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NOTE

Bis(diphenylphosphino)-ferrocene or -dicarba-*closo*-dodecaborane as ligands in gold and silver chemistry†

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The synthesis and properties of gold and silver complexes with bis(diphenylphosphino)-ferrocene or -dicarba-*closo*-dodecaborane, and other related derivatives, such as the corresponding partially degraded *nido*-carborane or bis{diphenylthio(or seleno)phosphoryl}ferrocene, as ligands are reviewed. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: gold; silver; ferrocene; carborane

1 INTRODUCTION

Gold and silver are very special elements, known and cherished by everybody. They have been present in man's life since the earliest civilizations and have occupied an important place in the history of mankind for over 7000 years, as we can see from the excellent goldsmith's work found, for instance, in American and Egyptian tombs.

The main differences between silver and gold are a consequence of relativistic effects, which are specially important for gold.[1] There is a contraction of the 6*s* orbitals and this stabilization diminishes the energy gap between these and the 5*d* orbitals, which also undergo an expansion. Both of these effects are much less pronounced in silver, with the result that the energy separation of the valence *d* and *s* shells of gold is significantly smaller than that in silver.[1] The consequences of these effects are:(a) the different colour of gold;[2] (b) the covalent radius of gold is smaller than that of silver;[3] (c) gold(I) forms two-coordinate complexes easily and silver(I) prefers the formation of three- and four-coordinate derivatives;[1] (d) gold(I) complexes form aggregates through gold–gold interactions (e) the oxidation state III is very stable in gold and it is almost absent in silver.[1]

Due to the high stability of ferrocene and carboranes and the well-established methods for their incorporation into more complex structures, they have became versatile building blocks for the synthesis of new types of ligands.[4,5] An important feature of the ferrocene-based ligands is their flexibility: they behave as a ball-joint, and so the bidentate representatives can adapt as chelating or bridging groups to different geometric requirements of the metal centre.[4]

There is a growing interest in the synthesis of ferrocene- or carborane-containing complexes, which are attractive for various specialized applications. Thus, ferrocene-containing complexes have a wide-spread utility, for example in organic synthesis, production of fine chemicals, homogeneous catalysis and materials chemistry.[5] Carboranes are used as boron sources in the preparation of tumour-seeking drugs for boron neutron-capture therapy (BNCT),[6] and for advanced boron-based ceramics,[7] high-temperature polymers[8] or derivatives with non-linear optical properties.[9]

Here we review the coordination properties on gold and silver of the ligands 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane (dppcc) and 1,1′-bis(diphenylphosphino)ferrocene (dppf).

2 BIS(DIPHENYLPHOSPHINO) DICARBA-*closo*-DODECABORANE AND -FERROCENE COMPLEXES

The observation that a number of silver or gold complexes with diphosphines have significant antitumour activities has increased interest in this type of derivatives.[10] The diphosphine dppcc shows

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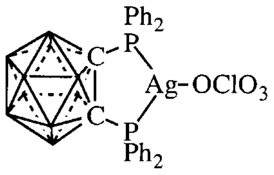
Table 1 X-ray data for the complexes with the diphosphines as chelating ligands

Compound	P-M-P (°)	M–P (Å)	Ref.
Four-coordinate			
[Ag(dppcc)(phen)]ClO_4	89.38(6)	2.463(2), 2.479(2)	11
[Ag(dppf)(phen)]ClO_4	110.59(3)	2.411(1), 2.507(1)	12
[Ag(dppnc)(phen)]	82.58(5)	2.465(2), 2.490(1)	33
[Ag(dppcc){$(SPPh_2)_2CH_2$}]ClO_4	84.56(5)	2.526(2), 2.532(2)	11
[Ag(dppnc)(dppcc)]	(*closo*) 84.90(6)	2.530(2), 2.575(2)	33
	(*nido*) 82.33(6)	2.511(2), 2.559(2)	33
[Au(dppnc)(dppcc)]	(*closo*) 89.25(4)	2.369(1), 2.487(1)	37
	(*nido*) 86.05(4)	2.394(1), 2.440(1)	37
$[Ag(dppf)_2]ClO_4$	105.71(4)	2.561(2), 2.584(2)	12
	98.39(4)	2.549(2), 2.602(2)	12
[Au(dppcc){$(SPPh_2)_2CH_2$}]ClO_4	89.72(6)	2.380(2), 2.389(2)	15
$[Au_4(S_2C_2B_{10})_2(dppcc)_2]$	95.52(8)	2.307(2), 2.427(2)	16
Three-coordinate			
$[Ag(dppf)(PPh_3)]ClO_4$	109.63(4)	2.431(1), 2.480(1)	12
$[Ag(dppnc)(PPh_3)]$	81.07(3)	2.488(1), 2.494(1)	33
$[Ag_2(HCO_2)_2(dppf)_3]$	109.3(2)	2.496(5), 2.523(5), 2.544(5)	13
$[Au(dppcc)(PPh_3)]ClO_4$	90.2(1)	2.405(1), 2.417(1)	14
$[Au(dppnc)(PPh_3)]$	84.91(4)	2.389(1), 2.395(2)	34
$[\{Au(dppnc)\}_2(dppp)]$	86.0(1)	2.365(3), 2.429(3)	34
	84.3(1)	2.374(3), 2.443(3)	34
$[Au(dppf)(PPh_3)]ClO_4$	109.5(1)	2.357(2), 2.409(2)	17
$[Au_2(dppf)_3](ClO_4)_2$	108.8(1)	2.377(3), 2.385(3)	17
$[Au_2(dppf)_3](NO_3)_2$	109.5(1)	2.383(3), 2.395(3)	30
[AuCl(dppomf)]	116.1(1)	2.316(3), 2.348(4)	21
$[Au_4(dppnc)_2(AsPh_3)_2]$	86.51(9), 89.10(8)	2.342(2)–2.373(2)	37
$[Au_4(dppnc)_2\{P(C_6H_4OMe)_3\}_2]$	82.73(4), 88.17(4)	2.359(1)–2.416(1)	38
Gold(III) complexes			
$[AuCl_2(dppnc)]$	87.53(7)	2.296(2), 2.306(2)	36

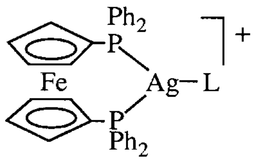
a great tendency to act as a chelating ligand and that has allowed us to prepare novel three- and four-coordinate complexes. Thus the substitution of perchlorate in $[Ag(OClO_3)(dppcc)]$ (**1**), obtained by reaction of the diphosphine $(PPh_2)_2C_2B_{10}H_{10}$ and silver perchlorate,[11] affords [Ag(dppcc)L]ClO_4 where, depending on the ligand, three-coordinate (L = PR_3, $AsPh_3$, $SPPh_3$) (**2**) or four-coordinate complexes [L = bipy, phen, $(SPPh_2)_2CH_2$, dppcc] (**3**) can be synthesized.[11] The reaction of complex **1** with dithiocarbamates, NaS_2CNR_2 ($NR_2 = NEt_2$, NC_4H_8) leads to neutral complexes $[Ag(S_2CNR_2)(dppcc)]$.[11] In the structure of the complexes with L–L = phen or $(SPPh_2)_2CH_2$ the silver atom exhibits a tetrahedral coordination (Table 1).

A similar behaviour is observed with the diphosphine structures **4–6** dppf, which reacts with $Ag(ClO_4)$ to give $[Ag(OClO_3)(dppf)]$ and when substituted for the perchlorate anion leads to three-coordinate, [Ag(dppf)L]ClO_4 (**4**) (L = PPh_3, $SPPh_3$), or four-coordinate complexes, $[Ag(dppf)(PPh_2Me)_2]ClO_4$, [Ag(dppf)L–L]$ClO_4$ (**5**) [L–L = bipy, phen, $(SPPh_2)_2CH_2$] or the homoleptic $[Ag(dppf)_2]ClO_4$.[12] The dppf is acting as a chelating ligand in the complexes with L = PPh_3 or L–L = phen or dppf (Table 1). However, dppf can also act as bridging ligand[13] (Table 2), as in the complex $[Ag(NO_3)(dppf)]_2$, obtained by reaction of $Ag(NO_3)$ and dppf, or in the complexes $[Ag_2(CH_3CO_2)_2(dppf)]_2$, $[Ag_2(C_6H_5CO_2)_2(dppf)]$ (**6**) or $[Ag_2(HCO_2)_2(dppf)_3]$, obtained by reaction of $Ag(NO_3)$ and dppf in the presence of the corresponding NaX.[13]

The reaction of dppcc with the gold derivative $[Au(tht)_2]ClO_4$ leads to [Au(tht)(dppc)]ClO_4. The tetrahydrothiophene (tht) in this complex can be easily substituted by other ligands L to afford three-coordinate [AuL(dppcc)]ClO_4 (L = PR_3, $SPPh_3$,



(**1**)



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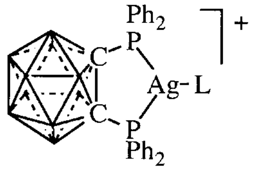

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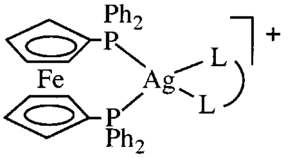

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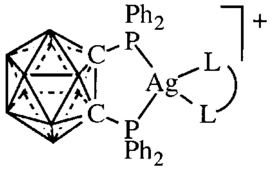

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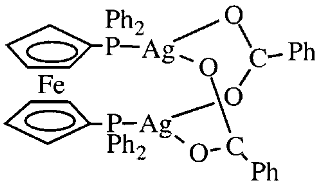
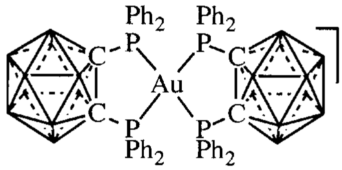


(**6**)

Table 2 X-ray data for the complexes with the diphosphines as bridging ligands

Compound	M–P (Å)	Ref.
$[(AuC_6F_5)(AuPPh_3)(dppnc)]$	2.300(2), 2.326(2)	35
$[Ag(NO_3)(dppf)]_2$	2.433(3), 2.435(3)	13
$[Ag_2(CH_3CO_2)_2(dppf)]_2$	2.344(2), 2.365(2)	13
$[Ag_2(C_6H_5CO_2)_2(dppf)]$	2.340(4), 2.364(5)	13
$[Au_2(dppf)_3(ClO_4)_2$	2.332(4)	17
$[Au_2(dppf)_3](NO_3)_2$	2.335(3)	30
$[(AuCl)_2(dppf)]$	2.222(3), 2.239(3)	19
$[(AuCl)_2(dppf)]$	2.226(1)	20
$[AuCl(dppf)]$	2.298(5), 2.309(6)	25
$[AuCl(dppf)]$	2.293(2), 2.323(2)	30
$[(AuI)_2(dppf)]$	2.240(8)	20
$[\{Au(C_{16}H_9)\}_2(dppf)]$	2.295(2)	22
$[Au_3(Spy)(dppf)(PPh_2Me)](OTf)_2$	2.239(5), 2.246(4)	20
$[S(Au_2dppf)]$	2.247(2)	26
$[S(Au_2dppf)(PPh_2Me)_2](ClO_4)_2$	2.263(6), 2.265(5)	26
$[S_2(Au_2dppf)_3](OTf)_2$	2.25(1)–2.27(1)	26
$[S(Au_2dppf)\{Au(C_6F_5)_3\}]$	2.244(3), 2.245(4)	28
$[S(Au_2dppf)\{Au(C_6F_5)_3\}_2]$	2.252(3), 2.254(3)	27
$[\{S(Au_2dppf)\}_2\{Au(C_6F_5)_2\}]$	2.243(4)–2.266(4)	28
$[Se(Au_2dppf)]$	2.25483), 2.263(3)	29
$[Se(Au_2dppf)_2](OTf)_2$	2.270–2.289	29
$[Se(Au_2dppf)\{Au(C_6F_5)_3\}]$	2.250(1), 2.259(1)	29



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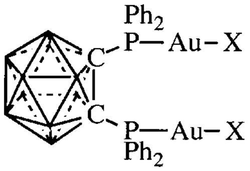
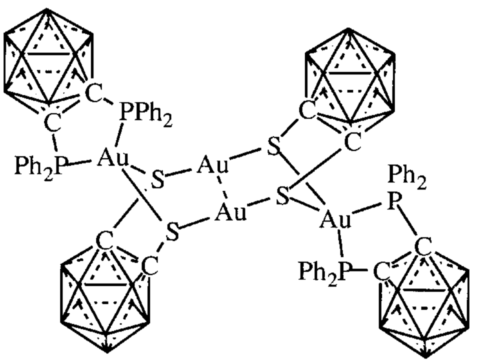


(**8**)

$AsPh_3$, C_5H_4NSH) or four-coordinate complexes (L = phen, dppcc (**7**), other diphosphines, diphosphine disulfides).[14,15] The structures of [Au(dppcc)(PPh_3)]ClO_4 and [Au(dppcc){$(SPPh_2)_2CH_2$}]ClO_4 confirm the trigonal or tetrahedral geometry, respectively, at the gold centre (Table 1). The restricted 'bite' of the diphosphine ligand represents the major deviation from ideal geometry. The large size of the carborane cage and the small bite angle of the diphosphine should encourage chelation; however it is also possible to obtain dinuclear gold complexes and the reaction of [AuX(tht)] (X = Cl, C_6F_5) with dppcc (molar ratio 2:1) leads to the dinuclear [$(AuX)_2$(dppc)] (**8**).[14]

The substitution of the chlorine ligands in the dinuclear complex [$(AuCl)_2$(dppcc)] with the dithiolate derivative $[1,2-S_2C_2B_{10}H_{10}]^{2-}$, obtained from $1,2\text{-}(SH)_2C_2B_{10}H_{10}$ in the presence of Na_2CO_3, does not afford the expected linear dinuclear compound, but the tetranuclear [$Au_4(S_2C_2B_{10}H_{10})_2(dppcc)_2$] (**9**). The structure has been confirmed by X-ray studies and shows an eight-membered Au_4S_4 ring with a short transannular gold–gold interaction [3,131(1) Å].[16]



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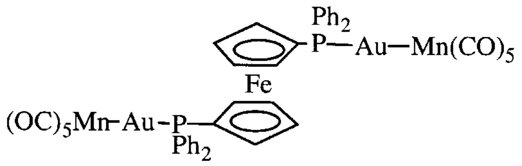
The diphosphine ferrocene has a pronounced tendency to act as a bridging ligand with gold centres (Table 2). Thus, the reaction with the complexes [AuX(SR_2)] (X = Cl or C_6F_5) or [AuL(SR_2)]ClO_4 (L = PR_3 or CH_2PR_3) leads to the dinuclear neutral, [$(AuX)_2$(dppf)], or cationic complexes, [$(AuL)_2$(dppf)]ClO_4.[17–19] The ^{197}Au and ^{57}Fe Mössbauer spectra confirm the presence of linear two-coordinate gold(I) in some of these derivatives.[18] The chloro compound [$(AuCl)_2$(dppf)] has at least three crystalline modifications; one of them shows a nearly linear P–Au–Cl unit and intermolecular gold–gold interactions of 3.083(1) Å,[19] whereas no gold–gold contacts have been found in the other two.[19,20] With the related diphosphine 1,1′-bis(diphenylphosphino) octamethylferrocene (dppomf), other similar dinuclear complexes, [$(AuX)_2$[(dppomf)] (X = Cl, C_6F_5), can be obtained.[21] Electrochemical studies show the formation of iron(III) derivatives of the metallophosphine gold(I) complexes, which can also be obtained by direct reaction of the precursors with electrochemically generated $[FeCp_2]^+$.[21]

Substitution reactions from [$(AuCl)_2$(dppf)] lead



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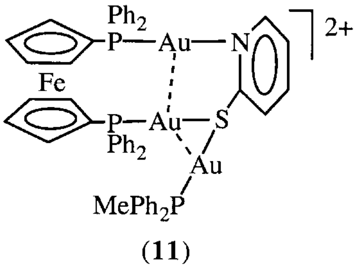

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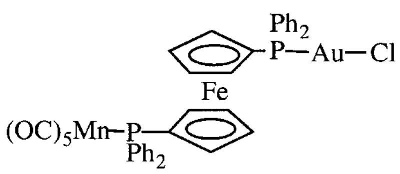

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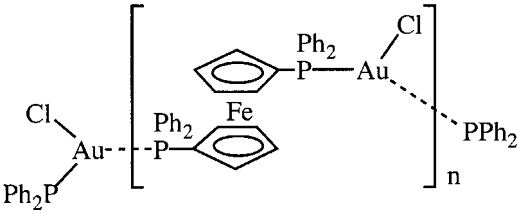

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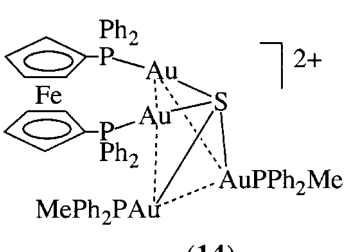
to the new dinuclear complexes [(AuX)$_2$(dppf)] (X = Br, I, 2-pyridinethiolate (Spy), S$_2$CNR$_2$,[20] Me, Ph, 1-naphhyl, 9-anthryl, pyren-1-yl (C$_{16}$H$_9$), C≡CPh, C ≡ CtBu[22])or to the heterometallic compounds [(Au{M(CO)$_5$})$_2$(dppf)] (M = Mn (**10**), Re).[23] The derivative [(AuSpy)$_2$(dppf)] can use its nitrogen donor atoms to incorporate [AuPPh$_2$Me]$^+$ units to give the polynuclear compounds [{AuSpy(AuPPh$_2$Me)}$_2$(dppf)](OTf)$_2$ or [{AuSpy(AuPPh$_2$Me)$_2$}$_2$(dppf)](OTf)$_4$ (OTf = CF$_3$SO$_3$). The latter decomposes in solution to give the trinuclear [Au$_3$(Spy)(dppf)(PPh$_2$Me)](OTf)$_2$ (**11**). It contains weak intramolecular gold–gold interactions of 3.098(1) and 3.210(1) Å.[20] The structure of the organogold compound [{Au(C$_{16}$H$_9$)}$_2$(dppf)] is similar to that of the chloro derivative.[22] The reaction of [(AuCl)$_2$(dppf)] with K$_2$[Pd(CN)$_4$] leads to ligand displacement and [{Au(CN)}$_2$(dppf)] is formed.[23] The complexes [M(CO)$_5$(dppf)] (M = Cr, Mo or W) behave like a monodentate phosphine ligand and react with [AuCl(SMe$_2$)] to aford the heterometallic [M(CO)$_5$ ($\mu-$dppf)AuCl] (**12**).[24]

A chain polymer based on trigonal ClAuP$_2$ units, [AuCl(dppf)]$_x$ (**13**), is obtained from the reaction of [(AuCl)$_2$(dppf)] and dppf, in a 1:1 molar ratio.[25]

Some interesting derivatives have been reported where [Au$_2$(dppf)]$^{2+}$ fragments coordinate around a central sulfur or selenium atom. The complex [S(Au$_2$dppf)], obtained by reaction of [(AuCl)$_2$(dppf)] with Li$_2$S (molar ratio 1:1), can incorporate new neutral or cationic gold(I) fragments to give trinuclear, [S{Au(C$_6$F$_5$)}(Au$_2$dppf)] or [S(AuL)(Au$_2$dppf)]ClO$_4$ (L = CH$_2$PPh$_3$, PPh$_3$, PPh$_2$Me), tetranuclear, [S(AuL)$_2$(Au$_2$dppf)](ClO$_4$)$_2$ (L = PPh$_3$, PPh$_2$Me (**14**)), or hexanuclear complexes, [S$_2$(Au$_2$dppf)$_3$](OTf)$_2$, in which two SAu$_3$ units are joined through the dppf ligand.[26] All these complexes display short gold–gold interactions. The reactions of [S(Au$_2$dppf)] with the gold(III) Au(C$_6$F$_5$)$_3$(OEt$_2$)] or [Au(C$_6$F$_5$)$_2$(OEt$_2$)$_2$]OTf afford the mixed-valence complexes [S(Au$_2$dppf){AuC$_6$F$_5$)$_3$}$_2$], [S(Au$_2$dppf){Au(C$_6$F$_5$)$_3$}] (**15**), or [{SAu$_2$dppf)}$_2${Au(C$_6$F$_5$)$_2$}]OTf.[27,28] The last two compounds show short gold(I)–gold(III) contacts [3.2195(8)–3.404(1) Å] which have been studied by theoretical calculations.[28]

Analogous complexes can be prepared from [Se(Au$_2$dppf)], obtained by reaction of [(AuCl)$_2$(dppf)] with SeC(NH$_2$)$_2$, followed by basic hydrolysis. It further reacts with [(AuOTf)$_2$(dppf)] or [Au(C$_6$F$_5$)$_3$(OEt$_2$)] to give the complexes [Se(Au$_2$dppf)$_2$](OTf)$_2$ or [Se(Au$_2$dppf){Au(C$_6$F$_5$)$_3$}] (**15**), respectively. The later also shows a gold(I)–gold(III) interaction of 3.541(1) Å.[29]

The diphosphines dppf and dppomf can also act as chelating ligands in gold chemistry. Thus, the



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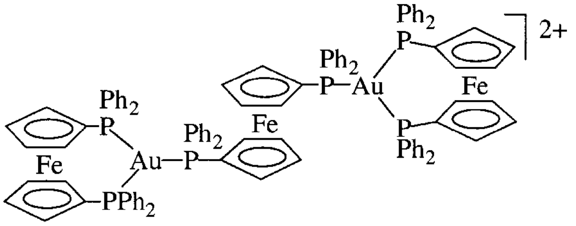

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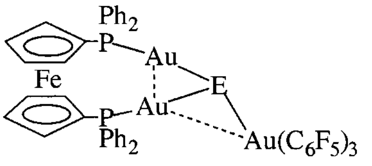

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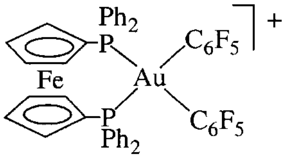


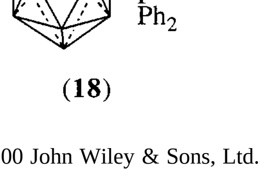
(**17**)

reaction of $[AuX(SR_2)]$ (X = Cl or C_6F_5), $[Au(tht)(PR_3)]ClO_4$ or $[Au(tht)_2]ClO_4$ with the diphosphines, in the appropriate molar ratio, gives three- or four-coordinate mononuclear derivatives, [AuX(dppomf)],[21] $[Au(dppf)(PR_3)]ClO_4$ or $[Au(dppf)_2]ClO_4$.[17] The crystal structures of [AuCl(dppomf)] and $[Au(dppf)(PPh_3)]ClO_4$[17,21] confirm a trigonal-planar Au coordination (Table 1). The M–P distances in $[M(dppf)(PPh_3)]ClO_4$ are shorter for M = Au than for M = Ag (Table 1). The four-coordinate derivative $[Au(dppf)_2]ClO_4$ undergoes a dimerization process with formation of $[Au_2(dppf)_3](ClO_4)_2$ (**16**) which involves bridging and chelating diphosphines.[16] The same cation is present in $[Au_2(dppf)_3](NO_3)_2$, obtained by reaction of the dinuclear $[(AuCl)_2(dppf)]$ with $AgNO_3$ and $NaHCO_3$.[30] Cyclic voltammetry of some of these compounds reveals one chemically reversible ferrocene-based oxidation.

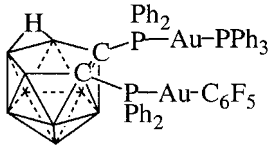
The gold(III) complexes $[\{Au(C_6F_5)_3\}(dppf)]$, $[\{Au(C_6F_5)_3\}_2(dppf)]$ or $[\{Au(C_6F_5)_2\}(dppf)]ClO_4$ (**17**), obtained by displacement of tetrahydrothiophene in $[Au(C_6F_5)_3(tht)]$ or $[Au(C_6F_5)_2(tht)_2]ClO_4$ by the dppf ligand, contain a diphosphine acting as a monodentate, bridging or chelating ligand, respectively.[17]

3 BIS(DIPHENYLPHOSPHINO)-DICARBA-*nido*-UNDECABORATE (1−) COMPLEXES

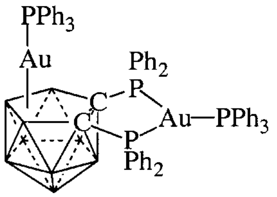
The *closo*-carboranes can be easily transformed into the corresponding *nido*-carborane anions through a partial degradation reaction, which consists of the removal of the boron atom nearest the carbon ones. However, the partial degradation of the bis(diphenylphosphino)dicarba-*closo*-dodecaborane is not an easy process, but the coordination of the ligand to a metal centre favours it. The *closo*-diphosphine can be converted to the 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate(1−) (dppnc, $[(PPh_2)_2C_2B_9H_{10}]^-$) by refluxing the metal complex in ethanol.[31,32]



(**18**)



(**19**)

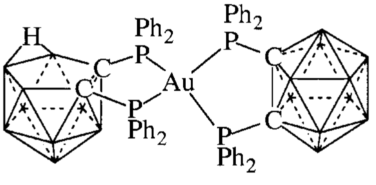


(**20**)

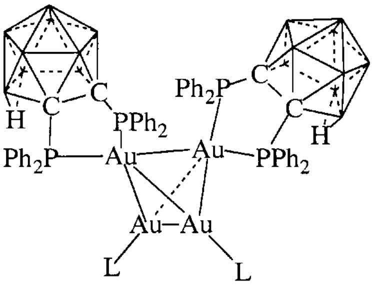
Thus, the reaction of the *closo*-diphosphine dppcc with $[Ag(OClO_3)(PR_3)]$ ($PR_3 = PPh_3$, PPh_2Me) in refluxing ethanol affords the neutral three-coordinate complexes $[Ag(dppnc)(PR_3)]$ (**18**).[33] The crystal structure analysis of the complex with $PR_3 = PPh_3$ confirms a trigonal-planar geometry for the silver centre. Other *nido*-diphosphine complexes, such as [Ag(dppnc)(L–L)] [L–L = phen, dppcc, $(SPPh_2)_2CH_2$], can be obtained from $[Ag(OClO_3)(dppcc)]$ through displacement reactions with bidentate ligands in refluxing ethanol.[33] These complexes are neutral and not cationic as were the *closo*-diphosphine complexes obtained in methylene dichloride at room temperature.[11] The silver atoms show a tetrahedral geometry, as has been confirmed in the crystal structure of the derivatives with L–L = phen or dppcc (Table 1).

In the ^1H NMR spectra a signal centred at −2 ppm corresponds to the bridging proton B–H–B. The chemical shift of this hydrogen atom does not change significantly from one compound to another. It always appears as a broad multiplet and it has a considerable mobility between the two boron atoms. The ^{31}P NMR spectra become more complicated due to the coupling with ^{107}Ag and ^{109}Ag nuclei.[33]

The reaction of the *closo*-diphosphine dppcc with the gold complexes $[AuCl(PR_3)]$ [$PR_3 = PPh_3$, PPh_2Me, $PPh_2(4\text{-}Me\text{-}C_6H_4)$, $P(4\text{-}Me\text{-}C_6H_4)_3$, $P(4\text{-}OMe\text{-}C_6H_4)_3$] in refluxing ethanol also affords the corresponding *nido*-diphosphine derivatives $[Au(dppnc)(PR_3)]$.[34] The gold centre in $[Au(dppnc)(PPh_3)]$ exhibits a trigonal-planar geometry with the *nido*-diphosphine anion acting as a chelating ligand; the restricted bite angle of the diphosphine represents the major deviation from ideal geometry.



(**21**)

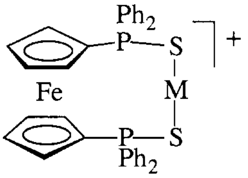


(**22**)

The Au–P distances are smaller than that the Ag–P ones in the analogous silver derivative (Table 1). The dppnc anion can also act as a *P,P′*-bidentate bridging ligand. Thus, the mononuclear complex [Au(dppnc)(PPh_3)] further reacts with [Au(C_6F_5)(tht)] to give the dinuclear derivative [(AuC_6F_5)($AuPPh_3$)(dppnc)] (**19**) which contains a short intramolecular Au…Au contact of 2.9885 (8) Å.[35] The reaction of [Au(dppnc)(PPh_3)] with NaH leads to the removal of the B–H–B proton and the open C_2B_3 face can coordinate a new $[AuPPh_3]^+$ unit, by reaction with [Au(PPh_3)(tht)](ClO_4), to give the metallocarborane [$(AuPPh_3)_2$ {$(PPh_2)_2C_2B_9H_9$}] (**20**).[34]

The gold(III) complex [$AuCl_3$(tht)] also reacts with the *closo*-diphosphine to give the neutral [$AuCl_2$(dppnc)].[32,36] A similar behaviour has been observed from the diphosphines 1,2-$(PR_2)_2$-1,2-$C_2B_{10}H_{10}$ (R = Et, ^{i}Pr or OEt).[32]

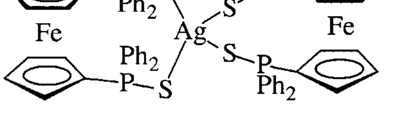
The reaction of the *closo*-diphosphine dppcc with [AuCl($AsPh_3$)] gives two very different complexes, depending on the molar ratio used. With an excess of phosphine (2:1 molar ratio), the four-coordinate [Au(dppnc)(dppcc)] (**21**), which contains the partially degraded dppnc phosphine, is obtained. However, when the molar ratio is 1:2, the tetranuclear cluster [Au_4(dppnc)$_2$($AsPh_3$)$_2$] (**22**) is formed. The Au–Au distances are in the range from 2.604 to 2.915 Å.[37] A pathway has been proposed through the formation of the intermediate three-coordinate [Au(dppnc)($AsPh_3$)]. This intermediate should be very reactive towards the displacement of the arsine ligand by the *closo*-diphosphine to give the four-coordinate derivative; alternatively it could react further with [AuCl($AsPh_3$)] to afford the tetranuclear cluster compound. Substitution reactions of the $AsPh_3$ ligand by phosphines PR_3 [$PR_3 = PPh_3$, P(4-Me-C_6H_4)$_3$ or P(4-OMe-C_6H_4)$_3$] leads to new tetranuclear complexes [Au_4(dppnc)$_2$(PR_3)$_2$] (**22**). In [Au_4(dppnc)$_2${P(C_6H_4OMe)$_3$}$_2$] the Au–Au distances range from 2.629(1) to 2.872(1) Å.[38]



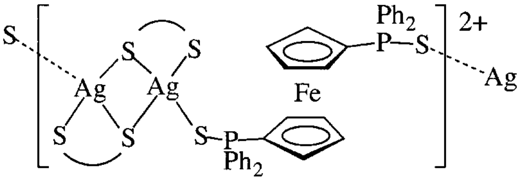
(**23**)

4 BIS{DIPHENYLTHIO(OR SELENO) PHOSPHORYL}FERROCENE COMPLEXES

The oxidation of dppf with sulfur or selenium leads to 1,1′-bis(diphenylthiophosphoryl)ferrocene (dptpf) or 1,1′-bis(diphenylselenophosphoryl)ferrocene (dpspf), which have a longer and more flexible backbone. The reaction of dptpf with [Au(tht)$_2$]OTf or AgOTf, in a 1:1 molar ratio, leads to the complexes [M(dptpf)]OTf (M = Au or Ag) (**23**)



(**24**)



(**25**)

with the dptpf acting as a *trans*-chelating ligand.[39] A similar compound, [Au(dpspf)]OTf, has been obtained from the reaction of the diseleno ligand and $[Au(tht)_2]OTf$.[40] The crystal structures of the three derivatives reveal a linear coordination geometry for the metal centre.[39,40] Short intermolecular Au–Au interactions of 3.091(1) Å, in the selenium derivative but not in the sulfur one, lead to the formation of a chain polymer.

Two- three- and four-coordinate complexes have been obtained with silver centres.[41] Thus, the reaction of the dptpf with $[Ag(OClO_3)(PPh_3)]$ in 1:1 or 1:2 molar ratio gives the three-coordinate $[Ag(dptpf)(PPh_3)]ClO_4$ or the linear $[(AgPPh_3)_2(dptpf)](ClO_4)_2$ derivative. The complex [Ag(dptpf)]OTf reacts with bidentate ligands to give the four-coordinate [Ag(bipy)(dptpf)]OTf or $[Ag(dptpf)_2]OTf$ (**24**) or the four-coordinate polymeric species $[Ag_2\{(SPPh_2)_2CH_2\}_2(dptpf)]_n(ClO_4)_{2n}$ [**25**, S–S = $(SPPh_2)_2CH_2$], which has been characterized by X-ray diffraction.[41]

5 CONCLUSIONS

Carboranes and ferrocene are versatile building blocks for the synthesis of potential ligands that have interesting chemical and physical properties. One of the more important features of the ferrocene-based ligands is their flexibility. The coordination properties of these ligands in gold and silver chemistry are at present attracting growing interest not only because of their potential applications, but also because of the novel structural situations. They can act: (a) as bridging ligands in dinuclear derivatives; (b) as chelating agents in gold(III) or in three- or four-coordinate gold(I) or silver(I) compounds (the rigid carborane backbone favours the formation of an important number of three and four-coordinate complexes); and (c) through a η^3-coordination of a $[AuPPh_3]^+$ unit to the open C_3B_3 face of the *nido*-carboranes.

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