An *arachno*-Metallacarbaborane Containing Intermolecular Hydrogen Bridges. Crystal and Molecular Structure of Bis-[11-triphenylphosphine-11-argenta-5,6-dicarbaundecaborane(11)]

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Summary The metallacarbaboranes $PPh_3AuC_2B_8H_{11}$, $PPh_3CuC_2B_8H_{11}$, and $(PPh_3)_2AgC_2B_8H_{11}$ have been prepared and $(PPh_3)_2AgC_2B_8H_{11}$ suffers a partial loss of triphenylphosphine on recrystallisation, to give '$PPh_3AgC_2B_8H_{11}$'; this last compound is shown from i.r. and *X*-ray data to have a dimeric structure comprising two enantiomeric *arachno*-AgC_2B_8 cages, linked by a pair of Ag–H–B bridges derived from terminal B–H groups, and analogous, though monomeric, *arachno*-structures are suggested for $PPh_3AuC_2B_8H_{11}$ and $(PPh_3)_2AgC_2B_8H_{11}$.

THE interactions between carbaborane ligands (particularly the isomeric $C_2B_9H_{11}^{2-}$ ions) and late transition metals have been the subject of several recent theoretical[1] and experimental investigations,[2] which have shown metallacarbaborane geometries to vary with (a) the electron configuration of the metal atoms, (b) the position of carbon atoms in the bonding face of the carbaboranes, and (c) the extent of any π-type interactions between the metal and its other (non-carbaborane) ligands. In order to assess the relevance of these factors to other systems, we have studied the interaction of 'electron-rich' d^{10} metal ions Cu^I, Ag^I, and Au^I, with the $C_2B_8H_{11}^-$ ligand. Several novel features are associated with the resulting metallacarbaboranes, $LMC_2B_8H_{11}$ (M = Cu, Ag, Au; L = PPh_3), notably the *arachno* structure of the AgC_2B_8 fragment, and the existence of intermolecular M–H–B bridge bonds leading to dimeric species in the solid state.

Reaction of equimolar quantities of $Na[5,6\text{-}C_2B_8H_{11}]$[3] and PPh_3AuCl in diethyl ether produced the auracarbaborane $PPh_3AuC_2B_8H_{11}$† (38% after recrystallisation from acetone) as a pale-yellow microcrystalline solid, and an analogous reaction with $[PPh_3CuCl]_4$ gave bright-yellow crystals (27%) of $PPh_3CuC_2B_8H_{11}$. The reaction between $Na[5,6\text{-}C_2B_8H_{11}]$ and $[PPh_3AgBr]_4$ gave low yields (*ca.* 29%) of a crystalline solid which, in contrast, analysed as the bis-phosphine complex $(PPh_3)_2AgC_2B_8H_{11}$, which is the first reported derivative of an argentacarbaborane. Much higher yields of this compound were obtained, however, when $(PPh_3)_2AgBr$ was used as the starting material. Recrystallisation of $(PPh_3)_2AgC_2B_8H_{11}$ from chloroform–hexane solution resulted in the partial loss of phosphine ligand, giving $PPh_3AgC_2B_8H_{11}$ as a cream-coloured crystalline solid; the latter was readily converted back into the bis-phosphine compound by treatment with triphenylphosphine in acetone.

The i.r. spectra of $PPh_3AuC_2B_8H_{11}$ and $(PPh_3)_2AgC_2B_8H_{11}$ (Nujol mulls) showed only normal ν (B–H terminal) absorption bands between 2600 and 2500 cm^{-1}, but the corresponding spectra of $PPh_3CuC_2B_8H_{11}$ and $PPh_3AgC_2B_8H_{11}$ both contained an additional strong, broad band between 2350 and 2300 cm^{-1}, and a low-temperature (173 K) single crystal *X*-ray study of the latter compound (acetone solvate) was undertaken, in an effort to determine the origin of this feature.

The structure (Figure) reveals a pair of enantiomeric $PPh_3AgC_2B_8H_{11}$ units dimerised about a crystallographic centre of symmetry *via* a pair of B–H–Ag hydrogen bridges derived from terminal B–H bonds [B(8)–H–Ag′ = 130(3)°, B(8)–H = 1·12(5), H–Ag′ = 2·19(5), B(8)–Ag′ = 3·033(6) Å]. Since co-ordination of B–H bonds to transition metals characteristically leads to lower B–H stretching frequencies,[4] the unusual i.r. absorption band is clearly accounted for. The H–Ag′ distance of 2·19(5) Å may be compared with other H–M parameters in other compounds containing M–H–B bonds; thus in $(PPh_3)_2CuBH_4$[5] and $\{[(PPh_3)_2Cu]_2B_{10}H_{10}\cdot CHCl_3\}$[6] the H–Cu distances are 1·82(3) and [1·88(6), 2·06(6)] Å respectively. In the recently described dimer $[(PPh_3)RhC_2B_9H_{11}]_2$,[7] where the Rh atom is linked to another $C_2B_9H_{11}$ cage *via* a Rh–H–B bond, the Rh–H distance is 1·77(6) Å, although there is also evidence of significant Rh–Rh bonding in this case.

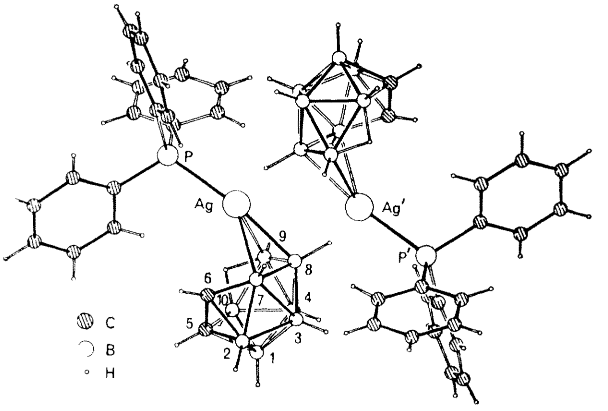

FIGURE. Molecular structure of $[PPh_3AgC_2B_8H_{11}]_2$ at 173 K.

Crystal data: $(PPh_3AgC_2B_8H_{11})_2(Me_2CO)$, M = 1041·5, triclinic, space group $P\bar{1}$, a = 10·5468(15), b = 11·0827(15), c = 12·6560(16) Å, α = 102·201(11), β = 108·325(10), γ = 107·100(11)°, D_c = 1·365 g cm^{-3}, Z = 1, μ(Mo-K_α) = 8·34 cm^{-1}. R is currently 0·045 for 5300 independent observed reflections.‡

Each silver atom is co-ordinated by a single intermolecular hydrogen bridge, by triphenylphosphine [Ag–P = 2·418(1) Å], and by three boron atoms of a C_2B_8 fragment [Ag–B(7) = 2·522(4), Ag–B(8) = 2·352(4), and Ag–B(9) = 2·420(7) Å], the resulting argentacarbaborane also containing an intramolecular B–H–B bridge in its open face, between borons (9) and (10). The Ag–C(6) distance of 2·827(6) Å suggests an essentially non-bonded interaction since the Ag–C σ-bond length in $[PhC{\equiv}CAgPMe_3]_2$ is 2·04 Å,[8] and in the weak π-complex $C_6H_6AgClO_4$ the Ag–C distances[9] are 2·50 and 2·63 Å. The AgC_2B_8 framework thus represents the first example of an 11-membered *arachno* cage-structure. Such a structure should be associated with 14 skeletal electron-pairs, (n + 3, where n = 11),[10] requiring the d^{10} silver(I) ion to contribute 2 electron-pairs, in keeping with previous findings[11] that, although up to 3 pairs of transition-metal d-electrons may be neglected for skeletal electron-counting purposes, any further valence-shell electron-pairs must be included in the total electron count, at least for the later transition elements.

An alternative view of the structure is one in which the phosphine–silver moiety replaces a bridging hydrogen in the proposed structure of the parent carbaborane $C_2B_8H_{12}$.[3] Similar replacements are already known in metalla-borane

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† Satisfactory elemental analyses have been obtained for all the compounds reported.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

chemistry, *e.g.* $(Ph_3P)_2CuB_5H_8$.[12] The ambiguity in the present structure which then arises is that the silver atom clearly bridges the face described by B(7)–B(8)–B(9), whereas the bridging hydrogen atom would conventionally be assigned to a bridging position between B(8) and B(9).

Analogous *arachno* structures are suggested for $PPh_3AuC_2B_8H_{11}$ and $(PPh_3)_2AgC_2B_8H_{11}$ on the basis of their ^{11}B n.m.r. spectra (Table) which correlate closely with those of $(PPh_3)AgC_2B_8H_{11}$ and $C_2B_8H_{12}$.[3] However, the absence of i.r. absorptions due to M–H–B bridge bonds suggests that the former two compounds may be monomeric in the solid state. The cage-structure of the cupracarbaborane $(PPh_3)CuC_2B_8H_{11}$ remains in doubt, since its ^{11}B and ^{1}H n.m.r. spectra differ substantially from those of the other compounds reported here.

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TABLE. ^{11}B and ^{1}H n.m.r. spectra[a]

$PPh_3AuC_2B_8H_{11}$[b]:	^{11}B; δ 5·24 (br, m, 4B), −3·97 (d, 1B), −10·06 (d, 1B), −27·15 (d, 1B), −31·46 (d, 1B). ^{1}H; δ 7·52 (m, 15H, PPh_3), 5·29 (s, 1H, carbaborane CH), 4·67 (s, 1H, carbaborane CH)
$PPh_3CuC_2B_8H_{11}$[c]:	^{11}B; δ 2·96 (d, 2B), 0·43 (d, 2B), −9·39 (d, 1B), −12·77 (d, 1B), −28·58 (d, 2B). ^{1}H; δ 7·44 (m, 15H), 3·93 (s, 1H), 4·74 (s, 1H).
$(PPh_3)_2AgC_2B_8H_{11}$[c]:	^{11}B; δ 1·86 (br, m, 4B), −4·18 (d, 1B), −11·08 (d, 1B), −30·30 (d, 1B), −33·40 (d, 1B). ^{1}H; δ 7·32 (m, 15H), 5·29 (s, 1H), 4·27 (s, 1H).
$PPh_3AgC_2B_8H_{11}$[d]:	^{11}B; δ 2·03 (br, m, 4B), −4·90 (d, 1B), −11·33 (d, 1B), −29·77 (d, 1B), −33·32 (d, 1B). ^{1}H; δ 7·34 (m, 15H), 5·31 (s, 1H), 4·43 (s, 1H).

[a] ^{11}B n.m.r. shifts are quoted in p.p.m. relative to external $BF_3{\cdot}Et_2O$, with downfield shifts given as +ve. ^{1}H and ^{11}B n.m.r. spectra were recorded at 90 and 28·9 MHz, respectively. [b] In $CDCl_3$. [c] In $(CD_3)_2CO$. [d] In CD_3CN.

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