DALTON

Silver complexes with the *nido*-diphosphine $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$

Olga Crespo,[a] **M. Concepción Gimeno,**[a] **Peter G. Jones**[b] **and Antonio Laguna** *[,a]

[a] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

[b] *Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany*

Silver complexes with the *nido*-diphosphine $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ have been synthesized. Reaction of $[Ag(OClO_3)(PR_3)]$ with $(PPh_2)_2C_2B_{10}H_{10}$ in refluxing ethanol affords the three-co-ordinate complexes $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PR_3)]$ ($PR_3 = PPh_3$ **1** or PPh_2Me **2**), whereas treatment of $[Ag(OClO_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]$ with L–L under the same conditions leads to the formation of $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(L\text{–}L)]$ [L–L = 1,10-phenanthroline **3**, bis(diphenylthiophosphoryl)methane **4** or 1,2-bis(diphenylphosphino)-1,2-dicarbadodecaborane(10) **5**]. The structures of complexes **1**, **3** and **5** have been established by X-ray crystallography. The silver atoms show a trigonal planar (**1**) or tetrahedral geometry (**3** and **5**).

Carbaboranes, despite their cost, are uniquely suitable for several applications.[1] Some of the latter are based on the properties of elemental boron: they are used as boron sources in the preparation of tumour-seeking drugs for boron neutron-capture therapy.[2–4] Others, such as the synthesis of polymers[5] or homogeneous catalysts,[6] are based on the specific properties of carbaborane clusters (rigid, bulky frameworks). The chemical and thermal stability of carbaboranes has been demostrated under the many reaction conditions used to prepare their derivatives, whereby the carbaborane cage remains intact. One of their better known reactions consists of the removal of the boron atom nearest to one of the carbons in *closo*-carbaboranes (partial degradation), as described as early as 1964 by Wiesboeck and Hawthorne[7] who prepared the anion $[7,8\text{-}C_2B_9H_{12}]^-$ by refluxing $1,2\text{-}C_2B_{10}H_{12}$ with KOH in methanol.

However, not much work has been done on the partial degradation of the diphosphine $1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$. At first it seemed that its co-ordination to a metal centre was required for retention of the C–P bond in the partial degradation reactions which afford the $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anion. Attempts to isolate these species by reaction of the *closo*-diphosphine with alkoxide led to the synthesis of $[7,8\text{-}C_2B_9H_{12}]^-$, whereas no reaction was observed in refluxing ethanol and other attempts using piperidine were unsuccessful.[8] Very recently Teixidor *et al.*[9] have isolated the partially degraded diphosphine $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ by refluxing the *closo*-diphosphine in ethanol for a long period of time with a large excess of piperidine.

We have previously described the synthesis of gold(I) complexes with this *closo*-[10] and *nido*-diphosphine[11] and silver(I) derivatives with the *closo*-diphosphine.[12] In this paper we report on the synthesis of silver(I) complexes with the anionic diphosphine, with the aim of comparison with the related *closo*-species. During the preparation of this manuscript the only reported complexes with the anion $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ were the copper derivatives $[Cu\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)]$ and $[NMe_4][CuCl\{(PPh_2)_2C_2B_9H_{10}\}(PR_3)]\cdot Me_2CO$, but in the meantime the synthesis of some transition-metal species,[13] including the complex $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)]$ (also described here), has been published, although no crystal structure determination was carried out.

Results and Discussion

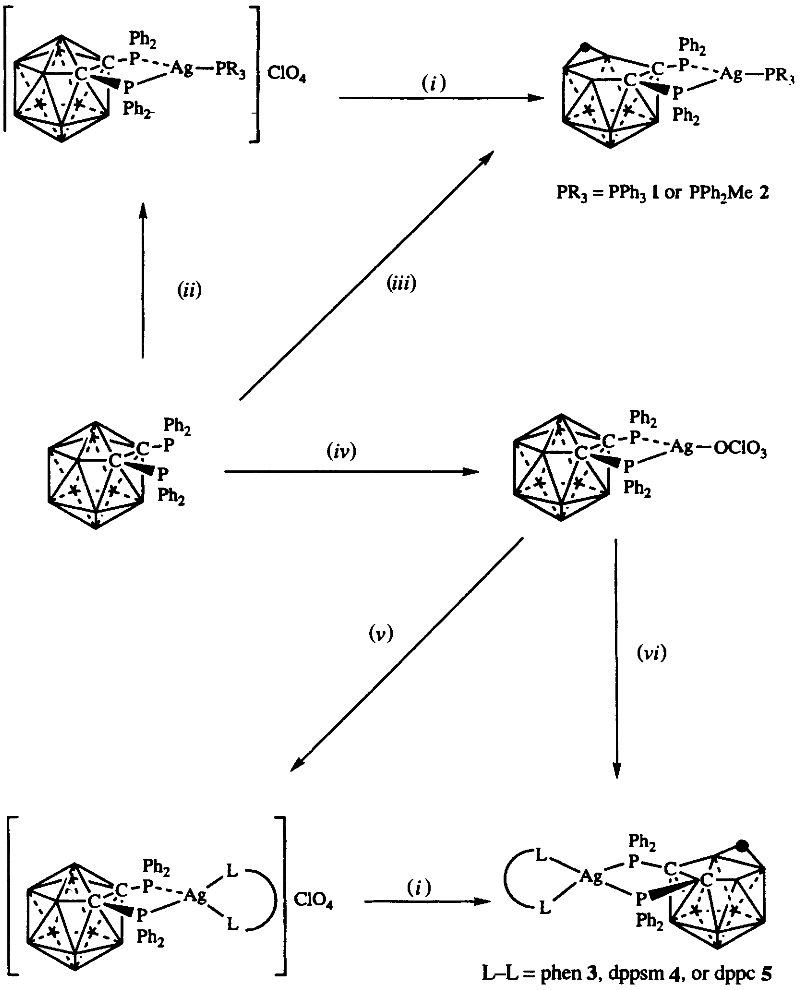
The complexes $[Ag(OClO_3)(PR_3)]$ react with $(PPh_2)_2C_2B_{10}H_{10}$ in refluxing ethanol to afford the neutral three-co-ordinate compounds $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PR_3)]$ ($PR_3 = PPh_3$ **1** or PPh_2Me **2**), in which one of the carbaborane boron atoms has been removed from the *closo* species to produce a *nido* system that incorporates a negative charge. These complexes are different from those obtained in methylene dichloride at room temperature[10] where cationic complexes containing the *closo*-diphosphine were obtained (Scheme 1).

Similarly, the reaction of $[Ag(OClO_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]$ with bidentate ligands such as 1,10-phenanthroline (phen), bis(diphenylthiophosphoryl)methane (dppsm) and 1,2-bis(diphenylphosphino)-1,2-dicarbadodecarborane(10) (dppc) affords the four-co-ordinate complexes $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(L\text{–}L)]$ (L–L = phen **3**, dppsm **4** or dppc **5**).

The first step in these reactions is co-ordination of the diphosphine to the metal centre, followed by removal of the boron atom. Upon co-ordination of the diphosphine there is a transfer of electron density from the metal to the cage. In such a situation one of the apical boron atoms is susceptible to nucleophilic attack, which leads to partial cluster opening. In this case ethanol is a suitable nucleophile. Correspondingly, derivatives **1**–**5** are also available from the complexes containing the *closo* ligands, $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(PR_3)]ClO_4$ or $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(L\text{–}L)]ClO_4$, under the same conditions of refluxing ethanol.

The IR and ^1H NMR spectra of complexes **1**–**5** confirm the removal of the boron atom. The former display the ν(B–H) absorption at lower energies (lower than 2535 cm^{-1}, except for complexes **1** and **5**) than for the analogous complex with the *closo*-diphosphine.[10] The ν(B–H) wavenumbers are summarised in Table 1. The spectrum of complex **4** also shows an absorption assigned to ν(P=S) at 603 cm^{-1}.

In the ^1H NMR spectra the signal centred at δ −2 assigned to the bridging proton B–H–B is consistent with the partially degraded nature of the diphosphine. The chemical shift of this hydrogen atom does not change significantly from one compound to another; it always appeared as a broad multiplet even when the experiments were carried out at low temperature. For a long time it was believed that this proton had two alternative positions, *e.g.* bridging involving the central boron atom or the one next to it. Theoretical calculations confirmed by X-ray diffraction and NMR studies indicate that it is strongly bonded to the central boron atom, although in solution it has considerable mobility between the two positions.[14,15] The signals of the other hydrogen atoms attached to the borons of the carbaborane cage are usually very broad and appear as a



Scheme 1 (*i*) EtOH, heat; (*ii*) $[Ag(OClO_3)(PR_3)]$, CH_2Cl_2; (*iii*) $[Ag(OClO_3)(PR_3)]$, EtOH, heat; (*iv*) $AgClO_4$, Et_2O; (*v*) L–L, CH_2Cl_2; (*vi*) L–L, EtOH, heat

Table 1 Analytical, conductivity and NMR data and $\tilde{\nu}$(B–H) values for complexes 1–5

Complex	Yield (%)	Analysis (%)[a] C	Analysis (%)[a] H	Λ_M[b]	$^{31}P-\{^1H\}$[c] δ(PP)	J[d]	δ (PR_3)	J[d]	$\tilde{\nu}$(B–H)/cm^{-1}
1 $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)]$	80	60.3 (60.6)	5.2 (5.2)	2	22.6	[255.2, 224.0] J(AB) = 69.5	19.3	[467.4, 410]	2589
2 $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PPh_2Me)]$	80	57.9 (57.85)	5.25 (5.35)	1	22.6 (ddd)	[293.5, 258.3] J(AX) = 68.2	−2.7 (ddt)	[512.5, 444.1]	2521
3 $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(phen)]$	61	57.8 (57.75)	4.85 (4.85)	3	17.5 (dd)	[368.5, 319.3]			2523
4 $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(dppsm)]$	78	57.85 (57.9)	4.5 (4.45)	38	14.4 (dd)	[300.1, 261.2]	38.4 (s)		2532
					δ(A)	δ(A′)	δ(B)	δ(B′)	
5 $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(dppc)]$[e]	59	52.75 (52.75)	5.3 (5.15)	5	20.8 J(AA′) = 7.0 J(AB) = 55.0 J(AB′) = 53.0 [224.0, 160.0]	20.0 J(A′B) = 17.0 J(A′B′) = 15.0 [770.0, 550.0]	18.7 J(A′B) = 12.0 [693.0, 495.0]	18.4 [215.0, 155.0]	2601

[a] Calculated values in parentheses. [b] In acetone Ω^{-1} cm^2 mol^{-1}. [c] Recorded in $CDCl_3$, values in ppm. [d] Coupling constants [$J(^{109}Ag–P)$, $J(^{107}Ag–P)$] in Hz; dd = two doublets, ddd = two doublets of doublets, ddt = two doublets of triplets. [e] Calculated values for $5{\cdot}CH_2Cl_2$. Chemical shifts (in ppm) and coupling constants, including [J^{109}Ag–P, J^{107}Ag–P] in Hz, for the spin sistem AA′BB′XY.

slight protuberance in the baseline between δ 1 and 3. The ^{11}B NMR spectra show the characteristic pattern for 7,8-dicarba-*nido*-undecaborate(1−) derivatives,[16–18] which usually present five resonances in a ratio 2:3:2:1:1. For these complexes only four signals appear, one of which has a shoulder. The resonances range from δ 0 to −35; the high-field signals are assigned to the boron atoms with high co-ordination number.

The complexes exhibit the cation/ion molecular peaks in the positive-ion fast atom bombardment (FAB) spectra at m/z =

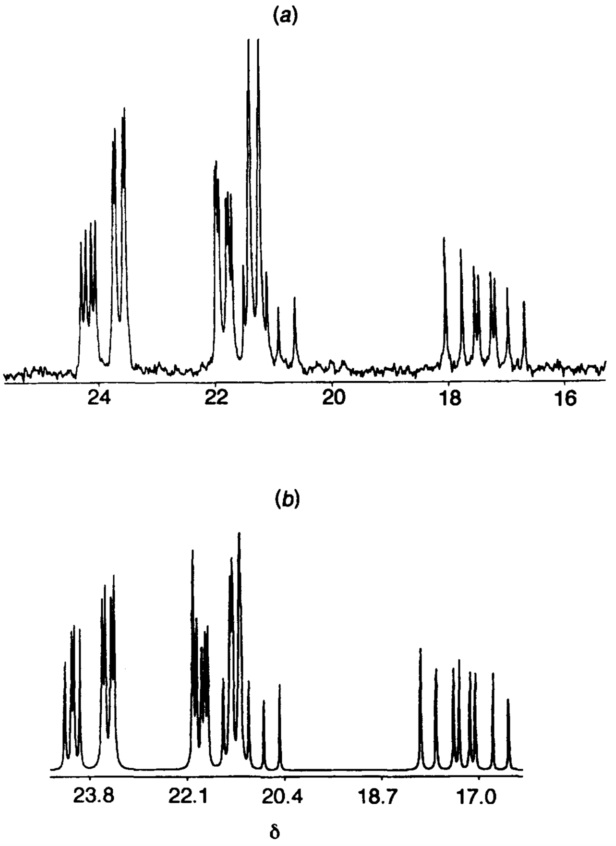


Fig. 1 (*a*) The ^{31}P-{^{1}H} NMR spectrum of complex **1** at −55 °C. (*b*) Spin simulation for an AB_2XY system

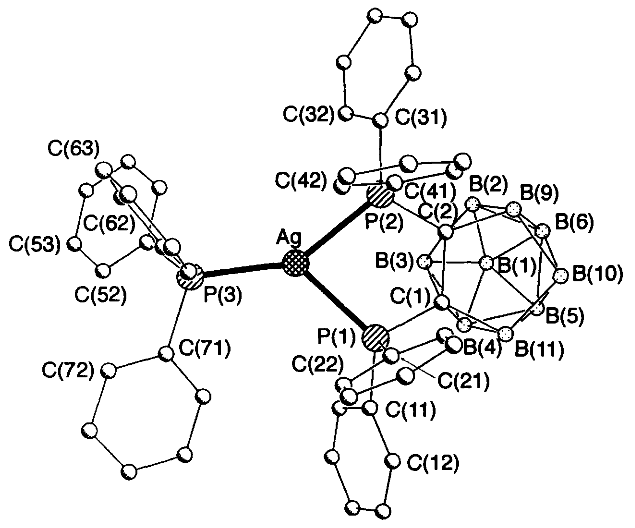


Fig. 2 Structure of complex **1** in the crystal: hydrogen atoms are omitted for clarity, and radii are arbitrary

871 (**1**, 66), 809 (**2**, 44), 789 (**3**, 18), 1059 (**4**, 6) and 1122 (**5**, 66%), with coincident experimental and isotopic distribution. Other fragmentation or association peaks are listed in the Experimental section.

The ^{31}P-{^{1}H} NMR spectrum of complex **1** is an AB_2 system with coupling of A and B with ^{107}Ag and ^{109}Ag nuclei; spin simulation of an AB_2XY system was in agreement with the observed spectrum (Fig. 1). However, the spectrum of **2** corresponds to an AX_2 system with coupling of A and X with the ^{107}Ag and ^{109}Ag nuclei. Thus, two doublets of doublets are shown for the X part (diphosphine phosphorus) and two doublets of triplets for the A part (phosphine phosphorus). The spectra of complexes **3** and **4** are less complicated. They present two doublets because of coupling of the phosphorus of the diphosphine with the ^{107}Ag and ^{109}Ag nuclei; **4** also shows a singlet arising from the phosphorus atoms of the dppsm ligand. A very complicated spectrum is observed for **5** because an AA′BB′ system with coupling to the silver nuclei appears; spin simulation for such a system was in agreement with the observed spectrum.

Notwithstanding the additional negative charge in the *nido*-diphosphine, the chemical shifts and coupling constants for the *closo*- and *nido*-derivatives are similar, except for complex **1** which displays a different system from that obtained for $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(PPh_3)]ClO_4$ (AB_2 and AX_2 with coupling to the silver nuclei, respectively). As expected, a high-field displacement of *ca.* 3 ppm is observed for the partially degraded derivatives.

The $J(^{109}Ag{-}P)$ and $J(^{107}Ag{-}P)$ coupling constants for the three-co-ordinate compounds **1** and **2** are smaller than those reported for [AgX(L–L)] {X = Cl, $SnCl_3$, ClO_4 or NO_3; L–L = 2,11-bis(diphenylphosphanyl)methylbenzo[*c*]phenanthrene},[19] and similar to those of the complex $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(PPh_3)]ClO_4$ containing the *closo*-ligand.[12] However, they are very different from those reported for $[Au(dppf)(PPh_3)]ClO_4$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene],[20] where the coupling constants to the mono- and bidentate phosphines are more similar, in accord with a more regular distribution of the Ag–P bond distances (see structural comments below). For the four-co-ordinate derivatives **3**–**5** the coupling constants are larger than those published for $[Ag(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$).[21]

Not many studies have dealt with the relation between coupling constants and co-ordination number. It seems clear that an increase in the co-ordination number should lead to a decrease in the value of the coupling constant and that shorter Ag–P distances should give longer coupling constants. As can be seen in Table 2, the three-co-ordinated complexes have, in general, higher coupling constants than the four-co-ordinated ones; the exception is $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)]$ but in this case two more factors affect the system, the narrower P–Ag–P angle and the longer Ag–P distances. Also it can be shown that when the nucleophilicity of the other ligand attached to silver decreases, an increase in the coupling constant is observed. For the tetrahedral derivatives the coupling constants range from 248.5 to 396.8 Hz. It seems clear that the main factor affecting the J(AgP) value is the Ag–P distance, because if we compare the complexes $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(phen)]^+$ (313.6 Hz), $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(phen)]$ (345.5 Hz) and $[Ag(dppf)(phen)]^+$ (396.8 Hz) the Ag–P bond lengths are shortest in the latter. However, considering the first two complexes, the second has the slightly longer Ag–P distance and narrower P–Ag–P angle which should lead to lower coupling constants, but they are higher; the reason could be the positive charge at the silver centre in the first derivative.

The crystal structures of complexes **1**, **3** and **5** have been established by X-ray diffraction. The molecule of $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)]$ **1** is shown in Fig. 2. The silver atom presents a somewhat distorted trigonal geometry, lying 0.305(1) Å out of the plane of the three phosphorus. The restricted 'bite' of the *nido*-diphosphine [81.07(3)°] represents the major deviation from ideal geometry; this angle is even narrower than those found for the analogous gold complexes[10,11] $[Au\{(PPh_2)_2C_2B_{10}H_{10}\}(PPh_3)]ClO_4$ (90.2°) and $[Au\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)]$ (89.91°).

The bond to the monodentate phosphine is shorter [2.3974(10) Å] than those to the diphosphine [2.4942(10) and 2.4881(10) Å] (Table 3); the values agree well with those obtained for three-co-ordinate silver complexes such as [AgX(L–L)] {L–L = 2,11-bis(diphenylphosphanyl)methylbenzo[*c*]phenanthrene,[19] X = Cl, $SnCl_3$, ClO_4 or NO_3}, which lie in the range 2.40(3)–2.455(1) Å, or $[Ag(dppf)(PPh_3)]ClO_4$[20] [2.4386(13)–2.4870(12) Å]. As we have commented before, the bridging

Table 2 Co-ordination geometries and $J(Ag–P)_{av}$ coupling constants for silver diphosphine complexes

Complex	Ag–P/Å	P–Ag–P/°	J_{av}/Hz	Ref.
1 $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PPh_3)]$	2.4881(10), 2.4942(10)	81.07(3)	239.7	This work
$[Ag(dppf)(PPh_3)]$	2.4312(12), 2.4802(12)	109.63(4)	399.4	20
$[AgCl(L–L)]$*	2.455(1), 2.412(1)	140.7(1)	440	19
$[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(dppsm)]^+$	2.5272(2), 2.532(2)	84.56(6)	296.2	12
$[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(phen)]^+$	2.463(2), 2.479(2)	89.4(1)	313.6	12
3 $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(phen)]$	2.465(2), 2.4906(14)	82.58(5)	345.5	This work
$[Ag(dppf)(phen)]^+$	2.4112(10), 2.5067(10)	110.59(3)	396.8	20
$[Ag(dppf)_2]^+$	2.549(2), 2.602(2)	113.15(14), 106.81(4)	250.8	20
$[Ag(dppe)_2]^+$	2.488(3), 2.527(3)	84.5(1), 83.8(1)	248.5	21

* L–L = 2,11-bis(diphenylphosphonyl)methylbenzo[*c*]phenanthrene.

Table 3 Selected bond lengths (Å) and angles (°) for complex **1**

Ag–P(3)	2.3974(10)	Ag–P(1)	2.4881(10)
Ag–P(2)	2.4942(10)	P(1)–C(1)	1.831(3)
P(2)–C(2)	1.852(3)	C(1)–C(2)	1.611(4)
C(1)–B(11)	1.622(5)	C(1)–B(3)	1.728(5)
C(1)–B(4)	1.738(5)	C(2)–B(9)	1.630(5)
C(2)–B(3)	1.717(5)	C(2)–B(2)	1.727(5)
B(9)–B(10)	1.857(6)		
P(3)–Ag–P(1)	128.53(4)	P(3)–Ag–P(2)	144.78(3)
P(1)–Ag–P(2)	81.07(3)	C(1)–P(1)–Ag	106.54(11)
C(2)–P(2)–Ag	106.28(11)	C(2)–C(1)–P(1)	116.5(2)

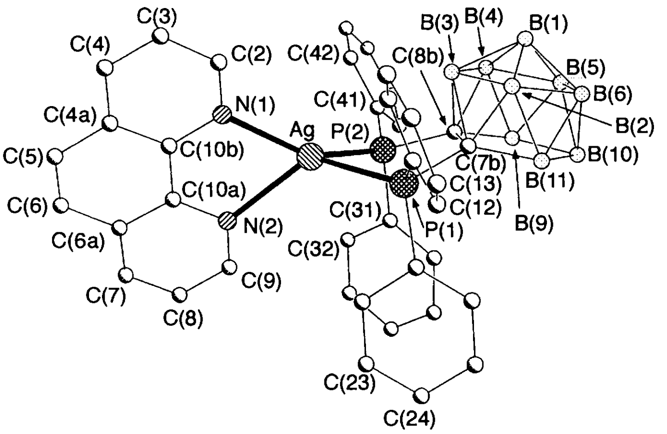


Fig. 3 Molecular structure of complex **3** showing the atom numbering scheme. Details as in Fig. 2

proton is strongly bonded to the central boron atom, B(10), of the C_2B_3 open face, but its contact to B(9) is 1.51 Å. Here, and in **3** and **5**, the bridged B–B bond is the longest.

The molecule of $[Ag\{(PPh_2)_2C_2B_9H_{10}\}(phen)]$ **3** is shown in Fig. 3; the silver atom is chelated by one diphosphine and one phenanthroline ligand; the geometry at the silver centre is somewhat distorted from tetrahedral, with ligand 'bite' angles P(2)–Ag–P(1) 82.58(5)° and N(1)–Ag–N(2) 71.5(2)° (Table 4), similar to those obtained for the *closo*-derivative[12] $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(phen)]ClO_4$ [P–Ag–P 89.38(6), N–Ag–N 72.7(2)°]. The P–Ag–P angle is also similar to that found for the *nido*-ligand in **1**. The dihedral angle between planes Ag, P(1), P(2) and Ag, N(1), N(2) is 73.40(1)° (79.2° for the *closo*-derivative).

The Ag–P bond distances are 2.465(2) and 2.4906(14) Å, of the same order as those in the *closo*-derivative[12] [2.463(2), 2.479(2) Å] and shorter than those in the four-co-ordinate silver complexes $[Ag(PPh_3)_4]X$[22–26] [2.650(2), 3 × 2.688(5) Å] and are at the extremes of those found in the *closo*-derivative [2.315(5), 2.333(5) Å] or in other tetrahedrally co-ordinated silver(I) complexes with macrocycles as ligands.[27] The central boron atom of the C_2B_3 open face is bonded to two hydrogen atoms with an H ⋯ B(9) contact of 1.57 Å.

Table 4 Selected bond lengths (Å) and angles (°) for complex **3**

Ag–N(1)	2.295(4)	Ag–N(2)	2.407(4)
Ag–P(1)	2.465(2)	Ag–P(2)	2.4906(14)
P(1)–C(7b)	1.841(5)	P(2)–C(8b)	1.838(5)
N(1)–C(2)	1.316(6)	N(1)–C(10b)	1.365(6)
N(2)–C(9)	1.316(6)	N(2)–C(10a)	1.352(6)
C(2)–C(3)	1.420(8)	C(3)–C(4)	1.359(7)
C(4)–C(4a)	1.401(7)	C(4a)–C(10b)	1.402(7)
C(4a)–C(5)	1.436(7)	C(5)–C(6)	1.351(7)
C(6)–C(6a)	1.422(7)	C(6a)–C(7)	1.390(8)
C(6a)–C(10a)	1.416(7)	C(7)–C(8)	1.367(8)
C(8)–C(9)	1.408(7)	C(10a)–C(10b)	1.437(7)
C(7b)–C(8b)	1.616(6)	C(7b)–B(11)	1.629(8)
C(7b)–B(2)	1.740(7)	C(7b)–B(3)	1.747(8)
C(8b)–B(9)	1.626(8)	C(8b)–B(3)	1.724(7)
C(8b)–B(4)	1.725(7)	B(9)–B(10)	1.862(9)
N(1)–Ag–N(2)	71.5(2)	N(1)–Ag–P(1)	121.99(11)
N(2)–Ag–P(1)	125.98(12)	N(1)–Ag–P(2)	146.38(11)
N(2)–Ag–P(2)	114.59(11)	P(1)–Ag–P(2)	82.58(5)
C(7b)–P(1)–Ag	107.3(2)	C(8b)–C(7b)–P(1)	115.8(3)
C(7b)–C(8b)–P(2)	117.6(3)		

The molecule of complex **5** is shown in Fig. 4. The structure was rendered less precise by the presence of five solvent molecules, but the basic features are clear. The silver centre is chelated by two different types of diphosphines, thus possessing a distorted-tetrahedral geometry. The distortions mainly arise from the restricted bites of the diphosphines, P(2)–Ag–P(1) 84.90(6) and P(4)–Ag–P(3) 82.33(6)° (Table 5), similar values to those noted for complexes **1** and **3**. The dihedral angle between the two planes defined by Ag, P(1), P(2) and Ag, P(3), P(4) is 68.5°. The five-membered chelate rings display an envelope conformation, with the silver atom 0.674 and 0.724 Å out of the plane of the other four atoms. The Ag–P distances lie in the range 2.511(2)–2.575(2) Å, longer than those in complex **3** but still shorter than those in $[Ag(PPh_3)_4]^+$. The bridging hydrogen is bonded to B(10), with a contact to B(11) of 1.42 Å.

Experimental

Instrumentation

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} solution, with a Philips 9509 conductimeter. The elemental analyses (C,H) were carried out with a Perkin-Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec, with the FAB technique, using nitrobenzyl alcohol as matrix, NMR spectra on Varian 300 Unity and Bruker ARX 300 spectrometers in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (external, ^1H), 85% H_3PO_4 (external, ^{31}P) and $BF_3{\cdot}OEt_2$ (external, ^{11}B). The yields, melting points, analyses, conductivities and $^{31}P-\{^1H\}$ NMR data for the new complexes are listed in Table 1.

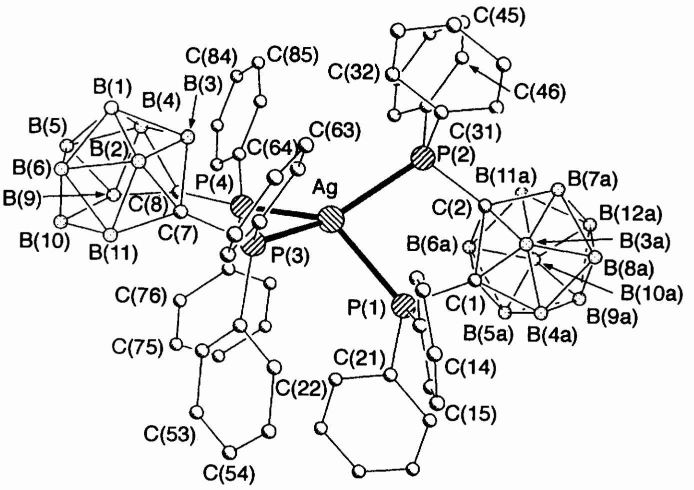


Fig. 4 Structure of complex **5** in the crystal. Details as in Fig. 2

Table 5 Selected bond lengths (Å) and angles (°) for complex **5**

Ag–P(4)	2.511(2)	Ag–P(2)	2.530(2)
Ag–P(3)	2.559(2)	Ag–P(1)	2.575(2)
P(1)–C(1)	1.865(7)	P(2)–C(2)	1.872(7)
P(3)–C(7)	1.837(6)	P(4)–C(8)	1.838(7)
C(1)–C(2)	1.750(9)	C(7)–C(8)	1.606(9)
B(10)–B(11)	1.853(11)		
P(4)–Ag–P(2)	126.64(6)	P(4)–Ag–P(3)	82.33(6)
P(2)–Ag–P(3)	133.91(6)	P(4)–Ag–P(1)	132.69(6)
P(2)–Ag–P(1)	84.90(6)	P(3)–Ag–P(1)	100.42(7)
C(1)–P(1)–Ag	107.3(2)	C(2)–P(2)–Ag	108.5(2)
C(7)–P(3)–Ag	107.3(2)	C(8)–P(4)–Ag	108.0(2)
C(2)–C(1)–P(1)	117.1(4)	C(1)–C(2)–P(2)	116.8(4)
C(8)–C(7)–P(3)	118.3(4)	C(7)–C(8)–P(4)	117.9(4)

Materials

The compound $(PPh_2)_2C_2B_{10}H_{10}$ was prepared following literature procedures.[28] The syntheses of $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(PR_3)]ClO_4$, $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(L–L)]ClO_4$ and $[Ag(OClO_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]$ were carried out as previously described by us;[12] $[Ag(OClO_3)(PR_3)]$[29] were also prepared following literature procedures.

Syntheses

$[Ag\{(PPh_2)_2C_2B_9H_{10}\}(PR_3)]$ (PR_3 = PPh_3 1 or PPh_2Me 2). These complexes can be synthesized by two procedures. (*a*) To a suspension of $[Ag(OClO_3)(PR_3)]$ [0.1 mmol; 0.047 (PR_3 = PPh_3) or 0.041 g (PR_3 = PPh_2Me)] in ethanol (30 cm^3) was added $(PPh_2)_2C_2B_{10}H_{10}$ (0.1 mmol, 0.051 g). The mixture was refluxed for 30 min. The complexes, as white solids, were filtered off. (*b*) A suspension of $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(PR_3)]ClO_4$ [0.1 mmol; 0.098 (PPh_3) or 0.092 g (PPh_2Me)] in ethanol (30 cm^3) was refluxed for 1 h. Complexes **1** and **2** were filtered off. NMR: ^1H, **1** δ, 7.7–7.1 (m, 35 H, Ph) and −2.0 [m, 1 H, br (width, $\Delta \approx 90$ Hz)]; **2** δ 7.7–7.0 (m, 30 H, Ph), 2.04 [d, 3 H, Me, *J*(PH) 5.7] and −2.1 [m, 1 H, br ($\Delta \approx 180$ Hz)]; ^{11}B NMR, **1** δ −7.8 (s, br, 2B), −12.3 [d, 3B, *J*(BH) 83.9 Hz], −15.7 (s, br, 2B), −30.5 (m, 1B) and −35.02 [d, 1B, *J*(BH) 130.3]; **2** δ −7.6 [d, 2B, *J*(BH) 123.3], −12.6 [d, 3B, *J*(BH) 127.7], −16.1 (s, br, 2B), −30.6 (m, 1B) and −35.0 [d, 1B, *J*(BH) 135.7 Hz]. Mass spectra (FAB+); **1**, m/z = 608 ($[M - PPh_3]^+$, 22), 871 ($[M]^+$, 66), 980 ($[M + Ag]^+$, 6) and 1242 ($[M + AgPPh_3]^+$, 7); **2**, m/z 608 ($[M - PPh_2Me]^+$, 13), 809 ($[M]^+$, 44) and 1117 ($[M + AgPPh_2Me]^+$, 3%).

$[Ag\{(PPh_2)_2C_2B_9H_{10}\}(L–L)]$ (L–L = phen 3, dppsm 4 or dppc 5). (*a*) In a similar manner, a suspension of $[Ag(OClO_3)\{(PPh_2)_2C_2B_{10}H_{10}\}]$ (0.1 mmol, 0.072 g) in ethanol (30 cm^3) was treated with L–L [0.1 mmol; 0.018 (phen); 0.044 (dppsm) or 0.051 g (dppc)]. The mixture was refluxed for 1 h, and then complexes **3**–**5** were filtered off. (*b*) A suspension

Table 6 Details of data collection and structure refinement for complexes **1**, **3** and **5**

	1	3	$5 \cdot 4.5CH_2Cl_2$
Chemical formula	$C_{44}H_{45}AgB_9P_3$	$C_{38}H_{38}AgB_9N_2P_2$	$C_{56.5}H_{69}AgB_{19}Cl_9P_4$
M	871.87	789.80	1504.31
Crystal habit	Yellow plate	Yellow plate	Pale yellow prism
Crystal size/mm	0.80 × 0.45 × 0.05	0.40 × 0.35 × 0.10	0.40 × 0.30 × 0.30
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	12.192(2)	15.482(2)	13.820(5)
b/Å	13.307(2)	13.766(2)	14.549(5)
c/Å	14.688(2)	17.242(3)	20.398(6)
α/°	78.528(10)	—	77.04(3)
β/°	68.511(14)	93.218(12)	71.99(2)
γ/°	73.704(14)	—	69.54(2)
$U/Å^3$	2115.8(6)	3668.8(10)	3623(2)
Z	2	4	2
$D_c/Mg\ m^{-3}$	1.369	1.430	1.379
F(000)	892	1608	1526
T/°C	−100	−100	−130
$2\theta_{max}/°$	50	50	50
$\mu(Mo\text{-}K\alpha)/mm^{-1}$	0.622	0.669	0.735
Transmission	0.859–0.938	—	0.807–0.908
No. reflections measured	7795	6587	15 683
No. unique reflections	7416	6364	12 807
R_{int}	0.048	0.048	0.074
R^a [*F*, where $F > 4\sigma(F)$]	0.039	0.046	0.082
$wR^b(F^2$, all reflections)	0.071	0.094	0.238
No. parameters	526	436	718
No. restraints	466	383	496
S^c	0.854	0.819	1.019
Maximum $\Delta\rho/e\ Å^{-3}$	0.519	0.594	2.75

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$ and *a* and *b* are constants adjusted by the program. [c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{\frac{1}{2}}$, where *n* is the number of data and *p* the number of parameters.

of $[Ag\{(PPh_2)_2C_2B_{10}H_{10}\}(L\text{–}L)]ClO_4$ [0.1 mmol; 0.089 (phen), 0.117 (dppsm) or 0.123 g (dppc)] in ethanol (30 cm^3) was refluxed for 1 h. The complexes **3**–**5** were filtered off. NMR: ^1H, **3**; δ 8.80 [d, 2 H, *J*(HH) 4.4], 8.38 [d, 2 H, *J*(HH) 7.9], 7.88 (s, 2 H), 7.76 [dd, 2 H, *J*(HH) 7.9, 4.4], 7.0–7.4 (m, 20 H, Ph), and −2.0 [m, 1 H, br (width, Δ ≈ 180 Hz)]; **4**, δ 7.8–6.8 (m, 40 H, Ph), 3.4 (m, 2 H, CH_2), and −2.2 [m, 1 H, br (Δ ≈ 108 Hz)]; **5**, δ 7.6–6.9 (m, 40 H, Ph) and −2.2 [m, 1 H, br (Δ ≈ 120 Hz)]; ^{11}B, δ −0.8 (s, br, 2B), −7.9 [d, 3B, *J*(BH) 103.5], −12.6 [d, 2B, *J*(BH) 121.9], −31.3 (m, 1B) and −34.5 [d, 1B, *J*(BH) 112.5]; **5**, δ 0.3 (s, br, 2B), −7.2 (s, br, 3B), −11.9 (s, br, 2B), −29.8 (m, 1B) and −34.5 [d, 1B, *J*(BH) 99.9 Hz]. Mass spectra (FAB+): **3**, *m*/*z* = 789 ($[M]^+$, 18); **4**, *m*/*z* = 1069 ($[M + B]^+$, 12), 1059 ($[M]^+$, 6%) and 557 ($[Ag(dppsm)]^+$, 100); **5**, *m*/*z* 1129 ($[M + Ag]^+$, 6), 1122 ($[M]^+$, 66), 620 ($[M - (PPh_2)_2C_2B_9H_{10}]^+$, 100) and 608 ($[M - (PPh_2)_2C_2B_{10}H_{10}]^+$, 12%).

Crystallography

Crystals of complexes **1**, **3** and **5** were mounted in inert oil on glass fibres. Data were collected using monochromated Mo-Kα radiation (λ = 0.710 73 Å). For **1** and **3**: Siemens P4 diffractometer with LT-2 low-temperature attachment, scan type ω, cell constants refined from setting angles of *ca.* 65 reflections to $2\theta_{max}$ 25°. For **5**: Stoe STADI-4 diffractometer, scan type ω–θ, cell constants from ±ω angles of 54 reflections to $2\theta_{max}$ 22°. Absorption corrections were applied on the basis of ψ scans for **1** and **5**.

Structures were solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL 93.[30] A system of restraints to light-atom displacement-factor components and local ring geometry was used. All hydrogen atoms of the carbaborane moieties were identified in difference syntheses; the BHs on the open carbaborane face were refined 'freely' (although heavily restrained with the command SADI). Other hydrogen atoms were included using a riding model. The fifth dichloromethane site in complex **5** was not well defined and was arbitrarily refined with occupation factor 0.5. The relatively high *R* factor for **5** is attributable to the high solvent content. Further details are given in Table 6.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/244.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (No. PB94-0079) and the Fonds der Chemischen Industrie for financial support.

References

1 J. Plesek, *Chem. Rev.*, 1992, **92**, 269.
2 M. F. Hawthorne, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 950.
3 R. F. Barth, A. H. Soloway and R. G. Fairchild, *Cancer Res.*, 1990, **50**, 1061.
4 *Clinical Aspects of Neutron Capture Therapy*, eds. R. G. Fairchild, V. P. Bond and A. D. Woodhead, Plenum, New York, 1989.
5 D. A. Brown, H. M. Colquhoun, J. A. Daniels, J. A. H. MacBride, I. R. Stephenson and K. Wade, *J. Mater. Chem.*, 1992, **2**, 793 and refs. therein.
6 M. F. Hawthorne, J. F. Liebman, A. Greenberg and R. E. Willians (Editors), *Advances in Boron and the Boranes*, VCH, New York, 1988, ch. 10, p. 225.
7 R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1642.
8 F. Teixidor, C. Viñas, M. M. Abad, M. López and J. Casabó, *Organometallics*, 1993, **12**, 3766.
9 F. Teixidor, C. Viñas, M. M. Abad, R. Nuñez, R. Kivekäs and R. Sillanpää, *J. Organomet. Chem.*, 1995, **503**, 193.
10 O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1992, 1601.
11 O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Inorg. Chem.*, 1996, **35**, 1361.
12 E. Bembenek, O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Chem. Ber.*, 1994, **127**, 835.
13 F. Teixidor, C. Viñas, M. M. Abad, R. Kivekäs and R. Sillanpää, *J. Organomet. Chem.*, 1996, **509**, 139.
14 J. Buchanan, E. M. J. Hamilton, D. Reed and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1990, 677.
15 L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, K. Nestor, M. Thornton-Pett, S. Hermánek, T. Jelinek and B. Stíbr, *J. Chem. Soc., Dalton Trans.*, 1990, 681.
16 D. V. Howe, C. J. Jones, R. J. Wiersema and M. F. Hawthorne, *Inorg. Chem.*, 1971, **10**, 2516.
17 F. Teixidor, C. Viñas and R. W. Rudolph, *Inorg. Chem.*, 1986, **25**, 3339.
18 D. Reed, *Chem. Soc. Rev.*, 1993, 109.
19 M. Barrow, H. B. Bürgi, M. Camalli, F. Caruso, E. Fischer, L. M. Venanzi and L. Zambonelli, *Inorg. Chem.*, 1983, **22**, 2356.
20 M. C. Gimeno, A. Laguna, C. Sarrroca and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1995, 1473.
21 S. J. Berners-Price, C. Brevard, A. Pagelot and P. J. Sadler, *Inorg. Chem.*, 1985, **24**, 4278.
22 S. J. Berners-Price and J. P. Sadler, *Struct. Bonding (Berlin)*, 1988, 27.
23 F. A. Cotton and R. L. Luck, *Acta Crystallogr., Sect. C*, 1989, **45**, 1222.
24 P. F. Batton, J. C. Dyason, P. C. Healy, L. M. Engelhardt, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1986, 1965.
25 H. Adams, N. A. Bailey, W. D. Carlisle, D. E. Fenton and G. Rossi, *J. Chem. Soc., Dalton Trans.*, 1990, 1271.
26 L. M. Engelhardt, C. Pakawatchai, A. H. White and P. C. Healy, *J. Chem. Soc., Dalton Trans.*, 1985, 125.
27 C. Stockhein, K. Wieghardt, B. Nuber, J. Weiss, U. Flörke and H. J. Haupt, *J. Chem. Soc., Dalton Trans.*, 1991, 1487.
28 R. P. Alexander and H. Schroeder, *Inorg. Chem.*, 1963, **2**, 1107.
29 F. A. Cotton, L. F. Falvello, R. Usón, J. Forniés, M. Tomás, J. M. Casas and I. Ara, *Inorg. Chem.*, 1987, **26**, 1366.
30 G. M. Sheldrick, SHELXL 93, A Program for Crystal Structure Refinement, University of Göttingen, 1993.

Received 5th June 1996; *Paper* 6/03959F