** in CD$_2$Cl$_2$, which results in rapid exchange of the permethylated carborane for the hexabromocarborane anion at the silver(I) center. The ^{1}H NMR spectrum of the resulting solution shows sharpening of the methyl signals, and chemical shifts identical to pure [NMe$_4$]**1**, while the ^{31}P{^{1}H} NMR spectrum shows evidence for the clean formation of [(PPh$_3$)Ag(1-*closo*-CB$_{11}$H$_6$Br$_6$)].[12] [1-*closo*-HCB$_{11}$Me$_{11}$] can thus be considered to be less nucleophilic than [1-*closo*-CB$_{11}$H$_6$Br$_6$], which itself is one of the least-coordinating anions known.[7]

Metal–alkane complexes are of considerable current interest,[10,24] but complexes isolated under standard laboratory conditions are rare.[25] Complexes such as **A**–**C**, which possess methyl groups that coordinate in an intermolecular fashion, are models for alkane complexes of the early transition metals. However, to our knowledge, no later d-block-metal complexes showing analogous interactions are known. Complex **2** represents the first example of a silver metal center interacting with an alkyl (CH$_3$) group in either an intra- or intermolecular fashion, and is thus a model for an interaction between a d^{10} metal center and an alkane.[24] The fact that these interactions are readily observed by ^{1}H NMR spectroscopy suggests that they will provide a useful spectroscopic marker in the development of the transition-metal chemistry of peralkylated carborane anions.

Experimental Section

2: Triphenylphosphane (60 mg, 0.23 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL) and added dropwise to a Schlenk flask charged with [Ag{CB$_{11}$Me$_{11}$H}][13] (92 mg, 0.23 mmol). The resulting solution was stirred in the dark for 16 h, cannula filtered, and the solvent removed in vacuo. The resultant white solid was redissolved in the minimum volume of CH$_2$Cl$_2$, layered with hexanes, then placed in a freezer overnight at −30 °C to afford colorless crystals (122 mg, 81 %).

^{1}H{^{11}B} NMR (300 MHz, CD$_2$Cl$_2$, 22 °C , assignments from ^{1}H{^{11}B-selective} experiments): $\delta = 7.66$–7.36 (15 H, m, Ph), 1.26 (1 H, s, C$_{cage}$-H), −0.14 (15 H, br s, BCH$_3$, B(7)CH$_3$–B(11)CH$_3$), −0.22 (3 H, br s B(12)CH$_3$), −0.28 ppm (15 H, br s, BCH$_3$, B(2)CH$_3$–B(6)CH$_3$). ^{11}B NMR (96 MHz, CD$_2$Cl$_2$, 22 °C, assignments from ^{11}B-^{11}B COSY): $\delta = -1.3$ (1 B, s, B(12)), −9.0 (5 B, s, B(7)–B(11)), −11.9 ppm (5 B, s, B(2)-B(6)). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$, 22 °C): $\delta = 133.9$ (s, C$_{phenyl}$), 132.3 (s, C$_{phenyl}$), 130.0 (s, C$_{phenyl}$), 128.2 (d, C$_{phenyl}$, J(CP) = 37 Hz), 61.3 (s, C$_{cage}$), −0.7–−6.0 ppm (br, CH$_3$). ^{31}P{^{1}H} (122 MHz, CD$_2$Cl$_2$, 22 °C): $\delta = 17.5$ ppm (dd, J(Ag^{109}P) 853 Hz, J(Ag^{107}P) 794 Hz). IR (KBr): $\tilde{\nu} = 2921$, 2895, 2829, 2736 cm^{-1} (CH$_3$); elemental analysis calcd for C$_{30}$H$_{49}$Ag$_1$B$_{11}$P$_1$: C 54.0, H 7.35 %; found: C 53.4, H 7.30 %.

Crystal data for **2**: triclinic, space group $P\bar{1}$, a = 9.18400(10), b = 13.6170(2), c = 15.1520(3) Å, $\alpha = 111.6370(10)$, $\beta = 95.0050(10)$, $\gamma = 100.3360(10)°$, $V = 1708.23(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.298$ Mg m^{-3}. Data were collected at 173(2) K on a Nonius kappaCCD diffractomter, Mo$_{K\alpha}$ radiation (0.71073 Å), 9965 measured reflections to $2\theta_{max} = 60.12°$, giving 7255 unique reflections ($R_{int} = 0.0417$). The structure was solved by direct methods, and refined against F^2 using all data.[26] The final discrepancy indices were $R_1 = 0.0378$, $wR_2 = 0.0941$. CCDC-187180 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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A Simple, Reliable, Catalytic Asymmetric Allylation of Ketones**

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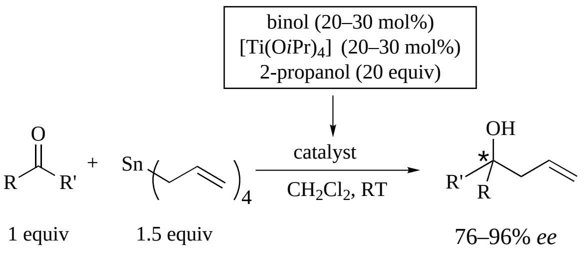
The asymmetric allylation of carbonyl groups to furnish homoallylic alcohols is a fundamental transformation in synthetic organic chemistry.[1–3] Several catalysts will promote the asymmetric allylation of aldehydes to give secondary homoallylic alcohols with excellent enantioselectivities.[4–15] The catalytic asymmetric allylation of ketones, however, has proven to be a more challenging transformation owing to the significant difference in reactivity between aldehydes and ketones. Thus, with one exception,[16] catalysts that promote the enantioselective allylation of aldehydes fail to catalyze the analogous reaction with ketones. In general, the enantioselective formation of quaternary stereocenters, as generated in the asymmetric allylation of ketones, is of considerable difficulty.[17,18]

To compensate for the reduced reactivity of ketones, a more reactive allylating agent was needed. Baba and co-workers found that tetraallylstannane added to ketones in the presence of methanol and 200 mol% binol to give the homoallylic alcohol in up to 60% *ee*.[19] An important discovery in the asymmetric allylation of ketones was recently reported by Casolari, D'Addario, and Tagliavini.[20] Their catalyst preparation involved the reaction of [Cl$_2$Ti(O*i*Pr)$_2$] and binol with allyltributylstannane. After mixing for one hour, tetraallylstannane and the substrate ketone were added. They observed the formation of the ketone allylation product with up to 65% *ee* at 20 mol% binol (80% *ee* with 40 mol% binol).

Based on the results of the Italian team,[20] Maruoka and co-workers[16] recently reported a system for the catalytic asymmetric allylation of aldehydes with a catalyst that is based on titanium, binol, and an achiral diamine spacer (2:2:1 ratio). This catalyst (60 mol% titanium and binol) was examined in the asymmetric allylation of only two ketones, acetophenone and methyl 2-naphthyl ketone, which underwent allylation with 90 and 92% *ee*, respectively.[16] More recently, Cunningham and Woodward[21] demonstrated that monothiobinaphthol will promote the allylation of acetophenone derivatives with a mixture of [RSn(allyl)$_3$]/[Sn(allyl)$_4$] (R = Et, Bu) with *ee* values as high as 92% (51% yield).

The ketone allylation reaction of Casolari, D'Addario, and Tagliavini[20] attracted our attention because of our interest in the mechanisms of titanium-based asymmetric Lewis acid catalysts[22–24] and the need for a more versatile and enantioselective catalyst for this important process. While investigating the catalyst structure of the Tagliavini system, we made several key observations that allowed us to develop the most general and enantioselective catalyst for the asymmetric allylation of ketones to date.

We repeated the catalyst preparation of Tagliavini[20] described above in CDCl$_3$ to probe the nature of the (binolate)Ti species by NMR spectroscopy. Like Tagliavini and co-workers,[20] we observed the production of tributyltin chloride. However, we were surprised to find that the major titanium-containing product was [(binolate)Ti(O*i*Pr)$_2$], which is dimeric in solution and trimeric in the solid state.[25,26] We prepared this compound on a gram scale simply by mixing titanium tetraisopropoxide and binol followed by removal of the solvent and liberated 2-propanol.[26] Using the isolated [(binolate)Ti(O*i*Pr)$_2$], we found that the enantioselectivities in the allylation reaction were about the same as those reported by Tagliavini and co-workers.[20] An important breakthrough was made when the catalyst was prepared directly from titanium tetraisopropoxide and binol (1:1, 20 or 30 mol%) *without removal of the liberated 2-propanol.* When we employed this catalyst preparation, the *ee* of the product formed from 3-methylacetophenone rose from 51% to 73%. These results suggested that the liberated 2-propanol had a beneficial impact on the enantioselectivity of the catalyst. We therefore prepared the catalyst with additional 2-propanol and observed a significant increase in the catalyst enantioselectivity [Eq. (1)].



(1)

The advantageous effect of the 2-propanol on the enantioselectivity of the catalyst reached a maximum when 20 equiv

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