Review

Carboranyl C-σ-bonded and C-functionalized carboranes as ligands in gold and silver chemistry

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A B S T R A C T

This report summarizes gold and silver chemistry with C-functionalized carborane ligands and also organometallic complexes with Au–C$_{carboranyl}$ σ bonds. The presence of different fragments bonded to the carbon atoms leads to ligands with different coordination preferences. Furthermore, through the partial degradation of the carborane cage the ligand charge can be modified and thus, anionic ligands are afforded. Consequently, for the synthesis of metal complexes, neutral and anionic ligands are available. These two aspects have been used to synthesise and stabilise a wide diversity of gold and silver coordination compounds. The use of carborane fragments as building blocks leads in some cases to unusual structures, clusters, rod like complexes and also to interesting properties like luminescent emissions.

Contents

1. Introduction

There has been a growing interest in gold and silver chemistry from the early 1980s. Different areas have been developed which are related to a wide diversity of research topics [1]. Silver and gold chemistries differ more than could be expected mainly due to the relativistic effects, found in heavy atoms, which display a maximum in gold [2]. These effects lead to the contraction of the 6s orbital (which is stabilized) and also to the expansion of the 5d orbital. Thus, the gap between the 5d and 6s orbitals decreases. These effects are much less pronounced in silver. Some of the consequences are: (i) the tendency of gold(I) towards the formation of linear di-coordinated complexes is higher than that in silver. Silver(I) coordination chemistry displays a wide diversity of unusual structures with many types of donor atom ligands. Silver also

displays a great tendency to form supramolecular compounds. Such versatility is not found in gold(I); (ii) stable silver(III) complexes are scarcely represented, whereas (III) is an stable oxidation state in gold; (iii) the *Aurophilic attraction*, one of the most striking observations in gold(I) chemistry [2e,2f] which, although not inherently relativistic, is considerably strengthened by relativistic effects and has been explained by Pykkö as an "*unusually strong van der Walls interaction*" [2d]. Aurophilic interactions lead to the association of mononuclear linear units or to the presence of gold-gold intra and/or intermolecular contacts in polynuclear complexes. The Au···Au distance found in these complexes lies between 2.7 and 3.3 Å. This range includes the distances between gold atoms in gold metal and approaches or even overlaps with the range of distances found in real Au–Au single bonds. The energy involved is comparable to a typical hydrogen bond (ca. 33 kJ mol^{-1}).

Dicarba-*closo*-dodecaboranes, commonly referred as carboranes (IUPAC name carbaboranes) have the general formula $(CH)_2B_{10}H_{10}$

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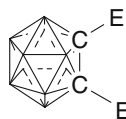
E = P, chalcogen , N... donor group

Fig. 1. Ligands derived from o-carborane.

and exist as *ortho*, *meta* or *para* isomers, which differ in the relative positions of the carbon atoms in the cluster. They are electronic deficient species which have been characterised as "pseudoaromatic" systems. The stability of the carborane cage under many reaction conditions, represents an important characteristic of these boron clusters [3]. The most widely studied is the *ortho* isomer, which remains stable up to 400 °C and is also stable in the presence of oxidizing agents, alcohols or strong acids. These properties have provided a wide range of applications for carborane derivatives [4], as the synthesis of polymers [4c], ceramics [4c], catalyst, [4d,4f,4g] complexes with non-linear optical properties [4e] or radiopharmaceuticals, although the medicinal chemistry of carborane has been mostly focused on the BNCT (Boron Neutron Capture Therapy) technique [4b].

Despite its stability a very well established reaction is the synthesis of 7,8- or 7,9-*nido*-undecaborate(-1) from the 'partial degradation' process. Alkoxide bases, amines, the fluoride ion or other reagents can react with the B3/B6 of *ortho*-carborane or the B2/B3 of *meta*-carboranes. As a result one boron atom of a closed (*closo*) cluster is removed and the resulting open (*nido*) cage is obtained. Another relevant reactivity is related with the CH groups in carboranes, which are weakly acidic and can be deprotonated resulting in nucleophiles. These nucleophiles can react with a wide range of electrophiles, leading to organometallic complexes, but also to C-substituted compounds which contain donor atoms. The latter may act as ligands in coordination chemistry (Fig. 1). This report summarizes gold and silver chemistry with C-functionalized carborane ligands and also organometallic complexes with Au–C$_{carboranyl}$ σ bonds. Outside the scope of this work are compounds where the gold centre is coordinated to the open face of the *nido* carborane anion. This coordination may take place via one boron atom or involve more atoms of the C$_2$B$_3$ face of the carborane cage. There have also been described heteropolynuclear species in which the gold atom is not directly coordinated to the carborane, but instead forms part of a

polynuclear skeleton that contains other metallic atoms bonded to the open face of the carborane [5].

2. Organometallic complexes with σ Au–C bond

As commented above, the CH hydrogen atoms of carborane are more acidic than those bonded to boron. Reaction of Li^{n}Bu and carborane in the corresponding molar ratio leads to mono or dinuclear organolithium complexes and further addition of [AuClL] affords organogold compounds [6] (Scheme 1). This is a general pathway not only for the synthesis of *ortho* but also of *meta* [6e] derivatives (Fig. 2a). The *ortho* isomer o-(CH)$_2$B$_{10}$H$_{10}$ reacts with [Au$_3$-(μ-O)(PPh$_3$)$_3$]$^+$ and NaH, leading to the monosubstituted [Au-(o-C$_2$B$_{10}$H$_{11}$)(PPh$_3$)] [7]. Table 1 resumes some crystallographic data. In the o-carborane derivatives [Au(1-R-o-C$_2$B$_{10}$H$_{10}$)L] the influence of the R substituent in the Au–C and C–C bond distances has been studied [6f]. It seems that an increment in the electron-withdrawing character of the R group leads to a longer Au–C distance and that the C–C distance in the carborane cluster increases when the R group gets bulkier. In the dinuclear compound [Au$_2$(o-C$_2$B$_{10}$H$_{10}$)(PPh$_3$)$_2$] the gold–gold distance is 3.567(1) Å, too long to be classified as an aurophilic interaction. It is interesting to compare this dinuclear derivative with the bis-carborane compound [Au$_2$(H$_{11}$B$_{10}$C$_2$–C$_2$B$_{10}$H$_{11}$)(PPh$_3$)$_2$] (Fig. 2b) that displays a gold···gold interaction of 3.119(2) Å [6c].

3. Complexes with C-functionalized *closo* or *nido* carboranes as ligands

Gold and silver coordination chemistry of C-functionalized carboranes (Fig. 1) has been widely developed, mostly with phosphines and chalcogenolates, although other ligands have also been explored. Here, we resume the reported complexes. A catego-
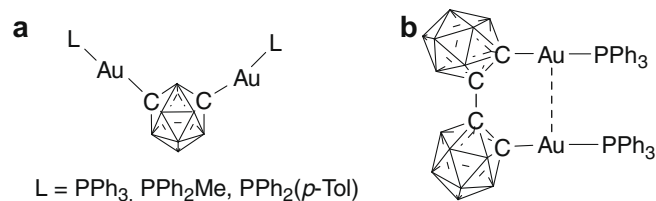

Fig. 2. Dinuclear organogold complexes.

R = MeOCH$_2$; L = PPh$_3$, PCy$_3$, PEt$_3$, P(o-Tol)$_3$, AsPh$_3$
R = Ph, L = PPh$_3$, PCy$_3$, AsPh$_3$
R = Me, L = AsPh$_3$
R = Si^{t}BuMe$_2$, L = PPh$_3$, PPh$_2$Me, AsPh$_3$
R = C$_5$NH$_4$, L = PPh$_3$
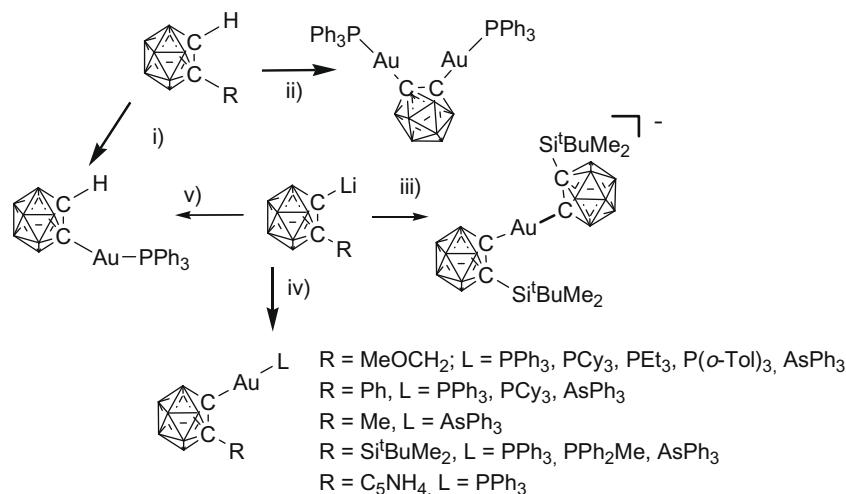
Scheme 1. (i) Li^{n}Bu; (ii) R = H, 2 Li^{n}Bu, 2 [AuCl(PPh$_3$)]; (iii) 1/2 PPN[AuCl$_2$]; (iv) [AuClL] and (v) R = H, NaH, [Au$_3$(μ-O)(PPh$_3$)$_3$]$^+$.

Table 1
Crystallographic data of organometallic carborane complexes with Au–C σ bonds.

Compound	C–M–E (°)[a]	Au–C (Å)	Au–E[a] (Å)	C–C (Å)	Ref.
Ortho complexes					
$[Au(1\text{-}MeOCH_2\text{-}o\text{-}C_2B_{10}H_{10})(AsPh_3)]$	177.05(21)	2.039(8)	2.3740(8)	1.667(11)	[6b]
$[Au_2(o\text{-}C_2B_{10}H_{10})(PPh_3)_2]$	178.9(4)	2.055(14)	2.270(4)	1.71(2)	[6c]
	174.2(4)	2.033(15)	2.273(5)		
$[Au(1\text{-}Si^tBuMe_2\text{-}o\text{-}C_2B_{10}H_{10})(PPh_3)]$	171.34(12)	2.050(4)	2.2718(13)	1.706(6)	[6d]
$[Au(1\text{-}C_5NH_4\text{-}o\text{-}C_2B_{10}H_{10})(PPh_3)]$	173.99(9)	2.069(3)	2.272(1)	1.684(5)	[6f]
$[Au_2(m\text{-}C_2B_{10}H_{10})(PPh_3)_2]$	179.3(2)	2.054(7)	2.265(2)	–	[6e]
	174.1(2)	2.047(7)	2.271(2)		

[a] E = P or As.
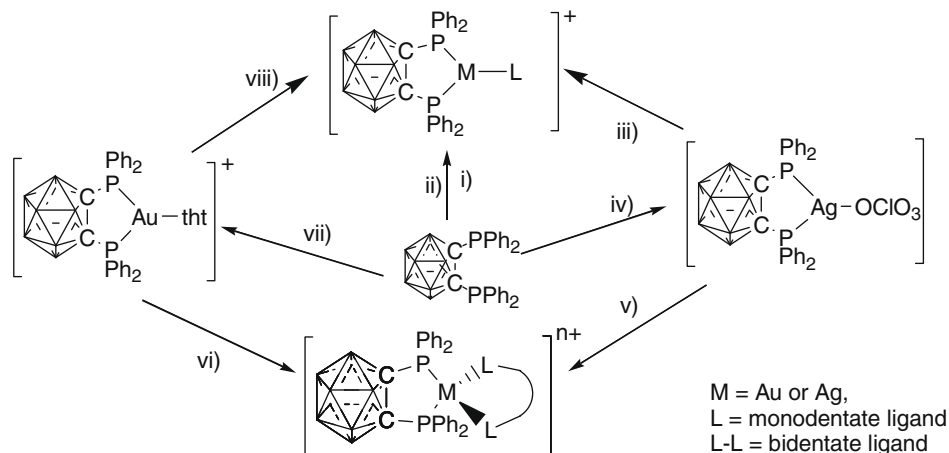
Scheme 2. (i) L = PR₃, [Ag(OClO₃)L], (ii) [AuL(tht)]ClO₄, (iii) L, (iv) AgClO₄, (v) L–L, (vi) L–L, n = 1 or Na(L–L), n = 0 (vii) [Au(tht)₂]ClO₄ and (viii) PR₃.

rization by the donor atom of the carborane ligand is presented bellow.

3.1. Complexes with phosphine ligands

The trend of the diphosphines $(PR_2)_2C_2B_{10}H_{10}$ to act in a chelate mode has lead to the synthesis of three- and four-coordinated gold and silver complexes. Gold and silver chemistry with $(PPh_2)_2C_2B_{10}H_{10}$ (dppcc) has been reviewed [8]. From the reaction of $[Au(tht)_2]ClO_4$ (tht = tetrahydrothiophene) or AgClO₄ with dppcc complexes $[Au(tht)(dppcc)]ClO_4$ or $[Ag(OClO_3)(dppcc)]$ are obtained. Both are excellent reactants in the synthesis of different three- or four-coordinated cationic complexes [9] (Scheme 2).
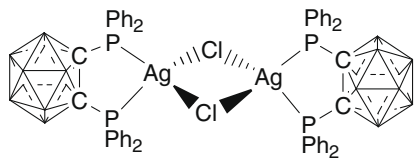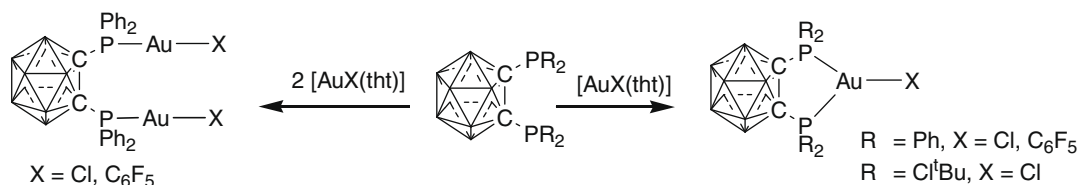

Fig. 3. [AgCl(dppcc)]₂.

Compound [AgCl(dppc)] crystallizes as a dimer in which the chloride ligands bridge two silver atoms (Fig. 3) [10]. Neutral gold compounds (Scheme 3) have also been obtained by reaction of the corresponding diphosphine with [AuX(tht)] (X = Cl, C₆F₅) [9a,11]. Many of these complexes have been characterised by X-ray diffraction studies confirming the expected geometry, some data are resumed in Table 2. The restricted chelate bite angle of the diphosphine is responsible for the major deviation of the ideal trigonal or tetrahedral geometry observed for the metal centres. In the trigonal distorted geometries, the narrower P–Au–P angle is opposite to the longer Au–P bond distance.

Heterometallic trinuclear clusters are obtained from the reaction of AgSCN and $(NH_4)_2MES_3$ (M = Mo, W; E = O, S) [12] (Scheme 4). In these clusters the metallic atoms display tetrahedral geometries, although two types of structures are afforded. Reactions with AgSCN and $(NH_4)_2MS_4$ lead to clusters in which the three metal centres are in linear conformation (Scheme 4A). The Ag–M distances are 2.8941(12), 2.9148(12) Å (M = Mo), 2.8016(12), 2.8401(11) Å (M = W), other data are resumed in Table 2. From AgSCN and $(NH_4)_2MOS_3$ butterfly shaped conformations (Scheme 4B) are afforded. The equilibrium $4[WOS_3]^{2-} \rightarrow 3[WS_4]^{2-} + [WO_4]^{2-}$ has been proposed and thus a complex of the same stoichiometry

$X = Cl, C_6F_5$

$R = Ph, X = Cl, C_6F_5$
$R = Cl^tBu, X = Cl$

Scheme 3.

Table 2
Crystallographic data for gold(I) and silver(I) three- or four-coordinated *closo*-complexes.

Compound	P–M–P (°)[a]	M–P[b] (Å)	Ref.
Closo three-coordinated			
[Au(dppcc)(PPh$_3$)]ClO$_4$	90.2(1)	2.405(1), 2.417(1)	[9a]
Closo four-coordinated			
[Ag(dppcc){(SPPh$_2$)$_2$CH$_2$}]ClO$_4$	84.56(5)	2.256(2), 2.532(2)	[9b]
[Ag(dppcc)(phen)]ClO$_4$	110.59(3)	2.411(1), 2.507(1)	[9b]
[Au(dppcc){(SPPh$_2$)$_2$CH$_2$}]ClO$_4$	89.72(6)	2.380(2), 2.389(2)	[9c]
[Ag$_2$Cl$_2$(dppc)$_2$]	89.90(5)	2.4784(14), 2.5052(14)	[10]
[Ag$_2$MoS$_4$(dppc)$_2$]	85.37(9) 85.34(9)	2.449(3)–2.582(3)	[12]
[Ag$_2$WS$_4$(dppc)$_2$] (**A**)	88.03(10) 87.23(9)	2.335(3)–2.481(3)	[12]
[Ag$_2$WS$_4$(dppc)$_2$] (**B**)	87.34(11) 84.70(11)	2.434(3)–2.579(4)	[12]

[a] Bite angle for the carborane diphosphine.
[b] Distances to the carborane diphosphine phosphorous.

[Ag$_2$WS$_4${(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}] but different geometry from that in **A** is obtained (Scheme 4B) for M = W. This compound is luminescent with a maximum of emission at 436 nm which has been attributed to ligand to ligand charge transfer (LLCT) processes. The Ag–W distances are 2.9314(12) and 2.9377(11) Å. The Ag–S distances in complexes **A** range from 2.356(3) Å to 2.525(3) Å, shorter than those found in compound **B** with M = W [2.530(4)–2.583(3) Å].

Although the carborane cage remains unchanged in a wide range of chemical conditions a well known reaction is the *partial degradation* of the carborane cluster. In this process one of the two boron atoms nearest to both carbon vertexes of the carborane is removed. The result is a *nido* carborane in which each boron and carbon atoms has its terminal hydrogen and one more hydrogen atom situated in the open face of the *nido* species. The latter bridges two of its boron atoms. Coordination of the carborane diphosphines [1,2-(PR$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$] to a metal favours the partial degradation process leading to complexes which contain the

M = Mo, E = O; M = W, E = S

Scheme 4.

M= Au or Au; R = Ph, ^{i}Pr, Et, OEt;
P-P = diphosphine; L-L= bidentate ligand
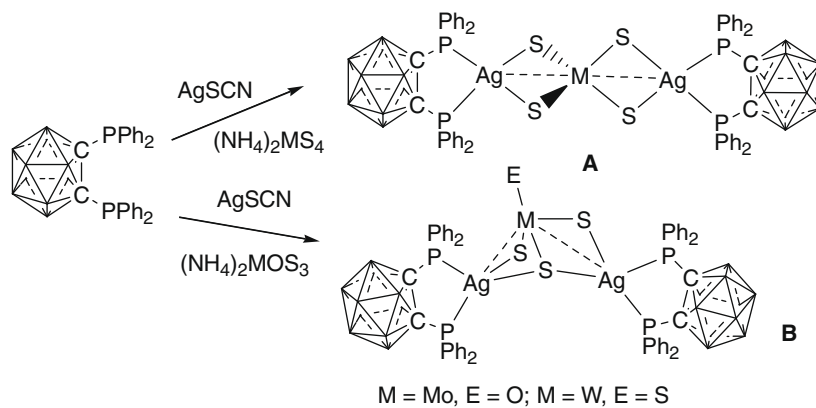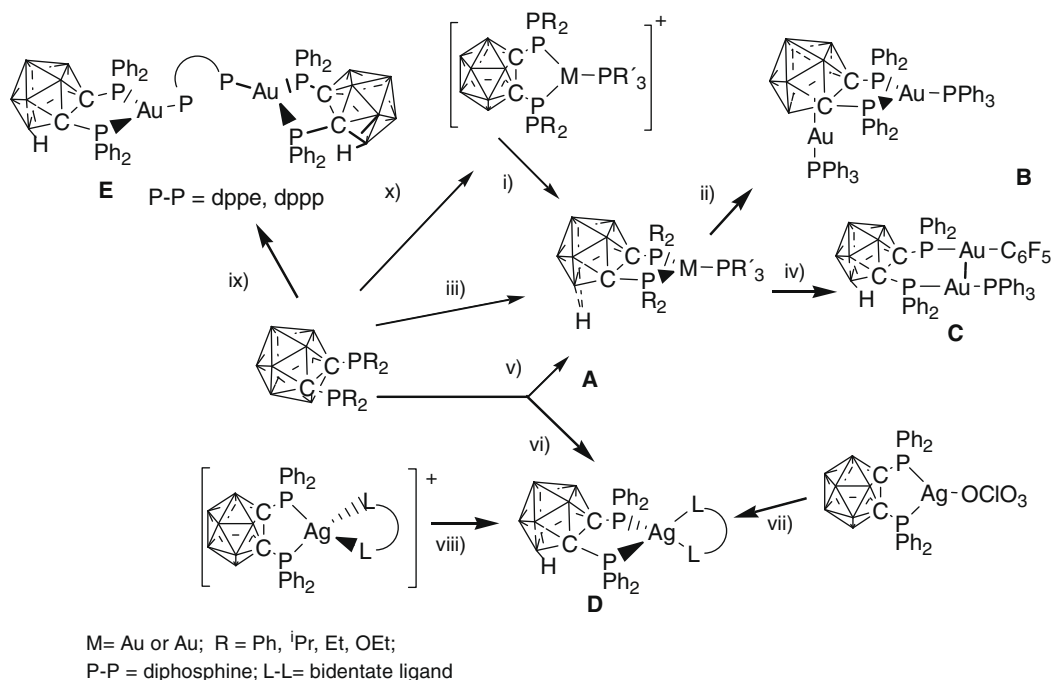
Scheme 5. (i) EtOH, Δ; (ii) NaH, [Au(PPh$_3$)(tht)]ClO$_4$; (iii) EtOH, Δ, [AuCl(PR′$_3$)] or [Ag(OClO$_3$) (PR′$_3$)], (iv) [Au(C$_6$F$_5$)(tht)], (v) EtOH, Δ, AgNO$_3$, PR$_3$; (vi) EtOH, Δ, AgNO$_3$, L–L; (vii) EtOH, Δ, L–L; (vii) EtOH, Δ, (viii) EtOH, Δ; (ix) [Au$_2$Cl$_2$(PP)] EtOH, Δ and (x) [Au(PR′$_3$)(tht)]ClO$_4$ or [Ag(OClO$_3$)(PR′$_3$)], CH$_2$Cl$_2$.

Table 3
Crystallographic data for gold and silver three- or four-coordinated *nido*-complexes.

Compound	P–M–P (°)[a]	M–P[b] (Å)	M–P[c] (Å)	B–H[d]	Ref.
Three-coordinated					
[Au(dppnc)(PPh$_3$)]	84.91(4)	2.389(1), 2.3952(12)	2.2831(13)	1.09 1.66	[13a]
[Au(dipnc)(PPh$_3$)]	90.38(2)	2.4083(6), 2.3073(6)	2.3791(6)	1.08 1.41	[14]
[Au$_2$(dppnc)$_2$(dppp)]	86.06(10) 84.35(9)	2.365(3)–2.443(3)	2.293(3), 2.288(3)		[13a]
[Ag(dppnc)(PPh$_3$)]	81.07(3)	2.488(1), 2.494(1)	2.3974(10)		[13b]
Four-coordinated					
[Au(dppnc)(dppcc)]	89.25(4)[e] 86.05(4)[f]	2.369(1), 2.487(1)[e] 2.394(1), 2.440(1)[f]	–		[16]
[Ag(dppnc)(dppcc)]	84.90(6)[e] 82.33(6)[f]	2.530(2), 2.575(2)[e] 2.511(2), 2.559(2)[f]	–		[13b]
[Ag(dppnc)(phen)]	82.58(5)	2.465(2), 2.490(1)	–		[13b]
Four-coordinated Au(III)					
[Au(dipnc)Cl$_2$]	88.30(6)	2.327(2), 2.313(2)	2.331(2), 2.334(2)		[13c]
[Au(dppnc)Cl$_2$]	87.53(7)	2.296(2), 2.306(2)	2.326(2), 2.335(2)		[19]

dppnc = [(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$]$^-$, dipnc = [(P^{i}Pr$_2$)$_2$C$_2$B$_9$H$_{10}$]$^-$.
[a] Bite angle for the carborane diphosphine.
[b] Distances to the carborane diphosphine phosphorous.
[c] Distances to the phosphorous atoms of no carborane ligands.
[d] B–H distances to the bridging hydrogen atom.
[e] *Closo* cage.
[f] *Nido* cage.

anionic ligand [7,8-(PR$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$. Thus, three- or four-coordinated neutral products (Scheme 5) [13,14] have been afforded by reaction, in refluxing ethanol, of the *closo*-diphosphine with either: the corresponding halogold precursor or the perchloratesilver compound or a mixture of AgNO$_3$ and the corresponding ligand. These complexes can also be synthesised by refluxing an ethanol suspension of the corresponding *closo* gold or silver compound. The structures of some of these complexes have been analysed by X-ray diffraction (Table 3). For some of them the bridging hydrogen at the open face has been located and the two boron–hydrogen distances compared. One of them may be longer than the other or both distances can be similar, then the hydrogen atom acts as a *real* bridge between the boron atoms. The bis-carborane compound [Au$_2$(PPh$_3$)$_2${7,7′-8,8′-(PPh$_2$)$_2$-7,7′-8,8′-(C$_2$B$_9$H$_{10}$)$_2$}] has also been reported [13c].

Complexes [Au{(PR$_2$)$_2$C$_2$B$_9$H$_{10}$}(PR′$_3$)] (R = Ph, ^{i}Pr) show intense emissions. The emission energies (ca. 520 nm) resemble those found in the corresponding free *nido*-diphosphines at about 480 nm. From theoretical studies the origin of this band has been assigned to intraligand transitions, perturbed by the presence of the gold atom. Nevertheless when R = Ph another emission at lower energy (ca. 630 nm) is observed, whose origin has been assigned to ligand to metal charge transfer transitions (MLCT) [14].

The hydrogen atom in the open face of the carborane in [Au{(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}(PPh$_3$)] may be removed with HNa. Further addition of [Au(PPh$_3$)(tht)]ClO$_4$ leads to the metallocarborane species [Au$_2${(PPh$_2$)$_2$C$_2$B$_9$H$_9$}(PPh$_3$)$_2$] (Scheme 5B) which contains one gold atom bonded to the open face and the other to both phosphorous atoms of the *nido* diphosphine. Reaction of [Au{(PPh$_2$)$_2$-C$_2$B$_9$H$_{10}$}(PPh$_3$)] with [Au(C$_6$F$_5$)(tht)] gives a dinuclear derivative in which the diphosphine bridges the fragments 'AuPPh$_3$' and 'Au(C$_6$F$_5$)' [15] (Scheme 5C).

The mixture of [AuCl(AsPh$_3$)] and (PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$ in refluxing ethanol does not lead to the expected [Au{(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}(AsPh$_3$)]. Depending on the molar ratio, two different complexes may be obtained [16]. From the 1:1 molar ratio reaction the four-coordinated [Au{(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}{(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}] which contains one *nido* and one *closo*-diphosphine is isolated. The 1:2 molar ratio reaction gives a tetranuclear gold cluster [Au$_4${(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}$_2$(AsPh$_3$)$_2$]
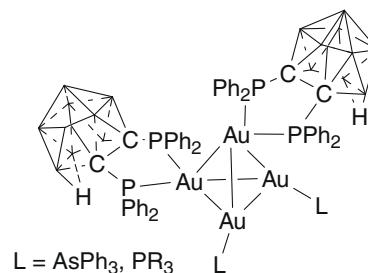

Fig. 4. Tetranuclear clusters with *nido*-carborane ligands.

(Fig. 4). Formation of [Au{(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}(AsPh$_3$)] could be the first step in both cases. This compound would react with more (PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$ or [AuCl(AsPh$_3$)] affording the homoleptic tetracoordinated compound or the tetranuclear cluster, respectively. Through displacement of the arsine ligand, by tertiary phosphines, in [Au$_4${(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}$_2$(AsPh$_3$)$_2$] complexes [Au$_4${(PPh$_2$)$_2$C$_2$-B$_9$H$_{10}$}$_2$(PR$_3$)$_2$] have been synthesised. The cluster [Au$_4${(PPh$_2$)$_2$C$_2$-B$_9$H$_{10}$}$_2$(PPh$_3$)$_2$] has also been obtained from the reaction of the diphosphine with [Au(NO$_3$)(PPh$_3$)] in refluxing ethanol [17]. The gold–gold distances in these clusters range from 2.6036(7) to 2.9606(16) Å (see other crystallographic data in Table 4). They display intense emissions whose maxima appear at about 630 nm. From theoretical calculations the charges assigned to the gold centres bonded to the diphosphine are 0 and those assigned

Table 4
Some crystallographic data of tetranuclear gold clusters with [(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$]$^-$ (dppnc).

Nido cluster complexes	P–M–P (°)[a]	M–P[b] (Å)	Ref.
[Au$_4$(dppnc)$_2$(AsPh$_3$)$_2$]	86.51(9), 89.10(8)	2.342(2), 2.373(2)	[16]
[Au$_4$(dppnc)$_2$(PPh$_3$)$_2$]	87.29(14), 85.89(16)	2.374(4)–2.406(4)	[17]
[Au$_4$(dppnc)$_2$-{P(4-OMe)-C$_6$H$_4$}$_2$]	82.73(4), 88.17(4)	2.359(11), 2.4164(11)	[18]

[a] Diphosphine chelate angle.
[b] Distances to the phosphorous of the diphosphine.

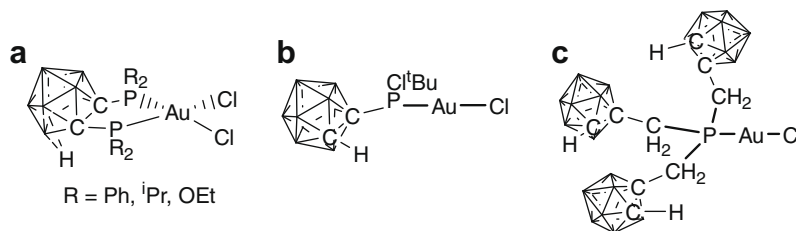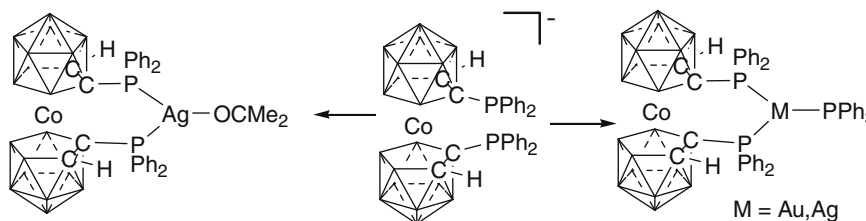**Fig. 5.** Gold(III) complexes with *nido*-diphosphines (a). Gold complexes with carborane monophosphines (b) and (c).

Scheme 6. (i) AgOTf, OCMe$_2$ and (ii) [MCl(PPh$_3$)].

to the gold atoms bonded to the monodentate ligand +1. The emission is assigned to a gold-centred spin-forbidden transition, which leads to coincident oxidation state assignment for the gold atoms to those obtained by theoretical calculations [18].

Gold (III) complexes of the type [AuCl$_2${(PR$_2$)$_2$C$_2$B$_9$H$_{11}$}] are synthesised by refluxing a mixture of the diphosphines (PR$_2$)$_2$C$_2$B$_{10}$H$_{10}$ (R = Ph, ^{i}Pr, OEt) with [AuCl$_3$(tht)] (tht = tetrahydrothiophene) or AuCl$_3$ · nH$_2$O [13c,19] in ethanol (Fig. 5a).

The diphosphine [(PPh$_2$)$_2$Co(C$_2$B$_9$H$_{10}$)$_2$]$^-$ belongs to the family of sandwich metallocarborane complexes (Scheme 6). Reaction of its salts with [MCl(PPh$_3$)] in refluxing ethanol or with AgClO$_4$ in ethanol/acetone at room temperature affords complexes in which the anionic diphosphine acts in as chelate mode [20]. In [Ag{(PPh$_2$)$_2$Co(C$_2$B$_9$H$_{10}$)$_2$}(PPh$_3$)] the silver atom may be considered as four-coordinated. The compound crystallizes with an acetone molecule which is weakly coordinated to the silver atom. Compound [Ag{(PPh$_2$)$_2$Co(C$_2$B$_9$H$_{10}$)$_2$}(OCMe$_2$)] displays intermolecular Ag–H interactions which lead to the formation of a one dimensional chain. The torsion angle C$_1$–c–c′–C$_1$′ (c and c′ are the centroids of the pentagonal C$_2$B$_3$ faces and C$_1$, C$_1$′ the carbon atoms bonded to the PPh$_2$ groups) changes from −102.3° in the free diphosphine to ca. −77° in the silver complexes and −54° in the gold derivative (see Table 5).

The monophosphines 1-(PCl^{t}Bu)-C$_2$B$_{10}$H$_{11}$ [3], 1-(PPh$_2$)-2-Ph-C$_2$B$_{10}$H$_{10}$ [21] and P(CH$_2$-1-C$_2$B$_{10}$H$_{11}$)$_3$ [22] (which contains three *closo*-carboranyl fragments) react with [AuCl(tht)] affording the corresponding di-coordinated complexes (Fig. 5b and c). Di-coordinated gold complexes with *nido*-monophosphines of stoichiometry

Table 5
Crystallographic data for complexes with the diphosphine [(PPh$_2$)$_2$-Co(C$_2$B$_9$H$_{10}$)$_2$]$^-$ (Ref. [20]).

Compound	P–M–P (°)[a]	M–P[b] (Å)	M–E[c] (Å)
[Au{(PPh$_2$)$_2$-Co(C$_2$B$_9$H$_{10}$)$_2$}(PPh$_3$)]	107.00(3)	2.3662(8) 2.4076(8)	2.3467(8)
[Ag{(PPh$_2$)$_2$-Co(C$_2$B$_9$H$_{10}$)$_2$}(PPh$_3$)]	111.21(3)	2.5507(9) 2.5470(10)	2.4713(10)
[Ag{(PPh$_2$)$_2$-Co(C$_2$B$_9$H$_{10}$)$_2$}(OCMe$_2$)]	114.746(19)	2.4894(6) 2.4933(6)	2.3895(17)

[a] Chelate angle of the diphosphine.
[b] Phosphorous atoms of the diphosphine.
[c] E = phosphorous atom of PPh$_3$ or oxygen atom of the OCMe$_2$.

Table 6
Some crystallographic data of complexes with carborane monophosphines.

Di-coordinated complexes with monophosphines	P–Au–P (°)	Au–P (Å)	Au–E (Å)[a]	Ref.
[Au{7-(PPh$_2$)-8-Me-C$_2$B$_9$H$_{10}$}(PPh$_3$)]	174.041(15)	2.3159(5)	2.3060(5)	[23c]
[Au{7-(PPh$_2$)-8-Ph-C$_2$B$_9$H$_{10}$}(PPh$_3$)]	174.68(8)	2.320(2)	2.312(2)	[23a]
[1-(ClAuPPh$_2$)-2-Ph-3-(p-cymene)-RuC$_2$B$_9$H$_9$]	176.1(2)	2.244(4)	2.285(4)	[23a]
[AuCl{1-(PPh$_2$)-2-Ph-C$_2$B$_{10}$H$_{10}$}]	175.84(12)	2.232(3)	2.279(3)	[21]
[Au{7-(PPh$_2$)-8-SBz-C$_2$B$_9$H$_{10}$}(PPh$_3$)]	173.28(5)	2.3186(13)	2.3051(13)	[23b]
[AuCl{P(CH$_2$-C$_2$B$_{10}$H$_{10}$)$_3$}]	178.21(5)	2.2163(12)	2.2804(13)	[22]

[a] E = P phosphorous of PPh$_3$ or Cl.

[Au{7-(PPh$_2$)-8-R-C$_2$B$_9$H$_{10}$}(PPh$_3$)] (R = Me, Ph, SBz, SEt) [23] have also been described and the crystal structures for R = Me, Ph, SBz elucidated (Table 6). [Au{7-(PPh$_2$)-8-Ph-C$_2$B$_9$H$_{10}$}(PPh$_3$)] has been used as reactant in the synthesis of metallocarborane derivatives. Its reaction with [RhCl$_2$L]$_2$ [L = p-cymene or C$_5$Me$_5$] gives mixed gold–rhodium complexes (this reactivity is resumed in Scheme 7 [23a]).
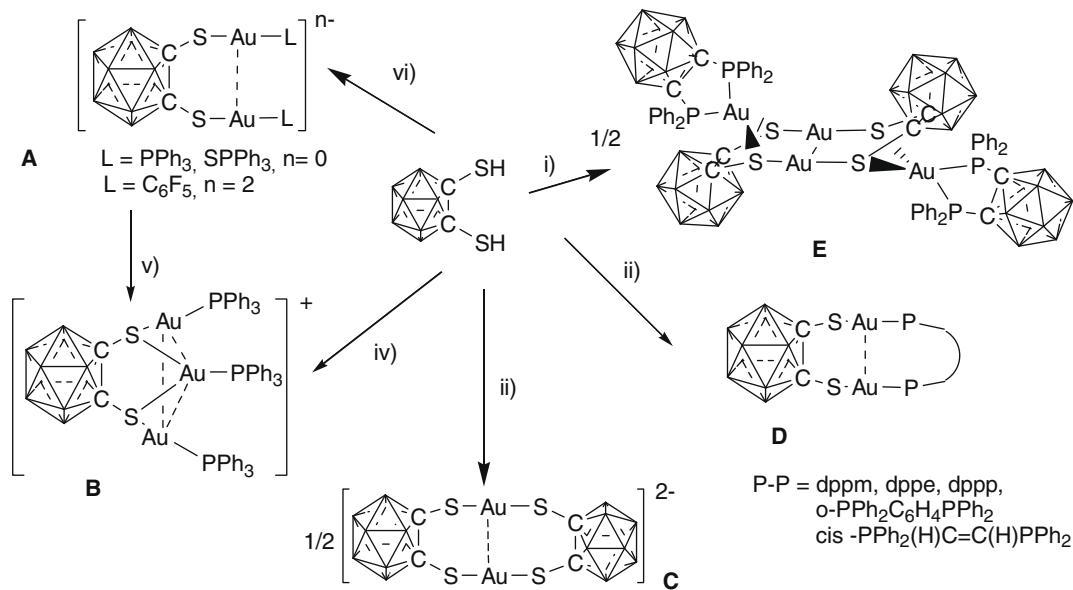
The complexes above contain the *ortho* isomer of the carborane cluster. The synthesis of the complexes [AuCl{1-(PPh$_2$)$_2$-1,12-C$_2$B$_{10}$H$_{10}$}], [Au$_2$Cl$_2${1,12-(PPh$_2$)$_2$-1,12-C$_2$B$_{10}$H$_{10}$}] and [Au{1,12-(PPh$_2$)$_2$-1,12-C$_2$B$_{10}$H$_{10}$}$_2$]Cl, which contain mono or diphosphines of the *para* isomer of carborane, have been reported [24].

3.2. Complexes with chalcogen atoms as donor ligands

The dithiolate 1,2-(SH)$_2$C$_2$B$_{10}$H$_{10}$ displays greater tendency to act in a bridging mode than the diphoshines previously commented. Reactions of this ligand with halogold (I) complexes not only lead to gold dinuclear compounds (Scheme 8), but also to the trinuclear species [Au$_3$(S$_2$C$_2$B$_{10}$H$_{10}$)(PPh$_3$)$_3$]OTf (Scheme 8B) [25]. From dinuclear halogold derivatives of stoichiometry [Au$_2$Cl$_2$(P–P)] (P–P = diphosphine) in 1:1 molar ratio complexes [Au$_2$(S$_2$C$_2$B$_{10}$H$_{10}$)(P-P)] in which the diphoshine and the dithiolate bridge two gold centres are afforded (Scheme 8D). This has been confirmed by X-ray studies for complexes with the diphosphines

R = Ph, Me

EtOH / Δ

[AuCl(PPh₃)]

NaH + [RuCl₂(p-cymene)]₂

+ Other

Scheme 7.

A   L = PPh₃, SPPh₃, n= 0
L = C₆F₅, n = 2

B

C

D   P–P = dppm, dppe, dppp,
o-PPh₂C₆H₄PPh₂
cis -PPh₂(H)C=C(H)PPh₂

E
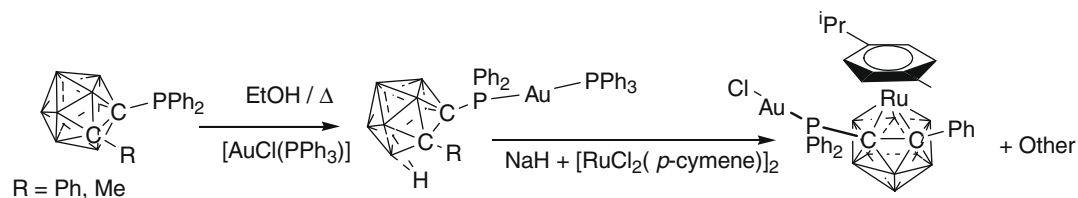
Scheme 8. (i) [Au₂Cl₂(dppcc)]; (ii) [Au₂Cl₂(P–P)]; (iii) [AuCl(tht)], NBu₄Br (iv) 3[Au(OTf)(PPh₃)], (v) [Au(OTf)(PPh₃)], (vi) 2[AuClL], n = 0, or 2[AuBr(C₆F₅)]⁻, n = 2.

1,2-bis(diphenylphosphino)benzene (dppph) or 1,2-bis(diphenyl-phosphino)ethylene (dppey) (Table 7). The same reaction with complex [Au₂Cl₂{μ-(PPh₂)₂C₂B₁₀H₁₀}] in 1:1 molar ratio leads to the formation of a tetranuclear derivative (Scheme 8E) [26]. The different result is probably due to the high tendency of this diphos-phine to act in a chelate mode and to its stereochemical hindrance. In this compound two gold centres are four-coordinated and the other two di-coordinated. The presence of aurophilic interactions has been confirmed for all the gold(I) complexes shown in Scheme 8 whose crystal structures have been determined (Table 7).

Table 7
Some crystallographic data of complexes with mono or dichalcogenolate ligands.

Gold(I) dithiolate	Au···Au (Å)	M–S (Å)	M–P (Å)	Ref.
[Au₂(S₂C₂B₁₀H₁₀)(PPh₃)₂]	3.0746(9)	2.329(2)	2.260(2)	[25]
[Au₂(S₂C₂B₁₀H₁₀)(dppph)]	2.9771(10)	2.313(2), 2.321(2)	2.257(2), 2.267(2)	[25]
[Au₂(S₂C₂B₁₀H₁₀)(dppey)]	3.0195(5)	2.301(2), 2.309(2)	2.249(2), 2.265(2)	[25]
[Au₄(S₂C₂B₁₀H₁₀)₂(dppcc)₂]	3.1311(12)	2.299(2), 2.298(2)[a]	2.307(2), 2.427(2)	[26]
		2.614(2), 2.584(2)[b]		
Silver (I) monothiolate	Ag···Ag (Å)[c]	Ag–S (Å)	Ag–P (Å)	Ref.
[Ag₄(μ₃-S₂C₂B₁₀H₁₁)₂(μ-OTf)₂(PPh₃)₄]	3.382	2.4252(12)	2.3772(13)	[29b]
		2.5467(14)	2.3841(14)	
		2.6508(14)		
Gold(I) monochalcogenolate	E[d]–Au–X[e] (°)	Au–E[a] (Å)	Au–X[b] (Å)	Ref.
[Au(2-Me-SC₂B₁₀H₁₀)(PPh₃)]	179.70(8)	2.311(2)	2.276(2)	[29c]
[Au(2-Me-SC₂B₁₀H₁₀)(AsPh₃)]	178.34(4)	2.272(2)	2.3399(8)	[29c]
[Au(2-C₅NH₄-SC₂B₁₀H₁₀)(PPh₃)]	174.86(4)	2.3052(10)	2.2616(10)	[29f]
PPN[AuCl(2-Me-SC₂B₁₀H₁₀)]	176.39(5)	2.260(2)	2.2794(14)	[29c]
[Au₂(SC₂B₁₀H₁₁)₂(dppe)]	176.06(3)	2.3071(11)	2.2621(9)	[29a]
[Au(SeC₂B₁₀H₁₁)(PPh₃)]	175.08(3)	2.4167(4)	2.2690(10)	[29d]
[Au(2-Me-SeC₂B₁₀H₁₀)(PPh₃)]	174.82(4)	2.4254(6)	2.2740(13)	[29e]

[a] To linear Au.
[b] To four-coordinated Au.
[c] Long for metallic interaction.
[d] E = S, Se.
[e] X = P, As, Cl.

L = E= C_6F_5, $C_6F_3H_2$, Cl; n = 1
E = Cl, C_6F_5; L = PPh_3; n = 0
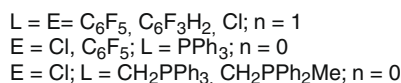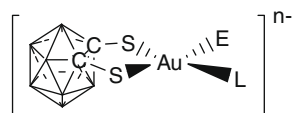E = Cl; L = CH_2PPh_3, CH_2PPh_2Me; n = 0

Fig. 6. Carborane-dithiolate gold (III) complexes.

Mononuclear gold (III) complexes shown in Fig. 6 have been obtained from the corresponding halogold (III) compound [27] and some structural data are resumed in Table 8). The partial degradation of one of two carborane cages in $[Au(S_2C_2B_{10}H_{10})_2]^-$ (Scheme 9A) leading to $[Au(S_2C_2B_{10}H_{10})(S_2C_2B_9H_{10})]^{2-}$ (Scheme 9B) or to $[Au(S_2C_2B_9H_{10})_2]^{3-}$ (Scheme 9C) has been achieved [28]. From the bond distances shown in Table 8 it can be proposed that the additional negative charge of the *nido* ligand leads to a slight reduction of the S–C bond length, and also to an increment in the Au–S distance (Table 9).

This chemistry has been extended to the monochalcogenolates $[1-E-C_2B_{10}H_{11}]^-$ (E = S, Se) and $[1-E-2-R-C_2B_{10}H_{10}]^-$ (E = S, R = Me, C_5NH_4; E = Se, R = Me) (Scheme 10) [29]. Table 7 resumes some structural data. Complexes $[Au\{1-Se-C_2B_{10}H_{11}\}(PPh_3)]$ and $[Au\{1-Se-2-Me-C_2B_{10}H_{10}\}(PPh_3)]$ crystallize as dimers [29d,29e]. The former through aurophilic interactions [Au⋯Au 3.3035(4) Å] (Fig. 7a), the latter through Au⋯Se contacts of 3.4783(6) Å (Fig. 7b). On the basis of theoretical calculations non-linear optical properties have been proposed for $[Au\{1-Se-C_2B_{10}H_{11}\}(PPh_3)]$ [30]. In the molecular structure of $[Au\{1-S-2-(C_5NH_4)-C_2B_{10}H_{10}\}(PPh_3)]$ the gold centre coordinates to the sulfur atom and is not connected to the nitrogen atom of the pyridine fragment. The crystal structure of the compound of empirical formula $[Ag_2\{SC_2B_{10}H_{11}\}(PPh_3)_2]^+$ (Scheme 10C, E = S) [18] consists of two "Ag(1-S-$C_2B_{10}H_{11}$)(PPh_3)_2"

units linked through two further Au–S bonds and two triflate anions (Fig. 8).

Anionic *nido*-mono or dithioethers react with AgNO_3 or [Ag(O-NO_2)L] (L = PPh_3, bipy) to afford silver derivatives which contain anionic thioether ligands [31]. Some of them have also been obtained from the reaction of [AgCl(PPh_3)_2] with the corresponding *closo* dithioether in refluxing ethanol. Different stoichiometries $[Ag(L)]$ [L = (7,8-(SCH_2S)-7,8-C_2B_9H_{10})^-$ $(L_{s2c5})^-$; $(7,8-\{S(CH_2)_2S\}-7,8-C_2B_9H_{10})^-$ $(L_{s2c6})^-$; $(7,8-\{SCH_2CH_2OCH_2CH_2OCH_2CH_2S\}-7,8-C_2-B_9H_{10})^-$ $(L_{s2c12})^-$; $(7,8-\{SCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2-CH_2S\}-7,8-C_2B_9H_{10})^-$ $(L_{s2c15})^-$], $[Ag(L)(PPh_3)]$ [L = $(L_{s2c5})^-$; $(L_{s2c6})^-$; $(7,8-\{SCH_2CH_2OCH_2CH_2S\}-7,8-C_2B_9H_{10})^-$ $(L_{s2c9})^-$; L_{s2c12}; $7,8-(SEt)_2-7,8-C_2B_9H_{10}$ (L_{s2n}); $7-(SEt)-8-Me-7,8-C_2B_9H_{10}$ (L_{s1})] and $[Ag(L)(bipy)]$ [L = L_{s2c6}, L_{s2n}, L_{s1})] have been found. The ligands coordinate to silver through the sulfur atoms but with different Ag–S distances. This fact favours the formation of polymeric structures. When the cyclic thioether contains oxygen atoms in the chain, coordination to one of the oxygen atoms can be observed. With strained ligands (as L_{s2c5}^-) coordination of the metal centre to the open face instead to the sulfur atoms is proposed. As a result of these factors the crystal structures show different patterns which are resumed

Table 9
Some bond distances (Å) for complexes with thioether ligands.

| Silver(I) thioether	Ag–S	Ag–O	Ag–P	Ref.
$[Ag(L_{s2c6})(PPh_3)]$	2.665(2), 2.584(2)	–	2.390(2)	[31b]
$[Ag(L_{s2c9})(PPh_3)]$[a]	2.505(5)[b], 2.611(4)[b]	2.627(9)[b]	2.377(5)[b]	[31c]
	2.530(6)[c], 2.555(4)[c]	2.58(1)[c]	2.364(5)[c]	
$[Ag(L_{s2c15})]$	2.503(3), 2.558(3), 2.711(3)	2.501(8)	–	[31b]
$[Ag(L_{s2c5})]$	2.520(4), 2.546(3) 2.600(3), 2.939(4)	–	–	[31a]

[a] Two conformers.
[b] Distances in one conformer.
[c] Distances in the other conformer.

Table 8
Crystal data for gold(III) dithiolate derivatives.

Gold(III) dithiolate	Au–S (Å)	C[a]–S (Å)	Au–Cl (Å)	Au–C (Å)	Ref.
PPN[AuCl_2(S_2C_2B_{10}H_{10})]	2.271(2)	1.782(6)	2.324(2)	–	[27]
	2.278(2)	1.785(6)	2.325(2)		
[AuCl(CH_2PPh_3)(S_2C_2B_{10}H_{10})]	2.2803(12)	1.772(4)	2.3223(12)	2.086(4)	[27]
	2.3245(13)	1.782(4)			
PPN[Au(S_2C_2B_{10}H_{10})_2]	2.319(2)	1.778(6)	–	–	[28]
	2.321(2)	1.784(6)			
[Au(S_2C_2B_{10}H_{10})(S_2C_2B_9H_{10})]^{2-}	2.3127(13)[b]	1.795(5)[b]	–	–	[28]
	2.3158(11)[b]	1.799(4)[b]			
	2.3264(12)	1.766(4)			
	2.3291(13)	1.780(4)			

[a] Carborane carbon atom.
[b] *Nido* carborane cage.
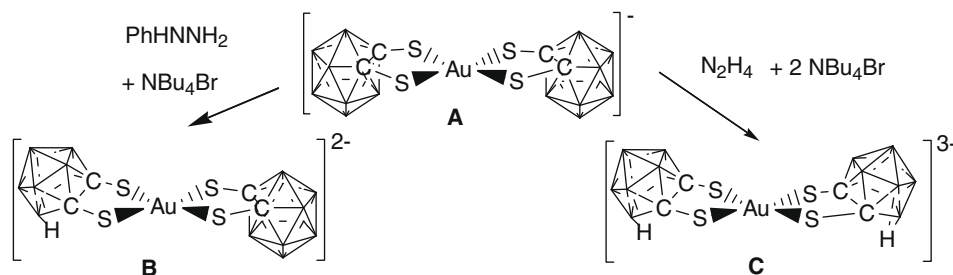
Scheme 9.
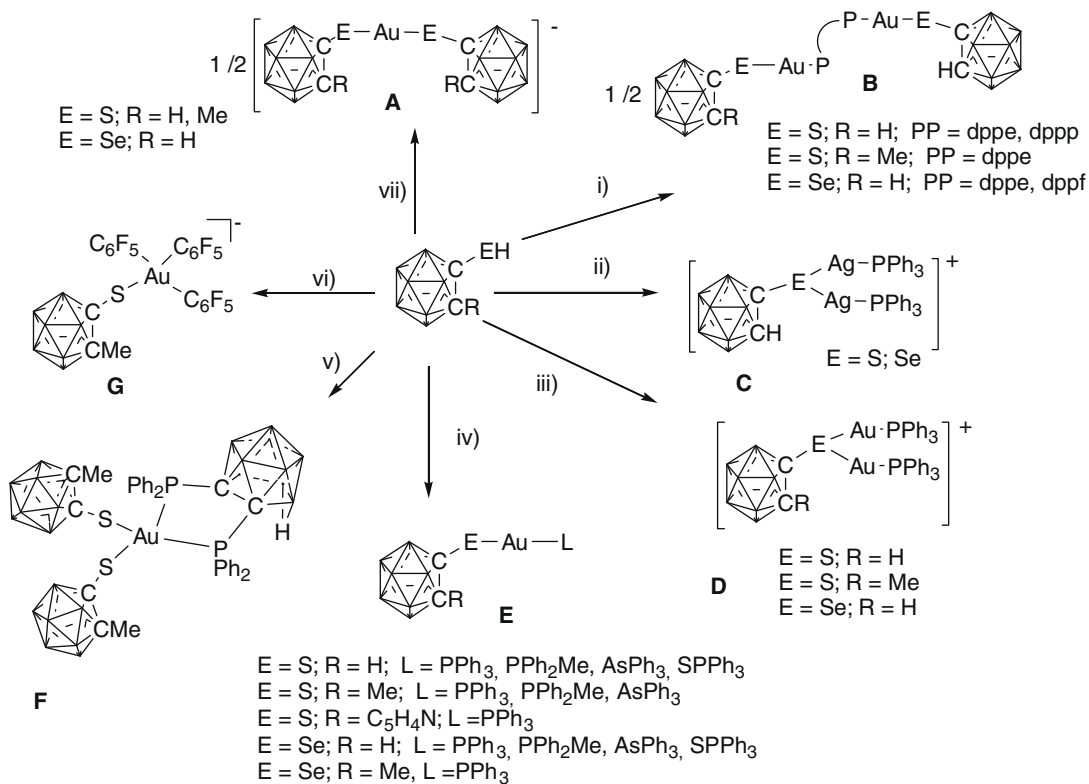
Scheme 10. (i) 1/2 [Au$_2$Cl$_2$(P–P)]; (ii) 2[Ag(OTf)(PPh$_3$)]; (iii) [Au$_3$(μ-O)(PPh$_3$)$_3$]$^+$; (iv) [AuClL]; (v) [AuCl$_2${(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}]; (vi) [AuCl(C$_6$F$_5$)$_3$]$^-$ and (vii) 1/2 PPN[AuCl$_2$].
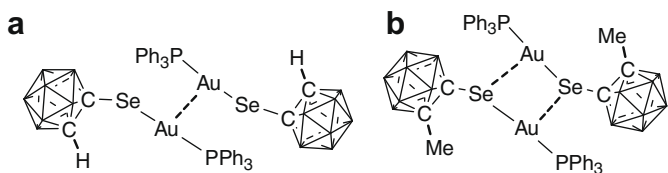

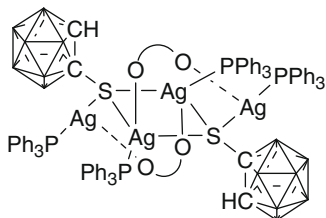**Fig. 7.** Dinuclear aggregation of carborane-monoselenolate gold (I) complexes.

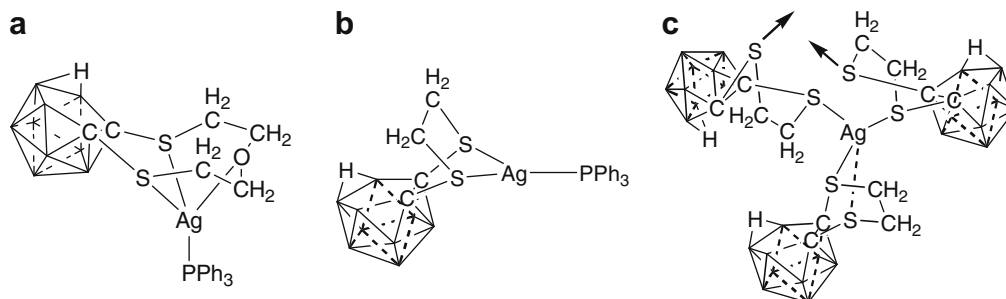**Fig. 8.** [Ag$_4${SC$_2$B$_{10}$H$_{11}$}$_2$(OTf)$_2$(PPh$_3$)$_4$].

in Fig. 9. Complexes [Ag(L$_{2SC5}$)] (Fig. 9c) and [Ag(L$_{2SC15}$)] are polymeric.

3.3. Complexes with other C-substituted ligands derived from o-carborane

The ligand 1,2-(NC$_5$H$_4$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$ has also been explored in gold and silver chemistry [32]. Substitution reactions with gold or silver reactants which contain labile ligands lead to three- or four-coordinated complexes in which the ligand may act both in a chelate or bridging fashion (Scheme 11). The Ag–N distances in [Ag{(NC$_5$H$_4$)$_2$C$_2$B$_{10}$H$_{10}$}(PPh$_3$)]OTf are 2.345(2), 2.350(2) Å and the Ag–P bond 2.3832(7) Å. The geometry towards the silver centre is trigonal distorted with a NAgN angle of 84.26(8)°.

Rigid-rod gold alkynyl derivatives of p-carborane have been synthesised by reaction of the bis(acetylide) 1,12-(HC≡C)$_2$-p-C$_2$B$_{10}$H$_{10}$ (decH$_2$) (Scheme 12) [33]. Some crystallographic data for PPN[Au(decH)$_2$] and [Au$_2$(μ-decH){P(4-OMe-C$_6$H$_4$)$_3$}$_2$] are resumed in Table 10. The crystal structure of compound PPN[Au-(decH)$_2$] (Scheme 12C) displays self assembling of the anions

Fig. 9. Carborane-dithioether silver complexes.
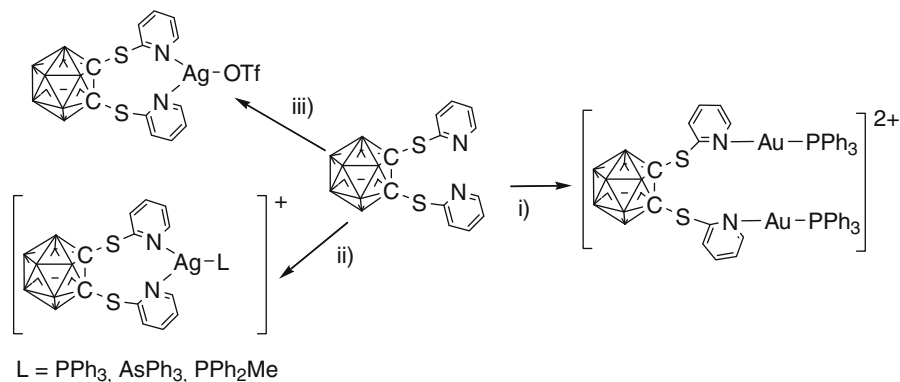
Scheme 11. (i) 2[Au(OTf)(PPh$_3$)], (ii) [Ag(OTf)L] and (iii) AgOTf.
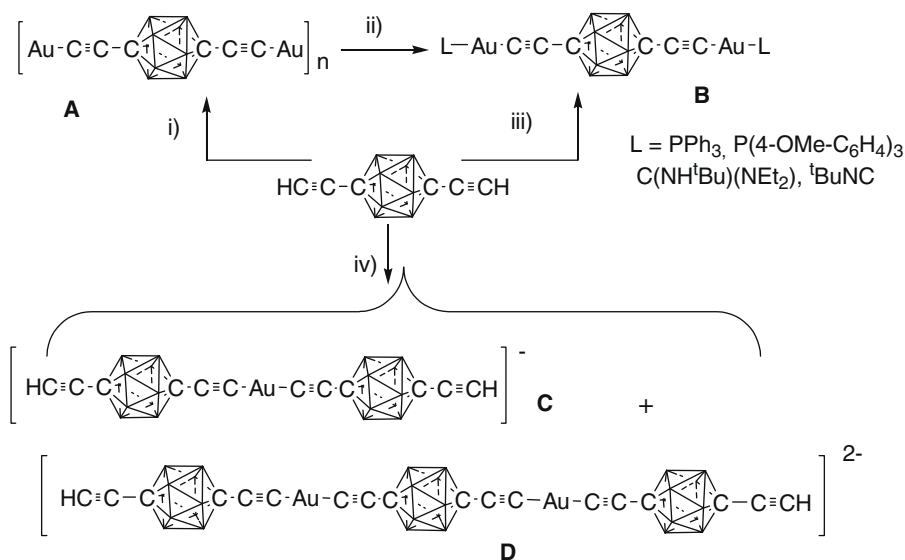
Scheme 12. (i) Not isolated. 2NEt$_3$, 2[AuCl(SMe$_2$)], (ii) ^{t}BuNC, (iii) 2 [Au(acac)L] and (iv) PPN[Au(acac)$_2$], a mixture of **C** and **D** is afforded.

Table 10
Some crystallographic data of bis(alkynyl)carborane gold derivatives (Ref. [33]).

Compound	Au–C (Å)	C≡C (Å)
[Au$_2$(μ-decH)(P(4-OMe-C$_6$H$_4$)$_2$]	2.007(5)	1.181(7)
PPN[Au(decH)$_2$]	1.999(7)	1.188(10)
	2.002(7)	1.166(9)

through two "C≡C–H···Au" and one "C≡C–H···π(C≡C)" intermolecular hydrogen bonding.

4. Conclusion

A wide number of silver and gold complexes have been reported with both Au–C$_{carboranyl}$ σ bond or C-substituted carboranes as ligands which include different nuclearities and geometries for the gold and silver centres. Carboranes have revealed as versatile and rigid building blocks. Fuctionalization of the carbon atoms with different fragments leads to different coordination preferences. Rigid diphosphines favour interesting structures, three or four coordination numbers in gold as well as the synthesis or gold clusters. Dithiolates usually act in a bridging mode. The partial degradation process opens an interesting door. This process leads to anionic ligands. Thus, for the synthesis of metallic compounds, anionic or neutral phosphines or thioetheres are available. Gold(I) three-coordinated complexes with *nido*-diphosphines, tetranuclear clusters [Au$_4${(PPh$_2$)$_2$C$_2$B$_9$H$_{10}$}$_2$L$_2$] and the butterfly shaped [Ag$_2$WS$_4${(PPh$_2$)$_2$C$_2$B$_{10}$H$_{10}$}] are intensely luminescent. The negative charge in *nido* thio- or dithio-ethers contributes to the stabilization of the final complexes. Other interesting points are the synthesis of gold and silver complexes with sandwich metallocarborane diphosphines *similar* to BINAP or ferrocene or the use of bis-acetylene ligands of the *para* isomer to build rod like gold derivatives. All these examples show that at present it is possible to direct the synthesis to a concrete desired compound with the aim of analysing or modifying different properties. In spite of the diversity of complexes known, the search of new ligands which could lead to the presence and/or modulation of interesting physical and chemical properties of the final complexes is still an open issue.

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