Silver Phosphanes Partnered with Carborane Monoanions: Synthesis, Structures and Use as Highly Active Lewis Acid Catalysts in a Hetero-Diels–Alder Reaction

Nathan J. Patmore, Catherine Hague, Jamie H. Cotgreave, Mary F. Mahon, Christopher G. Frost,* and Andrew S. Weller*[a]

Abstract: Four Lewis acidic silver phosphane complexes partnered with [1-*closo*-$CB_{11}H_{12}$]$^-$ and [1-*closo*-$CB_{11}H_6Br_6$]$^-$ have been synthesised and studied by solution NMR and solid-state X-ray diffraction techniques. In the complex [$Ag(PPh_3)(CB_{11}H_{12})$] (**1**), the silver is coordinated with the carborane by two stronger 3c–2e B–H–Ag bonds, one weaker B–H–Ag interaction and a very weak $Ag\cdots C_{arene}$ contact in the solid state. In solution, the carborane remains closely connected with the {$Ag(PPh_3)$}$^+$ fragment, as evidenced by ^{11}B chemical shifts. Complex **2** [$Ag(PPh_3)_2(CB_{11}H_{12})$]$_2$ adopts a dimeric motif in the solid state, each carborane bridging two Ag centres. In solution at low temperature, two distinct complexes are observed that are suggested to be monomeric [$Ag(PPh_3)_2$][$CB_{11}H_{12}$] and dimeric [$Ag(PPh_3)_2(CB_{11}H_{12})$]$_2$. With the more weakly coordinating anion [$CB_{11}H_6Br_6$]$^-$ and one phosphane, complex **3** [$Ag(PPh_3)(CB_{11}H_6Br_6)$] is isolated. Complex **4**, [$Ag(PPh_3)_2$-($CB_{11}H_6Br_6$)], has been characterised spectroscopically. All of the complexes have been assessed as Lewis acids in the hetero-Diels–Alder reaction of *N*-benzylideneaniline with Danishefsky's diene. Exceptionally low catalyst loadings for this Lewis acid catalysed reaction are required (0.1 mol%) coupled with turnover frequencies of 4000 h^{-1} (quantitative conversion to product after 15 minutes using **3** at room temperature). Moreover, the reaction does not occur in rigorously dry solvent as addition of a substoichiometric amount of water (50 mol%) is necessary for turnover of the catalyst. It is suggested that a Lewis assisted Brønsted acid is formed between the water and the silver. The effect of changing the counterion to [BF_4]$^-$, [OTf]$^-$ and [ClO_4]$^-$ has also been studied. Significant decreases in reaction rate and final product yield are observed on changing the anion from [$CB_{11}H_6Br_6$]$^-$, thus demonstrating the utility of weakly coordinating carborane anions in organic synthesis.

Keywords: carboranes · cluster compounds · cycloaddition · homogeneous catalysis · silver

Introduction

Monoanionic carborane anions based around [*closo*-1-$CB_{11}H_{12}$]$^-$ (**A**, see Scheme 1) are among the most inert and least coordinating anions currently known.[1, 2] The high chemical stability and low nucleophilicity of these ions means that they have been used to stabilise exotic cationic species, which are not isolatable with other, more coordinating, anions.[3–6] Such anions also have the potential to act as partners with cationic Lewis acidic transition metal complexes that take part in various catalytic processes. Somewhat surprisingly, given the almost ubiquitous use of [$B(C_6F_5)_4$]$^-$ and derivatives in such applications, there are only a few reports of anions such as **A** or related compounds utilised in catalytic processes,[7–10] despite their potential advantages over perfluorinated borates.[11, 12]

The coordination chemistry of cationic silver(I) phosphane complexes (combined with a range of anions) has been studied in some detail,[13–16] to the point that useful structural predications may be made on the basis of spectroscopic data.[17] Silver phosphanes *exo*-coordinated to polyhedral boranes are rarer,[18] but recent work, particularly from Stone et al.[19–21] has established this area. Related complexes in which *exo*-coordinated silver is bound to ligands other than phosphane,[22–25] or arene solvent molecules[26–29] or where the silver is partnered with halogeno-substituted carboranes[27, 30–33] are also known.

One of us has a current interest in the synthesis, structures and reactivity of Lewis acidic transition metal complexes partnered with anion **A** and derivatives.[24, 25] Concurrently, there is also interest in Lewis acid catalysis using silver(I) salts as effective promoters of a wide-range of organic transformations including allylation, aldol, ene and glycosylation

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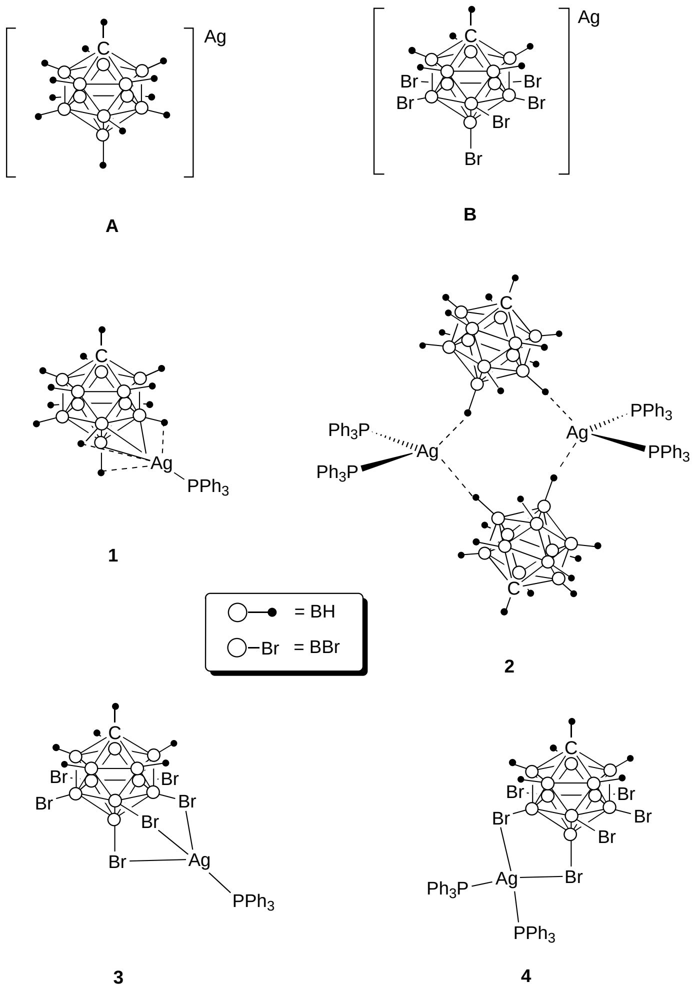


Scheme 1. Structures **A** and **B** and **1**–**4**.

reactions.[34] Of particular note is the use of silver(I) BINAP ([1,1′-binaphthalene]-2,2′-diylbis(diphenylphosphane)) complexes in asymmetric aldol reactions,[35–38] Mukaiyama aldol reactions,[39] asymmetric allylations[40] and hetero-Diels–Alder reactions.[41] It is well established that these reactions are accelerated by other Lewis acids (for example: Ti, B, Al, Sn complexes). However, many of these established catalysts are sensitive to air, water and product inhibition and consequently are used at a low substrate/catalyst ratio. The use of silver(I) phosphane complexes can provide a practical solution, with many precatalysts being stable in air and retaining activity in the presence of reaction product. Nevertheless, the best examples from the literature routinely employ high catalytic loadings (5–10 mol%) to achieve competitive rates and product yields. We are thus interested in developing silver(I) Lewis acids complexed with carborane anions in anticipation that the weakly coordinating nature of the anions will reveal enhanced activity for these systems. The hetero-Diels–Alder reaction is one of the most useful methods for the synthesis of bioactive heterocycles. Hence we chose to test our new complexes in this challenging reaction with the intention of identifying structure–activity relationships when the coordination sphere of the silver (number of phosphanes, anion) is systematically changed.

We report here the synthesis and solution and solid-state structural investigations for complexes of the formula $[Ag(PPh_3)_n(CB_{11}H_6Y_6)]$ ($n = 1$, 2; Y = H, Br) and their use as active catalysts in the hetero-Diels–Alder reactions of *N*-benzylideneaniline with Danishefsky's diene. Aspects of this work have been communicated previously.[42]

Results and Discussion

Synthesis and structures: Silver(I) salts of monoanionic carborane anions are readily prepared and are air stable and useful synthons for subsequent reactions. For example, they can be used in silver salt metathesis reactions to introduce a carborane anion into a metal's coordination sphere[23, 25, 29, 43, 44] or to generate synthetically useful salts.[28] In addition they often have significant solubility in aromatic solvents compared with other cations, facilitating more complete characterisation of the cation/anion pair. In principle, they also provide a useful starting point for the investigation of silver(I) complexes of the general formula $[Ag(L)_n(CB_{11}H_6Y_6)]$ (L = two electron donor; Y = H, halogen) as simple addition of the required ligand (L) results in complex formation.

Addition of slightly less than one equivalent (to avoid formation of **2**, vide infra) of PPh_3 to a suspension of $Ag[CB_{11}H_{12}]$ in CH_2Cl_2 results in the formation of $[Ag(PPh_3)(CB_{11}H_{12})]$, **1**, as an analytically pure solid in good isolated yield after recrystallisation (Tables 1 and 2). The solid-state structure of **1** is presented in Figure 1. The $\{AgPPh_3\}^+$ fragment interacts with the carborane anion through the three {BH} units that form the B(12)–B(7)–B(8) polyhedral face, a coordination motif seen previously in $[(Cp^*)ZrMe_2\text{-}\eta^3\text{-}(CB_{11}H_{12})]$.[10] The silver phosphane fragment does not sit over the centre of this face but is more localised towards B(8) and the corresponding Ag–B bond lengths reflect this: Ag(1)–B(8) 2.504(1) Å, Ag(1)–B(12) 2.569(3) Å, Ag(1)–B(7) 2.619(2) Å. These bond lengths are broadly similar to those previously reported for the related complex $[2,2,2\text{-}(CO)_3\text{-}2\text{-}PPh_3\text{-}7,12\text{-}\{Ag(PPh_3)\}\text{-}\mathit{closo}\text{-}2,1\text{-}MoCB_{10}H_9]$[20, 21] (2.552(4) Å and 2.589(4) Å), in which the Ag centre is bound dihapto by the cage and is the only other *closo*-polyhedral borane structure reported with an *exo*-$\{AgPR_3\}$ fragment, although there are others reported with ligands other than phosphane,[22] with Ag–metal bonds[21] and with *endo* coordination of a silver fragment.[18] The location of the silver phosphane fragment in relation to the B(8)–B(12) bond is such that the silver atom adopts a planar coordination motif with respect to P(1), B(8) and B(12) with the sum of relevant angles around Ag(1) 359.7°. P(1) essentially lies on the same plane formed by Ag(1), B(8) and B(12) (max deviation from plane 0.083 Å for P(1)), resulting in an apparent vacant coordination site *transoid* to H(7). Inspection of the extended lattice packing diagram shows that there are no Ag···H–B intermolecular interactions directed towards this vacant site.[18, 20] However, there is a long intermolecular interaction (3.348 Å) between Ag(1) and C(35)′ of a phenyl ring in a symmetry related molecule (Figure 2), and the arene carbon approaches the silver from the reverse of the trigonal

Table 1. Crystal data and structure refinement for **1**, **2** and **3**.

	1	**2**	**3**
empirical formula	$C_{19}H_{27}AgB_{11}P$	$C_{74}H_{84}Ag_2B_{22}P_4$	$C_{19}H_{21}AgB_{11}Br_6P$
M_r	513.16	1550.85	986.57
T [K]	150(2)	170(2)	150(2)
λ [Å]	0.71073	0.71069	0.71073
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	10.282(2)	11.6963(2)	8.89500(10)
b [Å]	10.988(2)	13.1668(2)	24.4140(4)
c [Å]	11.308(2)	14.1393(2)	14.4170(3)
α [°]	76.22(3)	96.8860(6)	90
β [°]	75.25(3)	106.8980(7)	102.0720(10)
γ [°]	75.61(3)	110.5370(8)	90
V [Å^3]	1175.7(4)	1890.30(5)	3061.60(9)
Z	2	1	4
ρ_{calcd} [mg m^{-3}]	1.450	1.362	2.140
μ [mm^{-1}]	0.932	0.646	8.554
$F(000)$	516	792	1848
crystal size [mm]	0.20 × 0.20 × 0.10	0.25 × 0.20 × 0.17	0.10 × 0.10 × 0.05
θ range [°]	2.96 to 27.50	3.38 to 27.50	3.71 to 27.88
reflections collected	20702	22570	23164
independent reflections	5374 [R(int) = 0.0387]	8605 [R(int) = 0.0250]	7253 [R(int) = 0.0519]
reflections observed (> 2σ)	4538	7964	5880
max and min transmission	0.9126 and 0.8355	1.027, 0.981	0.66 and 0.47
data/restraints/parameters	5374/0/302	8605/2/478	7253/0/349
goodness of fit on F^2	1.018	1.050	1.041
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0316$ $wR_2 = 0.0757$	$R_1 = 0.0289$ $wR_2 = 0.0738$	$R_1 = 0.0358$ $wR_2 = 0.0783$
R indices (all data)	$R_1 = 0.0417$ $wR_2 = 0.0813$	$R_1 = 0.0323$ $wR_2 = 0.0763$	$R_1 = 0.0521$ $wR_2 = 0.0855$
largest diff. peak and hole [e Å^{-3}]	0.544 and −0.923	1.727 and −0.584	1.081 and −1.181

Table 2. Selected bond lengths [Å] and angles [°] for the new compounds **1**–**3**.

Compound **1**			
Ag(1)–P(1)	2.3625(7)	P(1)–Ag(1)–B(7)	142.11(6)
Ag(1)–B(7)	2.619(3)	P(1)–Ag(1)–B(8)	158.23(6)
Ag(1)–B(8)	2.504(3)	P(1)–Ag(1)–B(12)	160.32(6)
Ag(1)–B(12)	2.569(3)	B(12)–Ag(1)–B(8)	41.26(8)
Ag(1)–H(7)	2.36(2)	B(12)–Ag(1)–B(7)	40.37(8)
Ag(1)–H(8)	2.14(2)	B(7)–Ag(1)–B(8)	40.98(8)
Ag(1)–H(12)	2.26(2)		
Compound **2**			
Ag(1)–P(1)	2.4698(3)	Ag(1)–H(12)′	2.17(2)
Ag(1)–P(2)	2.4741(3)	Ag(1)–H(7)	2.51(2)
Ag(1)–B(7)	3.494(2)	P(1)–Ag(1)–P(2)	130.90(1)
Ag(1)–B(12)′	2.892(2)	B(7)–Ag(1)–B(12)′	72.4(6)
Compound **3**			
Ag(1)–P(1)	2.4032(10)	P(1)–Ag(1)–Br(7)	117.44(3)
Ag(1)–Br(7)	2.8710(5)	P(1)–Ag(1)–Br(8)	155.55(3)
Ag(1)–Br(8)	2.6963(5)	P(1)–Ag(1)–Br(12)	93.31(3)
Ag(1)–Br(12)	3.0953(5)	P(1)–Ag(1)–Br(11)′	157.15(1)
Ag(1)–Br(11)′	3.4901(5)	Br(7)–Ag(1)–Br(8)	87.471(14)

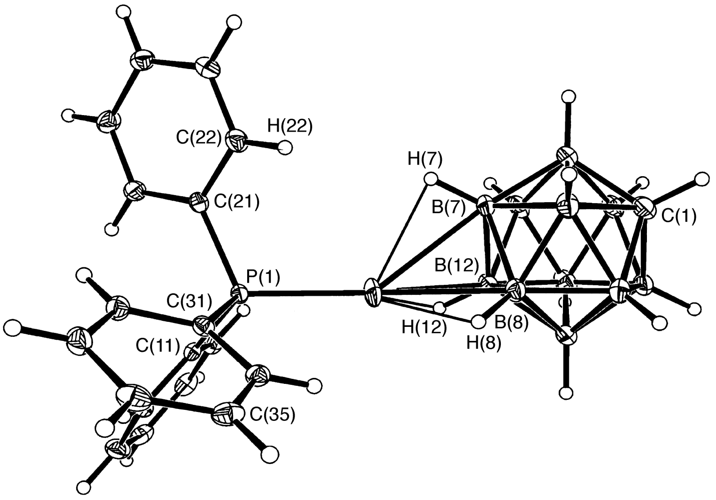


Figure 1. Molecular structure of complex **1**, showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

plane formed by B(8), B(12), Ag(1) and P(1). Although this distance is very long compared with other reported silver–arene bond lengths found in the solid-state structure of Ag carboranes (ca. 2.5–2.6 Å), we suggest that it may be significant, given the observed orientation of the silver phosphane fragment with respect to the cage. Indeed, gas-phase DFT calculations on **1** show that the silver adopts the expected tetrahedral geometry when there are no intermolecular interactions,[45] while comparable weak silver–arene contacts have been previously identified.[46, 47] The Ag(1)–P(1) distance, at 2.3625(7) Å, is at the shorter end of the range reported for [Ag(PPh$_3$)L] or [Ag(PPh$_3$)]X (X = counterion or two-electron ligand (L)) molecules[14, 16] suggesting a relatively strong AgP bond.

In solution, the ^{1}H{^{11}B} NMR spectrum of **1** shows a 1:1 ratio of phosphane to carborane anion. Resonances due to {BH} groups are observed at $\delta = 2.25$ and $\delta = 1.85$ in the ratio 1:10 (the latter is a 5+5 coincidence), with no high-field resonances potentially indicative of M–H–B interactions observed.[48] That only two {BH} resonances are observed suggests that the {AgPPh$_3$} fragment is fluxional over the surface of the cage and affords time-averaged C_{5V} symmetry in solution. This facile process is evidenced by no significant change observed in the spectrum when recorded at −90 °C.

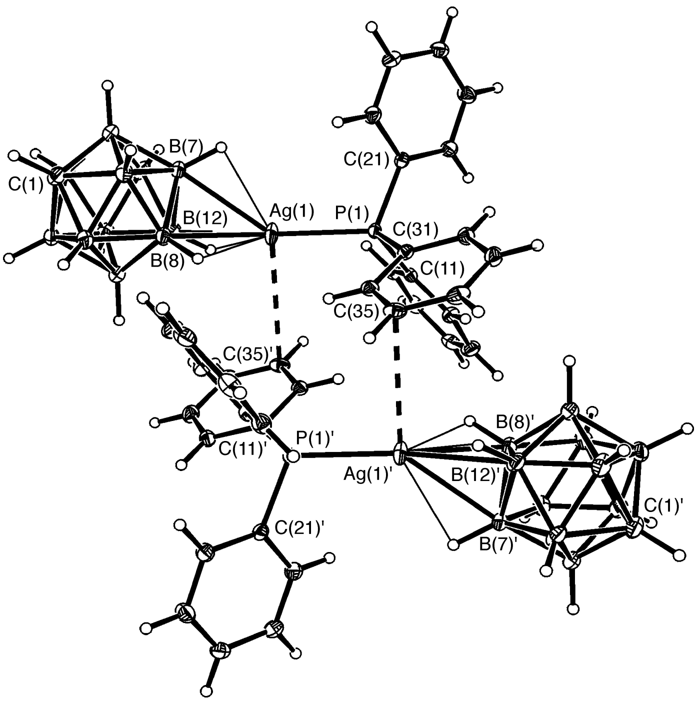


Figure 2. Dimeric unit formed in the extended lattice by $Ag\cdots C_{arene}$ contacts (Ag–C(35)′ 3.348 Å). Atom labelling and other details as in Figure 1.

Related metallaboranes with *exo*-coordinated $\{AgPPh_3\}$ fragments are also highly fluxional in solution.[20, 21] We were initially surprised to observe that the $^{11}B\{^1H\}$ NMR spectrum shows that both the antipodal [B(12)] and lower pentagonal belt [B(7)–(11)] borons undergo a significant upfield shift on complexation with the $\{AgPPh_3\}$ fragment when compared with $Ag[CB_{11}H_{12}]$ (Figure 3), while there is no significant shift in the {BH} resonances observed in the $^1H\{^{11}B\}$ NMR spectrum. This was unexpected as coordination of an *exo*-metal fragment results in significant upfield shifts of the *exo*-metal coordinated {BH} units in *both* the ^1H and ^{11}B NMR spectra in other systems.[25, 44] Specifically, in the $^{11}B\{^1H\}$ NMR spectrum, resonances are observed at $\delta = -10.3$, $\delta = -11.2$ and $\delta = -12.0$ in the ratio 1:5:5. This dichotomy between ^1H and ^{11}B chemical shifts may be indicative of the cage-silver bonding predominantly originating from Ag–B interactions,[49] with a reduced contribution (or perhaps a more electrostatic interaction) from the cage hydrogens. It is noteworthy that AgH interactions can be observed by ^1H NMR spectroscopy in certain cases and show both significant chemical shifts and AgH coupling constants,[50] neither of which are observed for complex **1**, or previously in related Ag cage compounds.[19–21]

Given that only the antipodal [B(12)] and lower pentagonal belt [B(7)–B(11)] boron atoms appear significantly perturbed in the ^{11}B NMR spectrum on coordination of the $\{AgPPh_3\}$ fragment, we suggest a mechanism to explain the observed fluxionality that incorporates the metal phosphane precessing around the five triangular faces formed between B(7)–B(11) and B(12). This mechanism is similar to that previously observed for the movement of $\{Rh(cod)\}^{+}$[44] or $\{Pt(tBu_2P(CH_2)_3PtBu_2)\}^{+}$[51] over the surface of [*closo*-$CB_{11}H_{12}]^-$. In the $^{31}P\{^1H\}$ NMR spectrum of **1**, a peak centred at $\delta = 18.70$ is observed as a pair of concentric doublets, due to ^{109}AgP and ^{107}AgP coupling, having an average value for $J(AgP)_{average}$ of 743 Hz. This large value is consistent with the strong AgP bond seen in the solid state and is also indicative of a low-coordinate silver phosphane species;[13] this suggests the observed solution and solid-state structures of **1** are similar.

Addition of two equivalents of PPh_3 to $Ag[CB_{11}H_{12}]$ gives complex **2**, having the empirical formula $[Ag(PPh_3)_2(CB_{11}H_{12})]$, which has been characterised by solution NMR spectroscopy and in the solid state by X-ray diffraction. The extra PPh_3 ligand has the effect of disturbing the silver-cage bonding from **1**, so that a dimeric, centrosymmteric, $[Ag(PPh_3)_2(CB_{11}H_{12})]_2$ unit is now observed (Figure 4), in which each carborane unit bridges two silver centres. Each cage interacts with the two silver centres through one shorter (Ag(1)–H(12)′ 2.17(2) Å, Ag(1)–B(12)′ 2.892(2) Å) and one longer (Ag(1)–H(7) 2.51(2) Å, Ag(1)–B(7) 3.494(2) Å) $Ag\cdots H–B$ interaction. This bonding mode to the two silver centres by the antipodal [B(12)] and a single lower pentagonal belt [B(7)] vertex is similar to that observed in the extended solid-state structure of $[Mo(Cp)(CO)_3I\cdot Ag(CB_{11}H_{12})]_2$.[24] Dimeric and tetrameric silver carborane complexes with cages other than $[CB_{11}H_{12}]^-$ have also been previously reported.[18, 20–22] As expected on moving to a higher coordination number in going from **1** to **2**, the Ag–P bond lengths are relatively longer in the latter complex (Ag(1)–P(1) 2.4698(3) Å, Ag(1)–P(2) 2.4741(3) Å). The P(1)–Ag(1)–P(2) angle of 130.90(1)° is similar to that observed in the three-coordinate complex $[Ag(PPh_3)_2(NCMe)][BF_4]$ (129.37(2)°).[14]

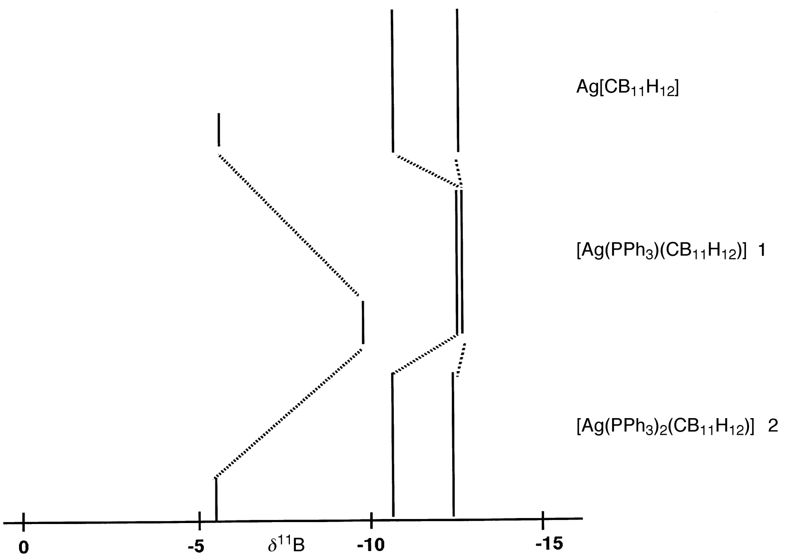


Figure 3. ^{11}B NMR chemical shift "stick" diagram comparing complexes **1** and **2** (solutions in CD_2Cl_2) with $Ag[CB_{11}H_{12}]$ (solution in $[D_6]$acetone).

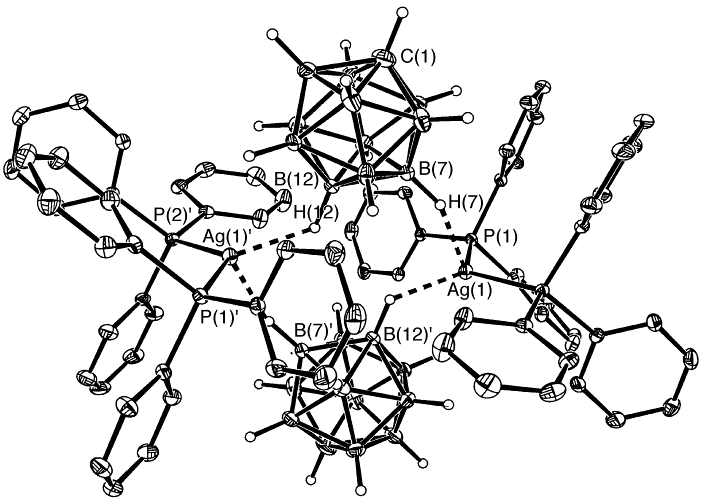


Figure 4. Molecular structure of complex **2**, showing the atom-numbering scheme. Phenyl hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

In solution at room temperature in **2**, the carborane does not interact significantly with the metal centre. This is evidenced in the ^{11}B NMR spectrum, which does not show any appreciable perturbation from that found for Ag[$CB_{11}H_{12}$], with three resonances observed at $\delta = -5.1$, -10.6 and -12.6 in the ratio 1:5:5 (Figure 3). These data reflect the significantly weaker Ag···H–B interactions apparent in **2**, relative to **1**, in the solid state. In the room-temperature $^{31}P\{^1H\}$ NMR spectrum of **2**, a single broad resonance centred at $\delta = 14.8$ is observed, suggesting that the phosphane ligands are undergoing an exchange process. Progressive cooling affords two broad singlets at $\delta = 15.4$ and $\delta = 13.2$ at 0 °C, which gradually sharpen into two sets of doublets at -60 °C, of approximately equal proportions, centred at $\delta = 13.7$ (J(AgP) = 333 Hz) and $\delta = 13.6$. The latter resonance is further observed as a pair of concentric doublets, showing coupling to both ^{109}Ag and ^{107}Ag ($J(\mathrm{AgP})_{\mathrm{average}} =$ 519 Hz). These changes in the NMR spectrum on cooling are consonant with the presence of two different complexes in solution at low temperature, which interconvert at ambient temperature. The species that reveals the larger AgP coupling constant has a value very similar to that reported for two-coordinate [Ag($PPh_3)_2$][BF_4] (J(AgP) = 530 Hz),[14] while the alternative species has a coupling constant intermediate between the three-coordinate [Ag($PPh_3)_2$Br] (J(AgP) = 385 Hz)[15] and four-coordinate [Ag($PPh_3)_4$][PF_6] ($J(^{107}$AgP) = 224 Hz)[13] silver phosphane complexes. On the basis of these observations, we tentatively suggest that, at low temperature an approximate 1:1 mixture consisting of the two-coordinate, ion-pair separated, species [Ag($PPh_3)_2$][$CB_{11}H_{12}$] and the dimeric [Ag($PPh_3)_2$($CB_{11}H_{12}$)]$_2$ is formed. No evidence for the disproportionation of **2** to form [Ag(PPh_3)][$CB_{11}H_{12}$] and [Ag($PPh_3)_3$][$CB_{11}H_{12}$] was seen in the low-temperature $^{31}P\{^1H\}$ NMR spectrum.[13] The low-temperature $^{11}B\{^1H\}$ NMR spectrum exhibits two broad peaks at $\delta = -5.8$ (1B) and $\delta = -11.6$(10B), essentially unshifted from room-temperature values.

The coordination chemistry of the anion [*closo*-$CB_{11}H_{12}$]$^-$ can be usefully compared with that of [*closo*-$CB_{11}H_6Br_6$]$^-$, in which the six lower hydrogen atoms in the cage are replaced with bromines, and it is considered to be significantly more weakly coordinating than [$CB_{11}H_{12}$]$^-$. While there are now a significant number of solid-state structural investigations on the silver salts of perhalogenated anions,[27, 30–33] there are few studies in which both the solution and solid-state structures of their transition metal complexes have been investigated. Addition of one equivalent of PPh_3 to a suspension of Ag[$CB_{11}H_6Br_6$] in CH_2Cl_2 affords the new complex [Ag(PPh_3)($CB_{11}H_6Br_6$)] (**3**). The solid-state structure of **3** is presented in Figure 5. On first inspection, the silver(I) centre is coordinated with the carborane anion through two shorter (2.6963(5) Å and 2.8710(5) Å) Ag–Br interactions and one longer one (3.0953(5) Å), all of which fall comfortably within the sum of the van der Waals radii for silver and bromine. These bond lengths are of similar values to those previously reported for silver complexes of [$CB_{11}H_6Br_6$]$^-$[31] and dibromoalkane complexes of silver.[52] The silver phosphane bond length (2.4032(10) Å) is slightly longer than that found in **1**. The phosphane phenyl groups adopt a relatively uncommon C_{2v} arrangement, a result of one phenyl group (C(2)–C(7)) twisting to minimise interactions with Br(12). Given that the silver is formally 4-connected in the asymmetric unit, the fact that it appears to adopt a *pseudo*trigonal planar, as opposed to a tetrahedral coordination motif (sum of relevant angles around Ag(1) is 360.5°) was on first inspection puzzling to us. However, similar to **1**, the packing diagram (Figure 6) reveals a long interaction (3.4901(5) Å) between Ag(1) and Br(11)′ on a symmetry related cage in the lattice; this bromine atom approaches Ag(1) approximately *trans* to Br(12) (Br(12)–Ag(1)–Br(11)′ 157.15(1)°). Although this distance is long, the coordination motif around the silver suggests that it is significant in the solid state. This interaction completes the coordination sphere at the silver centre. It also results in phenyl groups on symmetry related phosphanes having a close approach in the lattice (Figure 6), and the Ag(1)–P(1) vector being canted from lying equidistant between Br(7)

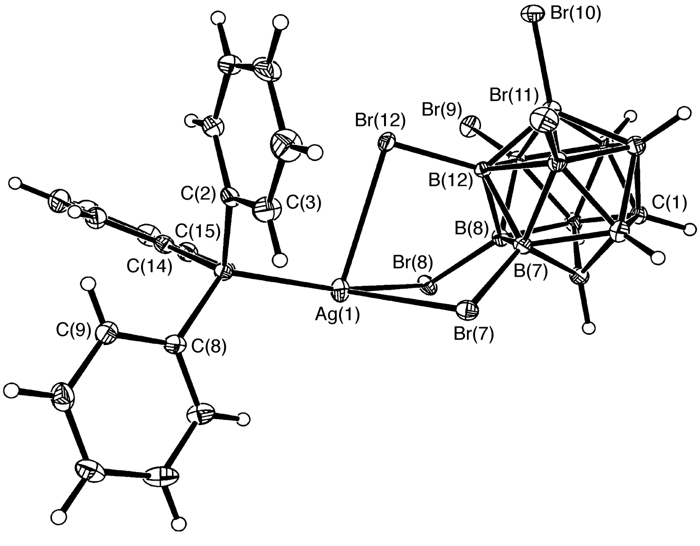


Figure 5. Molecular structure of complex **3**, showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

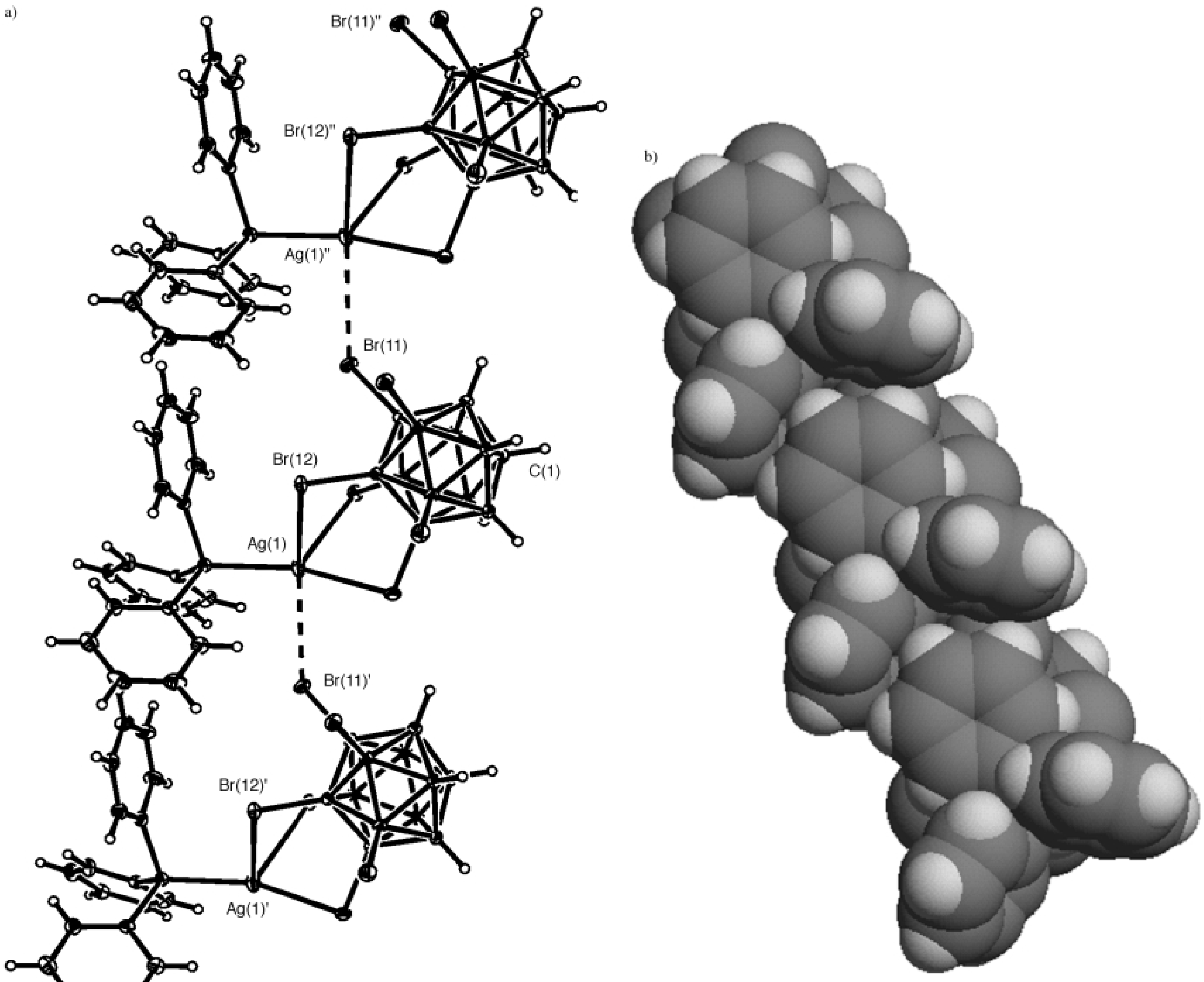
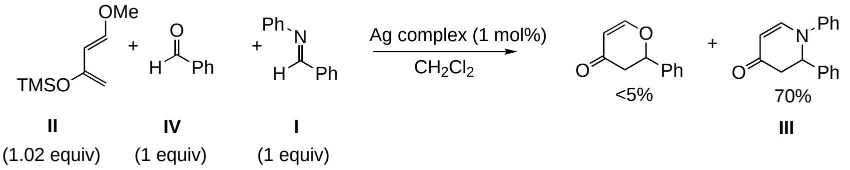


Figure 6. Extended solid-state structure apparent in complex **3**: a) showing weak axial Ag···Br interactions; b) space-filling diagram showing orientation of phenyl groups in the solid state.

and Br(8) (P(1)–Ag(1)–Br(8) 155.55(3)°, P(1)–Ag(1)–Br(7) 117.44(3)°).

In solution, C_{5v} symmetry is observed for the cage anion in the ^{11}B NMR spectrum, which shows that the $\{AgPPh_3\}^+$ fragment does not retain a rigid coordination motif with respect to the cage. The $^{31}P\{^1H\}$ NMR spectrum of **3** is similar to that of **1** with a resonance centred at $\delta = 16.52$ is observed as a concentric pair of doublets, $J(AgP)_{average} = 715$ Hz, suggesting that similar structures are adopted in solution for both complexes. This value is slightly smaller than that observed for **1**, in line with the slightly longer Ag–P bond observed in the solid state for **3** compared with complex **1**.[17]

Addition of two equivalents of PPh_3 to $Ag[CB_{11}H_6Br_6]$ results in the isolation of a white solid having the empirical formula $[Ag(PPh_3)_2(CB_{11}H_6Br_6)]$ (**4**). Despite repeated attempts, crystals suitable for X-ray diffraction could not be obtained, so characterisation of complex **4** was limited to NMR spectroscopy and microanalysis. In solution at room temperature, the $^{31}P\{^1H\}$ NMR spectrum of **4** has a broad singlet at $\delta = 12.9$, showing that the phosphane ligands are undergoing exchange under ambient conditions. The corresponding $^1H\{^{11}B\}$ NMR spectrum shows a 2:1 ratio of phosphane to cage, with no signals observed at high field. The low-temperature (−80 °C) $^{31}P\{^1H\}$ NMR spectrum shows that one species is present at this temperature, due to two concentric doublets centred around $\delta = 8.1$. The magnitude of the AgP coupling constant ($J(AgP)_{average} = 240$ Hz) is very small and of the same order of that associated with $[Ag(PPh_3)_4]^+$.[13] To account for this, a low-temperature limiting structure that has a sp^3 hybridised silver(I) centre is suggested, in which the hexabromo carborane anion is coordinated to the silver by two of the bromines on the cage. That there is a more intimate contact between the halogenated cage and silver in **4** compared with the silver-cage contact



Scheme 3. Activation of imines in the presence of aldehydes by silver complex **3**.

in **2** is further reflected in the relative catalytic activities of these two compounds, which will be presented later. While we have taken measures to use pure samples (recrystallised material used exclusively for NMR and catalysis experiments), we cannot completely rule out the presence of small amounts of free PPh_3 in **2** and **4**, which would lead to rapid phosphane exchange at room temperature.[13]

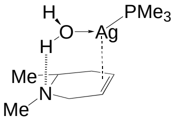
Catalysis: We have investigated the reaction between *N*-benzylideneaniline (**I**) and Danishefsky's diene (**II**) (Scheme 2) with the silver complexes **1** to **4**. Importantly, in the absence of any catalyst there was only a trace (less than 5%) of product after 24 hours at room temperature. Initial experiments using freshly distilled reagent grade solvents revealed that the addition of 1 mol% of silver complex promoted the efficient formation of the product (**III**) in less than one hour at room temperature (Table 3). On the bench under these conditions, complexes **1** to **4** were significantly more active than $[Ag(PPh_3)(OTf)]$ and $[Ag(PPh_3)(BF_4)]$ whilst $[Ag(PPh_3)(ClO_4)]$ was of comparable activity. Remarkably, the catalyst loading could be lowered to 0.1 mol% of complex **3** and the reaction was still complete in less than thirty minutes to afford an isolated yield of 99% product (>2000 turnovers $hour^{-1}$).

Table 3. Yields of compound **III**. Catalyst (1 mol%); imine **I** (1.1 mmol); Danishefsky's diene (**II**) (1.65 mmol). Yields reported are after reaction for 60 minutes at room temperature and workup (see Experimental Section for full details).

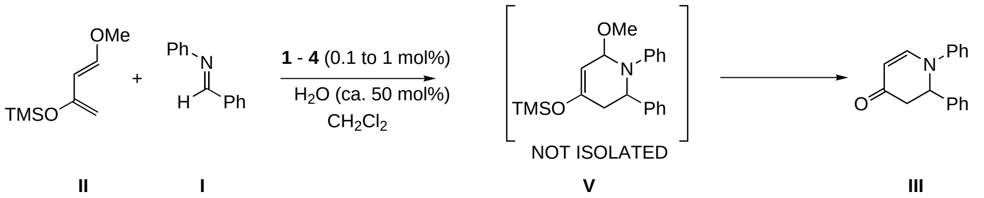
	Complex	Isolated yield of **III** [%]
1	$[Ag(PPh_3)(BF_4)]$	35
2	$[Ag(PPh_3)(OTf)]$	70
3	$[Ag(PPh_3)(ClO_4)]$	90
4	$[Ag(PPh_3)(CB_{11}H_{12})]$ (**1**)	98
5	$[Ag(PPh_3)_2(CB_{11}H_{12})]$ (**2**)	99
6	$[Ag(PPh_3)(CB_{11}H_6Br_6)]$ (**3**)	99
7	$[Ag(PPh_3)_2(CB_{11}H_6Br_6)]$ (**4**)	85

A competition experiment illustrated that silver complex **3** could preferentially activate imines in the presence of aldehydes (Scheme 3). When Danishefsky's diene (**II**) was added to a 1:1 mixture of benzaldehyde (**IV**) and imine (**I**) in the presence of 1 mol% of **3**, the product arising from the reaction, after 15 minutes at room temperature, was isolated in 70% yield whilst the aldehyde adduct was produced in only 5% yield. According to the classification system suggested by Kobayashi et al.,[53] the silver catalyst is thus an A-2 Lewis acid (active, imine selective).

Prompted by these results we decided to follow the reactions by ^1H NMR spectroscopy, using catalyst loadings of 0.1 mol%, in the anticipation of uncovering structure–activity relationships involving counterion and/or phosphane ligands. This initially resulted in the unexpected observation that the reaction between diene **II** and imine **I** did not proceed (no reaction after ca. two hours at room temperature) when in the NMR tube, using rigorously dried solvent (CD_2Cl_2 vacuum distilled from CaH_2). However, addition of a substoichiometric amount of water (ca. 50 mol%, 1 μL, unoptimised) to these solutions resulted in rapid initiation of the reaction. This is an example of a water-accelerated Lewis acid catalysed reaction; such reactions, in which water is an important partner, are being increasingly appreciated.[54] Pertinent to this observation, modest yield enhancements on addition of stoichiometric amounts of water to a hetero-Diels–Alder reaction catalysed by lanthanide trifluoromethanesulfonylamides[55] have been reported previously. Currently, we are unsure about the exact role of the water in the reaction. It is likely, however, that a polarised, silver-bound, water molecule acts as a Lewis assisted Brønsted acid, similar to that in lanthanide salt catalysed aromatic electrophilic substitutions.[56] It is also similar to the role metal-coordinated water is suggested to play in certain catalytic processes.[57] In support of this, preliminary DFT calculations on the model system $[Ag(Me_3P)(OH_2)(MeNH{=}CHMe)]^+$ indicate that a coordinated water molecule plays an important function in the silver promoted [2+4] addition of imine to diene. A putative intermediate in this process is shown in Scheme 4, in which the water molecule forms a hydrogen bond with the nitrogen atom.[45] This proposed intermediate accounts for both the observed dependence on trace amounts of water in this reaction and the strong counterion effect observed (vide infra), with both the Lewis assisted Brønsted acidity (OH⋯N hydrogen bond) and the need for a vacant site (alkene coordination) playing important roles. Experimentally, what is clear is that trace



Scheme 4. Proposed intermediate structure.



Scheme 2. Reaction between *N*-benzylideneaniline (**I**) and Danishefsky's diene (**II**) with the silver complexes **1**–**4**.

amounts of water are needed for this reaction to proceed, which is probably made available to the reaction, when at the bench, by adventitious water.

That a silver-bound water molecule is strongly implicated as a catalytic proton source in these reactions is demonstrated by the following control experiments. Addition of just water to a mixture of **I** and **II** affords no product, while under the standard conditions used for catalysis addition of the hindered base 2,6-di-*tert*-butyl-4-methylpyridine suppressed the reaction completely.[56] Moreover, water need not be the unique proton source. The reaction is easily repeated replacing an alcohol (methanol, 20 mol%) for water, resulting in essentially identical product yields and reaction times.

The results of these NMR experiments, in which water is added, are shown in Figure 7 for the new complexes **1** through **4** and for comparison the complexes $[Ag(PPh_3)(BF_4)]$, $[Ag(PPh_3)(ClO_4)]$[58] and $[Ag(PPh_3)(OTf)]$.[16] All of these experiments were carried out at 0.1 mol% catalyst loading with 50 mol% added water in solutions in CD_2Cl_2, with the diene in 1.5 molar excess. The final products in the NMR tube are a consistent mixture of intermediate **V** and final product **III** (ca. 90:10 ratio), which on workup gives only the final product. The reactions were monitored by selected peaks due to intermediate **V** and the final product (see Experimental Section). No hydrolysis of the imine to benzaldehyde was observed under the conditions used, while the consumption of imine **I** in each run followed the same time-dependent profile (although inversed) as the increase in **V** and **III**.

It is clear from Figure 7 that complex **3** gives the fastest rate of catalysis, complete conversion being apparent after 15 minutes. This equates to a turnover frequency (TOF) of 4000 hour^{-1}, which is excellent for a Lewis acid catalysed reaction of this type. Complex **1**, although a slower catalyst than **3**, also yields complete conversion of the imine after ≈40 minutes. Not unsurprisingly the monophosphane complexes, $[Ag(PPh_3)(ClO_4)]$ and $[Ag(PPh_3)(OTf)]$, which contain more nucleophilic counterions, are less active than **1** and **3**. The addition of an extra PPh_3 ligand would be expected to both reduce the Lewis acidity of the metal centre while also adding more steric bulk and blocking a potential vacant site. It is not unexpected then, that complexes **2** and **4** are significantly poorer catalysts than any of the monophosphane complexes. Interestingly the relative reaction rates for the bisphosphane complexes **2** and **4** are reversed from those seen for the monophosphane/carborane complexes. Complex **2**, which incorporates the $[CB_{11}H_{12}]$ anion, catalyses the reaction significantly faster than **4**. Although this is perhaps counterintuitive given the relative coordinating abilities of these two anions, when the solution structures at −60 °C are compared (vide supra), complex **4** shows a considerably smaller value for $J(AgP)$, suggesting a silver centre that has a higher formal coordination number in **4** than in **2**. This implies that the $[CB_{11}H_6Br_6]^-$ anion interacts significantly with the metal centre at this temperature in **4**. Although we do not have the solid-state structure of **4** to hand,[59] this correlation between the magnitude of $J(AgP)$ at low temperature and the relative rates of **2** and **4** is compelling. This difference in rate is also reflected in the relative product yields on the bench after one hour (entries 5 and 7 in Table 3).

The catalyst $[Ag(PPh_3)(BF_4)]$ ceases to function after only a few minutes of activity, giving only modest yields of cycloaddition product in both the NMR and the bench-top experiments (Figure 7 and Table 3, entry 1). We suggest that under the conditions used for catalysis (0.1 mol% catalyst, 50 mol% water), rapid (<2 minutes) silver(I) mediated hydrolysis of the $[BF_4]^-$ anion occurs to afford an oxyborate anion that binds strongly with the metal centre, shutting down the catalytic cycle dramatically. In support of this, hydrolysis of $[BF_4]^-$ to afford coordinated oxyborates has been reported previously.[60, 61]

Conclusion

The preparation of the four silver(I) phosphane complexes partnered with the carborane anions $[closo\text{-}CB_{11}H_{12}]$ and

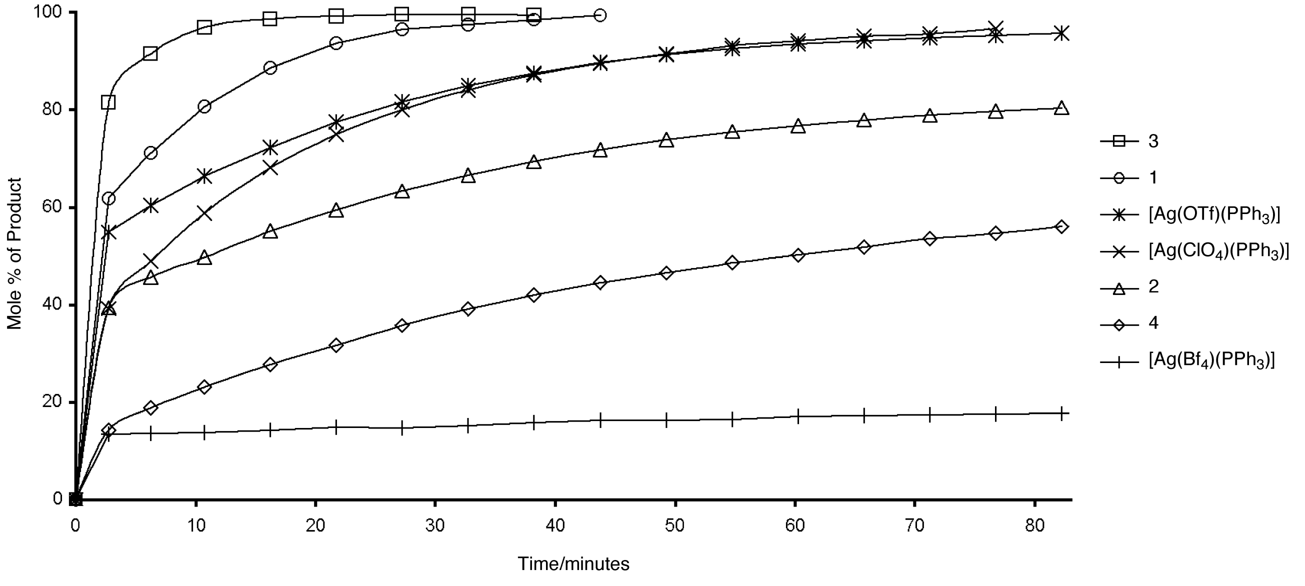


Figure 7. Chart showing relative rates of reaction between **I** and **II** by using 0.1 mol% of catalysts **1**–**4** and $[Ag(PPh_3)(Y)]$ [Y = OTf, BF_4, ClO_4] and 50 mol% added H_2O at room temperature in CD_2Cl_2. See text for other details.

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[*closo*-$CB_{11}H_6Br_6$] has allowed a study to be made of the relationship between solid and solution structures and performance as partners to cationic Lewis acids of these anions in an organic transformation. Not unsurprisingly, given the now well-documented[4, 5] inertness coupled with the low nucleophilicity of the hexahalageno anions and the precedent for pronounced counterion effects in Lewis acid catalysed cycloadditions,[62–64] the monophosphane complex **3** is a significantly better catalyst than both **1** and all of the other systems examined. In addition, compound **3** (and presumably the others, although not tested) is selective for imines and can be used at significantly lower catalyst loadings than previously reported for Lewis acid catalysed hetero-Diels–Alder reactions.

To us, the surprising result is that the relative ordering in rate of catalysis between [$CB_{11}H_{12}$] and [$CB_{11}H_6Br_6$] is reversed when two phosphanes are coordinated to the silver centre. Although this was unexpected, it is pleasing that a gross correlation exists between observable NMR properties in solution (magnitude of J(AgP)) and the catalytic activity. Thus, complexes **1** and **3**, which have large AgP coupling constants, are better catalysts than **2** and **4**, with the latter complex exhibiting the poorest performance and the lowest coupling constant by far (albeit measured at low temperature). Overall this suggests that when considering catalyst performance in these, and related systems, the influence of counterion and ligands are not independent and need to be considered together. It is however encouraging that useful catalyst performance indicators may be gleaned from simple NMR experiments, which could help in the identification of promising catalytic systems. To this end, we are currently investigating the applicability of complexes such as **3** in other Lewis acid catalysed reactions and will report on these in due course.

Experimental Section

General: All manipulations were carried out under an argon atmosphere by using standard Schlenk line or dry box techniques. CH_2Cl_2 was distilled from CaH_2 and hexane was distilled from sodium. Solution NMR spectra were measured on Varian 400 MHz and Bruker Advance 300 MHz FT-NMR spectrometers in solutions in CD_2Cl_2. Residual protio solvent was used as a reference (CD_2Cl_2, $\delta = 5.33$) in ^1H NMR, $BF_3 \cdot OEt_2$ (external) in ^{11}B NMR and 85% H_3PO_4 (external) for ^{31}P NMR spectra. Coupling constants are given in Hz. Elemental analyses were performed in-house at the Department of Chemistry. The complexes Ag[$CB_{11}H_{12}$][26] and Ag[$CB_{11}H_6Br_6$][13] were prepared by the published literature routes or variations thereof. All other chemicals were used as purchased from Aldrich.

Preparations

[Ag(PPh$_3$)(CB$_{11}$H$_{12}$)] (***1***): PPh_3 (0.163 g, 0.650 mmol) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a Schlenk flask charged with Ag[$CB_{11}H_{12}$] (0.155 g, 0.591 mmol), in the dark and with stirring. This solution was stirred overnight and then cannula filtered. The solvent was removed in vacuo to leave a pale yellow solid. Colourless crystals suitable for an X-ray diffraction study were grown by redissolving the product up in minimum CH_2Cl_2, layering with hexane, then placing the sample in a freezer overnight at −30 °C (0.281 g, 92% yield).

$^1H\{^{11}B\}$ (22 °C): $\delta = 7.52-7.29$ (m, 15H; C_6H_5), 2.55 (br s, 1H; CH_{cage}), 2.25 (br s, 1H; BH), 1.85 (10H; 5+5 coincidence, BH); selected $^1H\{^{11}B\}$ (−90 °C): $\delta = 2.59$ (br s, 1H; CH_{cage}), 2.34 (br s, 1H; BH), 1.94 (5H; BH), 1.76 (5H; BH); $^{11}B\{^1H\}$ (22 °C): $\delta = -10.3$ (sh br, 1B), −11.2 (br, 5B), −12.0 (5B); ^{11}B $\delta = -10.3$ (d, 5+1 coincidence, J(HB) = 118 Hz), −12.0 (d, J(HB) = 110 Hz, 5B); $^{31}P\{^1H\}$ (22 °C): $\delta = 18.70$ (dd, $J(Ag^{109}P) = 795$, $J(Ag^{107}P) = 691$ Hz, 1P); IR (KBr): $\tilde{\nu} = 2565$ (vs, BH), 2517 (sh s, BH), 2372 cm^{-1} (m, BH); elemental analysis calcd (%) for $C_{19}H_{27}B_{11}AgP$: C 44.5, H 5.30; found: C 44.3, H 5.19.

[Ag(PPh$_3$)$_2$(CB$_{11}$H$_{12}$)] (***2***): Ag[$CB_{11}H_{12}$] (0.075 g, 0.299 mmol) and PPh_3 (0.158 g, 0.602 mmol) were stirred together in CH_2Cl_2 (15 mL) in the dark for 1 hour. This solution was filtered and hexane (20 mL) added to the filtrate to induce crystallisation. The colourless product was isolated by decanting off the solvent and drying in vacuo (0.204 g, 88% yield). Crystals suitable for an X-ray diffraction study were grown by redissolving a portion of the solid product in a minimum of CH_2Cl_2, layering with hexanes and then placing in a freezer overnight at −30 °C to yield white crystals.

$^1H\{^{11}B\}$ (22 °C): $\delta = 7.45-7.18$ (m, 30H; C_6H_5), 2.21 (br s, 1H; CH_{cage}), 1.85 (br s, 1H; BH_a), 1.58 (br s, 10H; 5+5 coincidence, BH); $^{11}B\{^1H\}$ (CD_2Cl_2, 22 °C): $\delta = -5.1$ (br s, 1B), −10.6 (br s, 5B), −12.6 (br s, 5B); ^{11}B (22 °C): $\delta = -5.1$ (d, J(HB) = 128 Hz, 1B), −10.6 (d, J (HB) = 138 Hz, 5B), −12.6 (d, J(HB) = 158 Hz, 5B); $^{31}P\{^1H\}$ (CD_2Cl_2, 22 °C): $\delta = 14.8$ (s, br); $^{31}P\{^1H\}$ (−60 °C): $\delta = 13.7$ (br d, J(AgP) = 333 Hz), 13.6 (dd, $J(Ag^{109}P) = 554$, $J(Ag^{107}P) = 483$ Hz); IR (KBr): 2544 (vs, BH), 2442 (m, BH), 2396 cm^{-1} (m, BH); elemental analysis calcd (%) for $C_{37}H_{42}B_{11}AgP_2$: C 57.3, H 5.46; found: C 57.2, H 5.53.

[Ag(PPh$_3$)(CB$_{11}$H$_6$Br$_6$)] (***3***): PPh_3 (0.062 g, 0.236 mmol) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a Schlenk flask charged with Ag[$CB_{11}H_6Br_6$] (0.200 g, 0.276 mmol) in the dark and with stirring. The resulting solution was stirred overnight and filtered. The supernatent solvent was removed in vacuo to leave a clear oil. Crystals suitable for an X-ray diffraction study were grown by redissolving the product up in minimum CH_2Cl_2, layering with hexane, then placing the sample in a freezer overnight at −30 °C (0.194 g, 83% yield).

$^1H\{^{11}B\}$: $\delta = 7.52-7.22$ (m, 15H; C_6H_5), 2.73 (br s, 1H; CH_{cage}), 2.43 (5H; BH); ^{11}B: $\delta = -2.1$ (br s, 1B, B), −6.6 (br s, 5B, BBr), −16.9 (d, J(HB) = 157 Hz, 5B, BH); $^{31}P\{^1H\}$: $\delta = 16.52$ (d of d, $J(Ag^{109}P) = 766$, $J(Ag^{107}P) = 664$ Hz, 1P); IR (KBr): 2608 (vs, BH), 2593 cm^{-1} (s, BH); elemental analysis calcd (%) for $C_{19}H_{21}B_{11}AgPBr_6$: C 23.1, H 2.12; found: C 22.6, H 2.17.

[Ag(PPh$_3$)$_2$(CB$_{11}$H$_6$Br$_6$)] (***4***): The compounds Ag[$CB_{11}H_6Br_6$] (0.250 g, 0.345 mmol) and PPh_3 (0.181 g, 0.690 mmol) were stirred together in CH_2Cl_2 (20 mL) in the dark for 1 hour. The solution formed was filtered and solvent removed in vacuo to leave a white solid. This solid was redissolved in minimum CH_2Cl_2, layered with hexane and placed in a freezer overnight at −30 °C to afford a colourless microcrystalline powder (0.246 g, 57%).

$^1H\{^{11}B\}$: $\delta = 7.45-6.87$ (m, 30H; C_6H_5), 2.45 (br s, 1H; CH_{cage}), 2.21 (br s, 5H); ^{11}B: $\delta = 1.3$ (br s, 1B, B), −6.8 (s, 5B), −17.2 (d, J(HB) = 166 Hz, 5B); $^{31}P\{^1H\}$ (22 °C): $\delta = 8.1$ (br s); $^{31}P\{^1H\}$ (−80 °C): $\delta = 8.06$ (dd, $J(^{109}AgP) = 256$, $^{107}J(AgP) = 223$ Hz); IR (KBr): 2956 (vs, BH), 2587 cm^{-1} (s, BH); elemental analysis calcd (%) for $C_{37}H_{36}B_{11}AgP_2Br_6$: C 35.7, H 2.89; found: C 35.5, H 3.01.

General experimental procedure for catalytic studies: The imine **I** (0.200 g, 1.1 mmol) in dichloromethane (1.5 mL) at room temperature was added to a stirring solution of freshly recrystallised catalyst (1 mol%) in dichloromethane (3.5 mL). The reaction mixture was allowed to stir for 5 minutes then Danishefsky's diene (**II**) (320 µL, 1.65 mmol) was added dropwise. After 60 minutes, the reaction was quenched with aqueous sodium hydrogen carbonate and extracted with ethyl acetate. The crude product was purified by chromatography on silica gel (hexane/ethyl acetate 4:1) to afford the product **III**.

^1H NMR: $\delta = 7.67$ (dd, J(HH) = 1, 7 Hz, 1H), 7.35–6.99 (m, 10H), 5.27 (dd, J(HH) = 1, 7 Hz, 2H), 3.29 (dd, J(HH) = 7, 16 Hz, 1H), 2.77 (ddd, J(HH) = 1, 3, 16 Hz, 1H).

General procedure for NMR tube reactions: Solutions of catalyst were typically prepared by dissolving the compound (1 mg) in CD_2Cl_2 (1 mL) with the use of an ultrasound bath to ensure complete catalyst dissolution, although, by eye, the solids seemed to have dissolved completely. The relevant quantity of catalyst solution to give a 0.1 mol% catalyst concentration (i.e. 0.00011 mmol of catalyst) was taken from this standard solution and placed in an NMR tube previously charged with *N*-benzylideneaniline (20 mg, 0.11 mmol). Danishefsky's diene (32 µL, 0.17 mmol) and water (1 µL, 0.056 mmol) were added to the NMR tube, which was then shaken vigorously before being placed in the NMR spectrometer and measurements were taken at timed intervals. The disappearance of the peak at $\delta = 8.51$ due to PhN=C*H*Ph was monitored, along with the growth of the peaks centred at $\delta = 6.64$ and $\delta = 6.54$ [3H total, intermediate **V**] and $\delta = 5.27$ [1H total, final product **III**]. A plot for each catalyst, of time verses consumption of **I** and time verses total concentrations of **V** and **III** showed essentially the same profile. Repeat runs for all the catalysts tested showed the same time-dependent profiles.

Intermediate **V**: ^{1}H NMR: $\delta = 7.56$ (d, J(HH) = 13 Hz, 1 H), 7.42 – 7.40 (m, 2 H), 7.28 – 7.23 (m, 1 H), 7.10 – 7.01 (m, 3 H), 6.64 (m, 1 H), 6.54 (m, 2 H), 5.58 (d, J(HH) = 12 Hz, 1 H), 4.86 (q, J(HH) = 6 Hz, 1 H), 4.71 (d, J(HH) = 6 Hz, 1 H), 3.68 (s, 3 H), 2.94 (dd, J(HH) = 6 Hz, 22 H), 0.144 (s, 9 H).

X-ray crystallography: The crystal structure data for compounds **1** – **3** were collected on a Nonius KappaCCD. Structure solution followed by full-matrix least-squares refinement was performed by using the SHELX suite of programs throughout.[65] Hydrogens were included at calculated positions throughout, with the exception of H7 and H12 in compound **2**. These latter hydrogens were readily located in the penultimate difference Fourier map and refined at a fixed distance 1.12 Å from parent atoms B(7) and B(12), respectively. Plots were produced by using ORTEX.[66]

CCDC-171721 (**1**), 171769 (**2**) and 168828 (**3**) contain 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 e-mail: deposit@ccdc.cam.ac.uk).

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[59] Note added in proof: After the manuscript was submitted the solid-state structure of compound **4** was determined and it shows a monomeric $\{Ag(PPh_3)_2\}^+$ fragment bound to one $[CB_{11}H_6Br_6]$ cage

by two lower pentagonal belt bromine atoms, consistent with the structure proposed from the low-temperature $^{31}P\{^{1}H\}$ NMR spectrum.

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