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Three- and Four-Coordinate Gold(I) Complexes

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I. Introduction

Gold is a very special element; it has been known and cherished since the earliest civilizations. It has occupied an important place in the history of mankind for over 7000 years and still retains a special position in our cultures. However, in chemistry, gold has played a minor role and it was only during the last two or three decades that a rapid expansion took place. It has been during this spectacular development of the gold chemistry that new observations have become available, which confirm the unique character of this element. Not only were a great number of new coordination or organometallic compounds prepared, but new coordination numbers and novel structures were also discovered.[1−5]

We draw particular attention to the following important aspect. The stabilization of the 6s orbital, as a consequence of the relativistic effects on gold,[6,7] diminishes the energy gap between this and the 5d orbitals, the latter which also undergoes an expansion. As a result, the small difference of energy among the s, p, or d states leads to the efficient formation of s/d or s/p hybridizations, which are important in explaining the pronounced tendency of gold(I) to form linear two-coordinate complexes. This tendency to the two coordination is much greater than for other isoelectronic centers, such as platinum(0), silver(I), or mercury(II), who usually give compounds in higher coordination numbers.

The vast majority of gold compounds in the oxidation state +1 are two coordinate, linear, and 14-electron species. However, other complexes with different coordination numbers have also been characterized but are not as numerous; they are usually three-coordinate trigonal-planar complexes and tetrahedral four-coordinate complexes. While three- and four-coordinate gold(I) species are much less common than copper or silver species in the same oxidation state, they have some interesting properties. Actually this is an important field of research, but it has only been during the last two decades that a rapid expansion of this new field has taken place. For instance, as recently as 15 years ago it was thought that regular four-coordinate gold(I) complexes could not be synthesized and only a very few number of three-coordinate derivatives were known.[5] The interest in the preparation of three- and four-coordinate gold compounds is justified not only for the novel structural situations that present these derivatives, but also for the dynamic behavior in solution, for the discovery that three-coordinate derivatives generally are luminescent, and for the innovative synthetic approaches used in some of them.

This comprehensive review surveys the coordination compounds of gold(I) with higher than two coordination numbers, and the synthesis and properties of these derivatives are discussed and illustrated by recent examples. Other aspects of the chemistry of gold(I) and gold(III) have been recently treated.[2−4] Most of these complexes contain one or more phosphines as ligand, and for that reason the presentation of the material of this review follows an order of increasing number of phosphines, for the three- and four-coordinate derivatives, respectively. We have excluded most homo- and heterometallic clusters, containing gold atoms bonded to several metal centers through metal−metal bonds or through gold−gold interactions, because they have been treated recently elsewere.[3,7] However, some three-coordinate gold(I) complexes present "aurophilic" interactions and are mentioned in this review.

Because of the preponderant tendency to two coordination for gold(I), even in complexes of $[AuXL_2]$,

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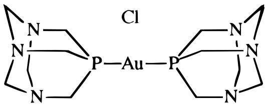
$[AuLL']^+$, or $[AuX'L]$ types ($X =$ anionic ligand, $L =$ neutral ligand, X' or $L' =$ potentially chelating anionic or neutral ligand, respectively), a careful structural study is always necessary. For example, several species of these types fail to achieve the three coordination. Thus, $[Au(PCy_3)_2]SCN$[8] or $[Au(TPA)_2]Cl$[9] (**1**) (TPA = 1,3,5-triaza-7-phosphaadamantane) have a linear coordination with the gold centers bound to the two phosphines, even in the presence of SCN or Cl, ligands which could be coordinated to gold. Furthermore, the usually bidentate S_2CNEt_2 ligand acts as monodentate in $[Au(S_2CNEt_2)(PPh_3)]$ (**2**).[10]

Three major methods have been employed to establish an expansion of the coordination shell in gold compounds: For complexes containing phosphine ligands, ^{31}P NMR spectroscopy is very useful



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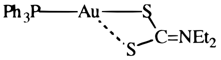


(**2**)

for structural and equilibrium studies in solution. ^{197}Au Mössbauer spectroscopy is applied to the characterization of solid complexes with a wide variety of ligands. However, a more important means of obtaining detailed structural information at the atomic level, for solid crystalline compounds, is the use of X-ray crystallographic methods. This tool has enjoyed extremely widespread use during the last two or three decades, probably as a consequence of the development of fast, accurate, and accessible diffractometers, computers, and software.

$^{31}P\{^1H\}$ NMR studies provide convincing evidence that two-, three-, and four-coordinate gold(I) complexes containing phosphines are readily formed in solution. Addition of phosphines (PR_3) to solutions of the linear complexes $[AuX(PR_3)]$ ($X =$ anionic ligand) or $[Au(PR_3)_2]X$ leads to the formation of new species, such as $[Au(PR_3)_3]X$ or $[Au(PR_3)_4]X$, which are in equilibrium, as it is shown in eq 1. The stoichiometry and exchange behavior of these systems depend critically on the steric and electronic properties of the ligand. When a bulky phosphine, such as PCy_3, is added to dichloromethane or chloroform solutions of $[AuBr(PCy_3)]$, only the two-coordinate cation $[Au(PCy_3)_2]^+$ is observed. When PBu_3, $P(p\text{-}Tol)_3$, or $PPh_2\{CH_2CH_2(o\text{-}C_5H_4N)\}$ are used, both $[Au(PR_3)_2]^+$ and $[Au(PR_3)_3]^+$ are formed; but with smaller phosphines, such as PEt_3, PMe_2Ph, or $PMePh_2$, the two-, three-, and four-coordinate species are detected.[11-15]

$$[AuX(PR_3)] \xrightleftharpoons{PR_3} [Au(PR_3)_2]X \xrightleftharpoons{PR_3} [Au(PR_3)_3]X \xrightleftharpoons{PR_3} [Au(PR_3)_4]X \quad (1)$$

The ^{31}P NMR chemical shifts for some $[Au(PR_3)_n]^+$ cations are collected in Table 1. These complexes are, however, labile on the NMR time scale at room temperature and the chemical shifts have been measured at low temperature to observe individual species. The signals move to a higher field when increasing the coordination number around the gold atom and this is a general behavior for complexes with a gold(I) center bound to two, three, or four phosphorus atoms. Phosphorus−phosphorus coupling constants decrease from three-coordinate to four-coordinate complexes. However, in three-coordinate complexes of the type $[Au(S\text{-}S)(PPh_3)]$ (S-S = dithiolate ligand) the resonance of the phosphorus of the phosphine appears at lower fields than in the corresponding linear derivatives.[16]

The successive formation of cationic complexes through analogous equilibria, as represented in eq 1, has also been observed by using other techniques, such as electronic spectroscopy.[17] Addition of the phosphite $L = P(OCH_2)_3CEt$ to acetonitrile solutions of $[Au(MeCN)_2]ClO_4$ or $(NBu_4)[AuX_4]$ ($X =$ Cl, Br) leads to the formation of $[AuXL]$, $[AuL(MeCN)]ClO_4$, $[AuL_2]ClO_4$, or $[AuL_4]ClO_4$.[17]

Table 1. ^{31}P NMR Chemical Shifts for $[Au(PR_3)_n]^+$ Species

PR_3	$[Au(PR_3)_2]^+$	$[Au(PR_3)_3]^+$	$[Au(PR_3)_4]^+$	ref
PCy_3	63.8			11
PBu_3	32.7	29.5		11
ppye[a]	39.6	36.7		14
PEt_3	43.3	38.3	−5.7	15
PMe_2Ph	15.6	−22.7	−35.1	11
$PMePh_2$	26.0	13.8	−5.8	11

[a] ppye = $PPh_2\{CH_2CH_2(o\text{-}C_5H_4N)\}$.

^{197}Au Mössbauer spectroscopy is also useful for the characterization of two-, three-, and four-coordinate gold(I) complexes.[12,18−21] The isomer shift (IS) is a measure of the total electron density at the gold nucleus and a decrease in the s electron density causes a decrease in IS. Consequently and for a given ligand, increase in the coordination number results in a decrease in IS (as p or d orbital participation in the hybridization of the gold atom increases) by 1−2 mm s^{-1} (three-coordinate complexes) or 2−4 mm s^{-1} (four-coordinate complexes). Thus, for $[Au(PPh_3)_n]ClO_4$ ($n = 2, 3, 4$) the IS decreases from 5.40 to 2.99 to - 0.17 mm s^{-1} as the coordination number increase from 2 to 4.

The quadrupole spliting (QS) reflects the symmetry of the electron distribution about the gold nucleus. Thus, QS for three-coordinate complexes is expected to be very similar to that for the two-coordinate derivatives, while that for complexes with the same four ligands, such as $[Au(PPh_3)_n]ClO_4$ (tetrahedral), is zero, and a single line spectrum results. Other complexes, such as $[AuX(PPh_3)_3]$, have lower symmetry, and a splitting of the spectrum is observed, but they are easily recognized by their low IS.

Sometimes the ^{197}Au Mössbauer spectra suggest an intermediate situation between two and three coordination. This is the case, for instance, for the complexes [AuL(L-L)]ClO_4 (L = tetrahydrothiophene, PPh_3; L-L = bipy or phen).[22] The Mössbauer parameters lie on a part of the IS-QS diagram[20] close to the two-coordination region, but toward the three-coordinate complexes, indicating an asymmetrical coordination of the bidentate ligand, in agreement with the crystal structure reported for the cation $[Au(PPh_3)(bipy)]^+$.[23]

Recently electrospray mass spectrometry has been used for the characterization of three-coordinate cationic complexes of the type $[Au(PR_3)_3]^+$.[24] However, the use of X-ray crystallographic methods has permitted a more detailed structural information and most of the discussion below is based in these data.

II. Three-Coordinate Complexes

Most of the three-coordinate gold(I) complexes are neutral or cationic derivatives with one, two, or three phosphines. Their structures vary from highly distorted ones, with an almost linear arrangement of the gold center with two of the three donor atoms (T-shaped coordination), to a regular trigonal-planar geometries. Some examples are collected in Table 2. It is clear that in the presence of a sufficiently rigid bidentate ligand, and taking into account the tendency of gold(I) to two coordination, the coordination of one donor atom to the gold center results in the other donor atom being fairly close to that center. However, the strength (and length) of these two bonds are often different and one is stronger than the other. The more important criteria to describe a complex as three coordinate is the deviation from linearity of the two stronger bonds at the gold atom, but also the distance of the gold to the more weakly bound donor atom must be taken into consideration. Thus, for example, complex **2** is considered as two coordinate, because of the P−Au−S angle being almost linear (175.7°) and one Au−S distance being much longer than the other (3.015 and 2.338 Å).[10] A similar situation occurs in the thioamide complex $[Au(C_{13}H_{11}N_2OS)(PPh_3)]$ [$C_{13}H_{11}N_2OS$ = [[(2-methoxyphenyl)imino](2-pyridyl)methyl]thio],[25] with a P−Au−S angle of 172.1° and an Au···N interaction of 2.574(5) Å.

Table 2. L−Au−L Angles of Some Examples for Three Coordination of Gold(I)

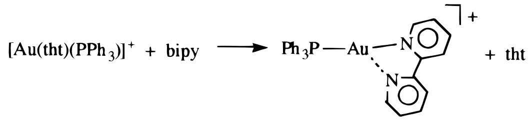
complex	L−Au−L (deg)			ref
$[C_4S_4(AuPPh_3)_2]$	162.4	111.6	85.9	26
$[AuCl(PCy_2Ph)_2]$	158.2	108.7	92.6	27
$[Au(PPh_3)(bipy)]^+$	157.1	130.4	71.4	23
$[Au(PMe_2Ph)_2(SnCl_3)]$	153.8	104.0	104.0	28
$[AuCl(PPh_3)_2]$	132.1	118.7	109.2	29
$[Au(PPh_3)_3]^+$	125.4	119.2	115.2	30
$Au_7P_{10}I$ (AuP_3 moieties)	118.5	118.5	118.5	31
$[Au(PCy_2Ph)_3]^+$	119.9	119.9	119.9	32
$Au_2Tl_6I_{10}$ (AuI moieties)	120	120	120	33

The most regular three coordination is observed in compounds when all the three ligands are identical. This is the case, for example, for the mononuclear $[Au(PCy_2Ph)_3]ClO_4$[32] or for the ternary compounds $Au_7P_{10}I$[31] or $Au_2Tl_6I_{10}$[33] which contain AuP_3 or AuI_3 moieties, respectively. Salts of the cationic complexes $[Au(PPh_3)_3]Q$ show small differences in the structures for the anions Q = $B_9H_{19}S^-$,[34] BPh_4^-,[30] NO_3^-,[35] SiF_5^-,[36] or $[Mo(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]^-$.[37]

A. Monophosphine Complexes

Some neutral, anionic, or cationic three-coordinate gold(I) complexes containing one phosphine as ligand are known. The cationic derivatives, $[Au(N\text{-}N)(PR_3)]^+$, contain a dinitrogen bidentate ligand, such as 2,2′-bipyridyl or 1,10-phenanthroline,[22] and the neutral or anionic ones, $[Au(L\text{-}L)(PR_3)]$, $[(MX_4)(AuPR_3)_2]$ or $[(MX_4)(AuPR_3)]^-$, have an anionic bidentate ligand, such as 8-hydroxyquinolinate[38] or, more often, a ligand with sulfur or selenium atoms. They can be obtained by the following general procedures:

A bidentate ligand displaces a weakly coordinated ligand in linear gold complexes,[22] as in equation 2. A similar procedure exists for the reaction of the ligand (or the corresponding HL) with the oxonium salt $[O(AuPR_3)_3]^+$.[38]



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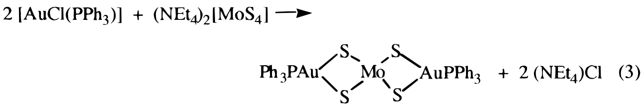
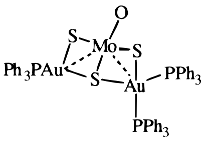
A second procedure is reaction of $[AuCl(PPh_3)]$ with salts of the anionic bidentate ligands, as in the example of eq 3.[39]



(3)

Some X-ray data for these monophosphine complexes are collected in Table 3. The reaction of the cation $[Au(PBuPh_2)]^+$ with the potentially tridentate ligand $[(SPPh_2)_3C]^-$ leads to the formation of $[Au\{(SPPh_2)_3C\}(PBuPh_2)]$ in which the tris(diphenylthiophosphinoyl)methanide ligand is coordinated to the gold center through two of the S atoms.[40] The complex has a T-shaped geometry.

Some complexes containing one or two three-coordinate gold centers, $[MX_4(AuPR_3)_2]$, $[MX_4(AuPR_3)]^-$ (M = Mo, W; X = S, Se), have been prepared by reaction of $[AuCl(PR_3)]$ with salts of $[MX_4]^{2-}$ anions (eq 3). The gold atoms are bound to the phosphine and to two S or Se atoms in a slightly distorted trigonal geometry.[38,41−45] The distances Mo−Au or W−Au in these complexes are short (2.795−2.872 Å) and suggest the presence of a direct metal−metal interaction. The binuclear complex $[C_4S_4(AuPMePh_2)_2]$,[26] prepared from $[AuCl(PMePh_2)]$ and the anion of the tetrathiosquaric acid, has a similar structure to $[MX_4(AuPR_3)_2]$ with the two gold centers bridged by the $C_4S_4^{2-}$ ligand in a distorted trigonal environment [Au−S distances 2.364(3) and 2.952(3) Å]. The reaction of $[AuCl(PPh_3)]$ with $Cs_2[MoOS_3]$ leads to the trinuclear complex $[MoOS_3(AuPPh_3)\{Au(PPh_3)_2\}]$[38] (**3**) which contains two different gold environments, one of them has a trigonal geometry while the other is tetrahedrally coordinated, with one triply bridging sulfur atom. Another example with three- and four-coordinate gold centers is found in $[WSe_4(AuPPh_3)\{Au(PPh_3)_2\}]$.[44]



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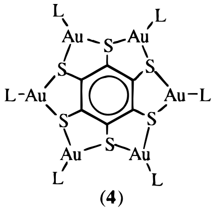


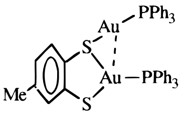
(**4**)

Some interesting complexes with dithiolate ligands have recently been reported. Thus, the reactions of Na_2dmit (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate, $C_3S_5^{2-}$) with 1 equiv of $[AuCl(PR_3)]$ (PR_3 = PMe_3, $PMePh_2$, PPh_3), in the presence of $(NBu_4)Br$, lead to mononuclear three-coordinate complexes, $(NBu_4)[dmit(AuPR_3)]$.[16b] The reaction of benzenehexathiol, $C_6(SH)_6$, with $[AuCl(PPh_3)]$ gives a hexanuclear derivative $[\{CSAu(PPh_3)\}_6]$[46] (**4**) whose wheellike structure shows a hexagon of carbon atoms of the benzene ring surrounded by a hexagon of sulfur atoms which are bonded to a hexagon of three-coordinate gold centers (Au−S−Au angles 131.9−142.7°, S−Au−S angles 80.7−82.7°).

There are some examples of three-coordinate gold centers which are additionally involved in short gold−gold interactions. This occurs in the dithiolate dinuclear complexes $[(S\text{-}S)(AuPPh_3)_2]$ [S-S = 3,4-$S_2C_6H_3Me$ (**5**),[16a] 1,2-$S_2C_6H_4$,[47a] dmit[16b] or 1,2-dicyanoethene-1,2-dithiolate[47]]. The structures contain an irregular three-coordinate gold(I) center, bound to the two sulfur atoms and the phosphine, and a "normal" two-coordinate, linear gold(I) center. The Au···Au contacts are in the range 3.081 to 3.115 Å. Addition of a $[AuPPh_3]^+$ unit to $[(3,4\text{-}S_2C_6H_3Me)(AuPPh_3)_2]$ gives the trinuclear $[(3,4\text{-}S_2C_6H_3Me)(AuPPh_3)_3]^+$ (**6**) which also contains a three-coordinate center with two Au···Au interactions of 2.962(1) and 3.196(1) Å. The trinuclear derivative $[(CH_2S)_2(AuPPh_3)_3]BF_4$,[48] obtained by reaction of ethane-1,2-dithiol with $[O(AuPPh_3)_3]BF_4$, has a similar structure; the central gold atom is three coordinate and the peripheral golds are linear, with Au···Au contacts at 3.284(1) and 3.129(1) Å. Recently, another three-coordinate environment has been found in one of the four gold atoms of $[(Ph_3PAu)SCH_2CHS(AuPPh_3)CH_2S(AuPPh_3)_2]BF_4$ [49] (Au···Au contacts 3.201(1) and 3.227(1) Å).

Table 3. X-ray Data for Three-Coordinate Monophosphine Complexes

complex	Au−P (Å)	P−Au−L (deg)		ref
$[Au(bipy)(PPh_3)]$	2.212(1)	157.1(1)	130.4(1)	23
$[Au\{(SPPh_2)_3C\}(PBuPh_2)]$	2.275(4)	161.4(1)	90.0(1)	40
$[MoS_4(AuPEt_3)_2]$	2.277(4)	133.1(1)	127.8(1)	41
	2.275(4)	131.4(2)	129.6(2)	
$[MoS_4(AuPPh_3)_2]$	2.272(2)	134.7(1)	126.0(1)	39
	2.272(1)	133.3(1)	127.5(1)	
$[WS_4(AuPPh_3)_2]$	2.251(2)	135.7(1)	125.9(1)	42
	2.254(2)	134.0(1)	127.7(1)	
$(PPh_4)[MoSe_4(AuPMe_2Ph)]$	2.272(3)	133.21(7)	122.27(7)	44
$(PPh_4)[WSe_4(AuPMe_2Ph)]$	2.272(2)	133.83(5)	122.37(5)	44
$[WSe_4(AuPMePh_2)_2]$	2.252(10)	130.6(4)	126.6(4)	45
	2.265(13)	129.9(4)	127.4(4)	
$[C_4S_4(AuPMePh_2)_2]$	2.270(3)	162.4(2)	111.4(2)	26
$(NBu_4)[C_3S_5(AuPPh_3)]$	2.235(2)	142.78(9)	127.20(9)	16b
$[C_3S_5(AuPPh_3)_2]$	2.257(1)	159.32(4)	115.05(4)	16b
$[(3,4\text{-}S_2C_6H_3Me)(AuPPh_3)_2]$	2.252(3)	160.84(9)	113.56(9)	16a
$[5,6\text{-}\mu\text{-}(AuPR_3)\text{-}nido\text{-}B_{10}H_{13}]$	2.309(2)	158.8(3)	154.7(3)	52
$[(AuPPh_3)(9\text{-}SMe_2)(C_2B_9H_{10})]$	2.255(1)	166.8(1)	144.9(1)	53



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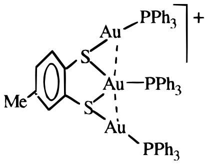

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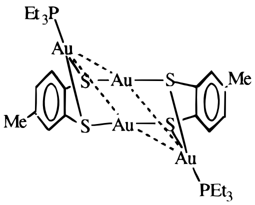

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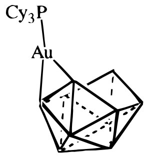
The tetranuclear $[Au_4(S\text{-}S)_2(PEt_3)_2]$ [S-S = 3,4-$S_2C_6H_3Me$ (**7**) or 1,2-$S_2C_6H_4$], obtained by reaction of $[AuCl(PEt_3)]$ with 3,4-dimercaptotoluene or benzene-1,2-dithiol, respectively,[47] contains two three-coordinate gold centers and the other two are linear. The molecule is a rectangular array of the four gold atoms which are in the same plane with Au···Au interactions ranging from 3.02 to 3.23 Å.

Some borane− or carborane−gold complexes can also be considered as three-coordinate derivatives, as the result of the replacement of μ-H atoms of the



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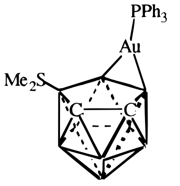


(**9**)

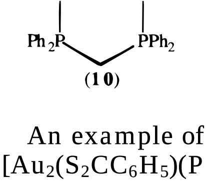
borane cages by the isolobal [μ-AuPR$_3$] fragments. Thus, the complexes [5,6-μ-(AuPR$_3$)-*nido*-$B_{10}H_{13}$] (**8**) [PR_3 = PCy_3, P(*o*-Tol)$_3$],[50–52] obtained by reaction of [AuMe(PR$_3$)] with the borane $B_{10}H_{14}$, or [10,11-μ-(AuPPh$_3$)-9-SMe$_2$-*nido*-7,8-$C_2B_9H_{10}$] (**9**),[53] obtained by reaction of [AuCl(PPh$_3$)] with Tl[9-SMe$_2$-*nido*-7,8-$C_2B_9H_{10}$], show an irregular trigonal coordination around the gold centers, with the AuPR$_3$ unit bridging asymmetrically an B−B edge.

B. Bisphosphine Complexes

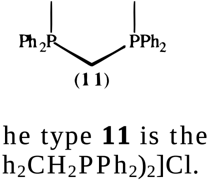
Some X-ray data for three-coordinate diphosphine gold(I) derivatives are collected in Table 4. Complexes of the type [AuX(PR$_3$)$_2$] show Au−P distances rather longer than those in two-coordinate or monophosphine three-coordinate compounds, and P−Au−P angles ranging from 127.8 to 161.2°. The extent of the distortion depends of the nature of the phosphines and the anionic ligands X. Other neutral or cationic complexes, such as [AuX(P-P)] (X = Cl, C_6F_5) or [Au(P-P)L]$^+$ (L = tht, PR$_3$, CH$_2$PR$_3$, SPPh$_3$, AsPh$_3$), have been prepared by using the diphosphine chelate ligands P-P = 1,1′-bis(diphenylphosphino)ferrocene (dppf),[58] (C$_5$Me$_4$)$_2$Fe(PPh$_2$)$_2$,[59] or 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane [(PPh$_2$)$_2$C$_2$-B$_{10}$H$_{10}$].[60,61]

Some of the three-coordinate bis(phosphine) gold(I) complexes luminesce in the solid state, as well as in solution.[57,62,63] Lifetimes are nanoseconds in duration. It is believed that the luminescence in these complexes originates from ligand excitation centered in the n−π* transition.

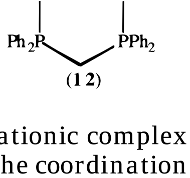
Some [Au$_2$(P-P)$_2$]$^{2+}$ (P-P = bidentate phosphine) complexes associated with halide or pseudohalide anions have been described in various configurations (**10**−**12**). Derivatives of the type [Au$_2$(P-P)$_2$X$_2$], with P-P = PPh$_2$CH$_2$PPh$_2$, X = Cl,[64,65] Br,[66] NO$_3$;[67] P-P = PPh$_2$C(=CH$_2$)PPh$_2$, X = Cl[68] or P-P = PPh$_2$C(=C=CH$_2$)PPh$_2$, X = Cl[69] contain two three-coordinate gold(I) centers. The coordination of the halide or pseudohalide ligand is nearly perpendicular to the P−Au−P axis, which is approximately linear (Table 4). The molecules contain short Au···Au contacts.



(**10**)



(**11**)



(**12**)

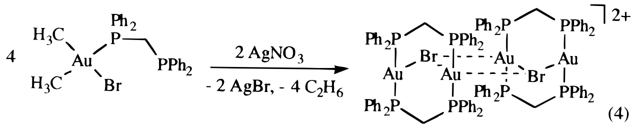
Table 4. X-ray Data for Three-Coordinate Diphosphine Complexes

complex	Au−P (Å)		P−Au−P (deg)	ref
[AuCl(PPh$_3$)$_2$]	2.336(4)	2.317(4)	135.7(1)	54
[AuCl(PCy$_2$Ph)$_2$]	2.324(1)	2.300(1)	158.24(5)	27
[AuBr(PPh$_3$)$_2$]	2.323(2)	2.323(2)	132.45(8)	54
[AuI(PPh$_3$)$_2$]	2.333(2)	2.333(2)	132.13(7)	54
[Au(SCN)(PPh$_3$)$_2$]	2.346(4)	2.349(4)	127.8(1)	55
[Au{C(CN)$_3$}(PPh$_3$)$_2$]	2.290(2)	2.300(2)	161.23(9)	56
[Au(S$_2$COEt)-{P(CH$_2$CH$_2$CN)$_3$}$_2$]	2.306(1)	2.349(1)	145.3(1)	57
[Au(S$_2$COEt)(PPh$_3$)$_2$]	2.310(2)	2.315(2)	130.1(1)	57
[AuCl{(PPh$_2$)$_2$Fe(C$_5$Me$_4$)$_2$}]	2.316(3)	2.348(4)	116.1(1)	59
[Au$_2$Cl$_2$(PPh$_2$CH$_2$PPh$_2$)$_2$]	2.332(3)	2.299(3)	164.9(1)	65
[Au$_2$(NO$_3$)$_2$(PPh$_2$CH$_2$PPh$_2$)$_2$]	2.302(3)	2.316(3)	170.6(1)	67
	2.324(3)	2.327(3)	176.7(2)	

An example of the type **11** is the cationic complex [Au$_2$(S$_2$CC$_6$H$_5$)(PPh$_2$CH$_2$PPh$_2$)$_2$]Cl. The coordination geometries of the two gold centers are different.[70] The bonds across one of the gold atoms are nearly linear, but the other is three coordinate. The dithiobenzoate ligand is coordinated to only one metal center through one of its sulfur atoms. Side-on coordination of chlorine is also found in [Au$_2$Cl{PPh$_2$C(CH$_2$CH$_2$)PPh$_2$}$_2$]Cl[71] or in [Au$_2$Cl{PPh$_2$CH(CH$_2$OCH$_3$)PPh$_2$}$_2$]Cl[71] which have only one coordinated chlorine, but with a weak interaction with the metal, as shown by the long Au−Cl distances of 2.807(3) and 2.963(4) Å, respectively (Au−Cl = 2.28 Å in [AuCl(PPh$_3$)] and 2.50 Å in [AuCl(PPh$_3$)$_2$][29,54]). The Au−Au−Cl angles are 75 and 176°, respectively. A similar situation occurs in [Au$_3$Cl{(PPh$_2$)$_3$CH}$_2$](ClO$_4$)$_2$, obtained by reduction of K[AuCl$_4$] with the triphosphine (PPh$_2$)$_3$CH.[72] The structure consists of three metal atoms arranged in a nearly equilateral triangle with the Au−Au−Au angles close to 60° and intramolecular Au···Au contacts of 2.922−3.089 Å. Two of the gold atoms are linearly coordinated to two phosphorus atoms, but the coordination geometry of the other gold center is similar to the preceding examples and the Au−Cl bond (2.642(6) Å) is nearly perpendicular to the P−Au−P axis. Excitation of an acetonitrile solution of this trinuclear complex at 300−400 nm at room temperature leads to an observed photoluminescence centered at *ca.* 537 nm with a lifetime of 11 ns.

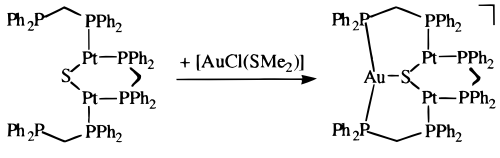
In the binuclear complex [Au$_2$I(PPh$_2$CH$_2$PPh$_2$)$_2$]I,[66] obtained by reaction of CH$_3$I with [Au$_2$(PPh$_2$CHPPh$_2$)$_2$], the coordinated iodide symmetrically bridges the two metals (Au−I = 3.127(2) and 3.196(2) Å; Au−Au−I = 66°), as in **12**. However, the same cation in [Au$_2$I(PPh$_2$CH$_2$PPh$_2$)$_2$][Au(CN)$_2$],[73] obtained from the reaction of the luminescent [Au$_2$(PPh$_2$CH$_2$PPh$_2$)$_2$](BH$_3$CN)$_2$ and NaI, contains an asymmetrically bridging iodide with Au−I distances of 3.161(3) and 3.342(3) Å and Au−Au−I = 73°. This difference has been attributed to different packing forces in the two compounds. The dinuclear derivative [Au$_2$(PPh$_2$CH$_2$PPh$_2$)$_2$](BH$_3$CN)$_2$ also reacts with NaS$_2$CNEt$_2$ to give [Au$_2$(S$_2$CNEt$_2$)(PPh$_2$CH$_2$PPh$_2$)$_2$](BH$_3$CN) which contains a nearly symmetrically bridging dithiocarbamate ligand.[73]

A new example of the type **12**, but further aggregated, has recently been prepared.[74] The reaction of the gold(III) derivative [AuMe$_2$Br(PPh$_2$CH$_2$PPh$_2$)$_2$] with AgNO$_3$ undergoes reductive elimination of ethane and leads to a tetranuclear ionic complex (eq 4). The dication is composed of two binuclear units [Au$_2$Br(PPh$_2$CH$_2$PPh$_2$)$_2$]$^+$ with the bromide bridging the two gold centers. External Au−Br contacts are responsible for the aggregation of these units into dimers.



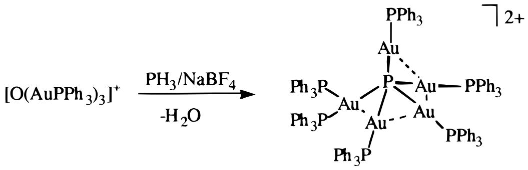
(4)

A new type of complex with a three-coordinate gold(I) center is the trinuclear $[Pt_2Au(\mu_3\text{-}S)(\mu\text{-}PPh_2CH_2PPh_2)_2]Cl$,[75] obtained from $[Pt_2(\mu\text{-}S)(\mu\text{-}PPh_2CH_2PPh_2)(\eta^1\text{-}PPh_2CH_2PPh_2)]$ (which acts as a tridentate ligand) and $[AuCl(SMe_2)]$, according to eq 5. Although the Au−S distance of 2.621(8) Å is long, the P−Au−P angle of 143.9(3)° clearly shows a deviation from linearity.



(5)

The reaction of $[O(AuPPh_3)_3]BF_4$ with PH_3 gas leads to a mixture of products, one of which is the pentanuclear $[PAu_5(PPh_3)_6](BF_4)_2$[76] (eq 6). The cationic cluster is centered by a five-coordinate phosphorus atom in an irregular coordination geometry. In the crystal one of the five gold atoms is attached to two triphenylphosphine ligands in a three-coordinate environment. In solution rapid ligand exchange renders the ligands equivalent on the NMR time scale.



(6)

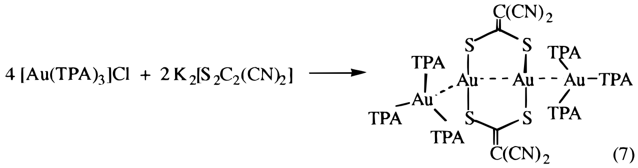
C. Trisphosphine Complexes

Some examples of trisphosphine gold(I) complexes are collected in Table 5. The most regular three coordination is observed in derivatives with three identical phosphines, $[Au(PR_3)_3]^+$. Despite the cations, in $[Au(PPh_3)_3]^+$ salts, being formally the same, small differences are observed in the structures with different anions.

Luminescence from a three-coordinate gold(I) center is a general phenomenon[62,63] and the origin of the emission has been assigned to a metal-centered transition $a_2''(p_z) \rightarrow e'(d_{x^2-y^2}, d_{xy})$. The water-soluble ligands TPA and TPPTS (TPA = 1,3,5-triaza-7-phosphaadamantane, TPPTS = 3,3′,3″-phosphinidynetris(benzenesulfonate)) have been used to synthesize a series of complexes AuLX, AuL_2X, AuL_3X, and AuL_4X (X = Cl). Only the three-coordinate derivatives $[Au(TPA)_3]^+$ and $[Au(TPPTS)_3]^{8-}$ show a strong luminescence both in the solid state and in solution.[77a] The long lifetimes and large Stokes shifts observed for these complexes imply that the emission is a phosphorescence from a triplet excited state. Addition of stoichiometric amounts of ligand to the nonluminescent two-coordinate complex $[Au(TPA)_2]X$ (**1**) causes the appearance of an emission band corresponding to the formation of the three-coordinate species. Addition of further equivalents of TPA quenches the luminescence as the four-coordinate, nonluminescent $[Au(TPA)_4]X$ is formed.

The TPA can be methylated at one of the nitrogen sites to form [MeTPA]I. It reacts with $[AuCl(SMe_2)]$ (molar ratio 3:1) to give the water-soluble complex $[AuI(MeTPA)_3]I_3$.[77b] The coordination environment of the three phosphines around the gold(I) center is approximately trigonal planar (Table 5), where the gold lies out of the P_3 plane by 0.375 Å toward the iodine. The iodine is weakly coordinated to the gold atom at a distance of 2.936(1) Å. This complex is luminescent as are other three-coordinate complexes and shows an interesting temperature-dependent emission spectrum in the solid state. It gives a yellow emission (598 nm) at 77 K and an orange emission (686 nm) at 140 K. $[AuI(MeTPA)_3]I_3$ undergoes an unusual phenyl-transfer reaction with $NaBPh_4$ to form $[AuPh(MeTPA)]BPh_4$. An analogous phenyl-transfer reaction has been observed between the closely related complex $[Au(TPA)_3]Cl$ and $NaBPh_4$, which leads to [AuPh(TPA)].[77b]

Trigonal-planar species can participate in the formation of Au···Au interactions even in unbridged systems. This is the case for the tetranuclear Au_4 chain complex $[\{(TPA)_3Au\}_2Au_2\{S_2C_2(CN)_2\}_2]$, obtained by addition of $K_2[S_2C_2(CN)_2]$ to MeCN−MeOH solutions of $[(TPA)_3Au]Cl$ (eq 7).[78] This complex strongly luminesces orange as a solid and yellow orange in acetone under an UV source. The structure shows the $[Au(TPA)_3]^+$ units interacting with each of the two gold atoms of $[Au_2\{S_2C_2(CN)_2\}_2]^{2-}$ through Au···Au contacts. The AuP_3 coordination of the $[Au(TPA)_3]^+$ units is very nearly trigonal planar; the Au···Au interactions perturb this planarity only slightly.

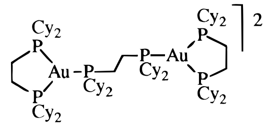


(7)

Diphosphines can act as chelating or bridging ligands. Thus the displacement of tetrahydrothiophene (tht) from $[Au(tht)(PR_3)]ClO_4$ with diphosphines, such as 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane $[(PPh_2)_2C_2B_{10}H_{10}]$ or 1,1′-bis(diphenylphosphino)ferrocene (dppf), leads to mononuclear three-coordinate complexes of the type $[Au(P\text{-}P)(PR_3)]ClO_4$.[58,60] Examples with dppf ligands acting both as chelate and bridging ligand are the binuclear derivatives $[(\mu\text{-}dppf)\{Au(dppf)\}_2]X_2$ (X = ClO_4[58] or NO_3[79a]), obtained by decomposition of the four-coordinate $[Au(dppf)_2]ClO_4$ or by reaction of $[Au(NO_3)(dppf)]_x$ with HCO_2Na, respectively. The two gold centers are in trigonal-planar environments, bound to one chelating diphosphine, and linked to one another by one bridging ligand. An analogous situation has been found in the binuclear cation of $[(\mu\text{-}dcpe)\{Au(dcpe)\}_2][Au(CN)_2]_2$ (**13**), obtained by reaction of AuCN with the diphosphine $(PCy_2)CH_2CH_2(PCy_2)$ (dcpe).[80] Emission was observed for this complex both as a solid and in acetonitrile solution at room temperature, but the probable four-coordinate $[Au(dcpe)_2]^+$ is nonemissive (solution or solid).[63]

Table 5. X-ray Data for Three-Coordinate Triphosphine Complexes

complex	Au−P (Å)			P−Au−P (deg)			ref
$[Au(PPh_3)_3]BPh_4$	2.365(3)	2.384(3)	2.403(3)	115.2(2)	119.3(2)	125.4(2)	30
$[Au(PPh_3)_3](B_9H_{12}S)$	2.384(7)	2.389(6)	2.37(1)	112.3(2)	121.5(2)	124.1(2)	34
$[Au(PPh_3)_3]SiF_5$	2.367(2)	2.379(2)	2.382(2)	116.39(8)	121.55(9)	123.86(8)	36
$[Au(PPh_3)_3][Mo(SC_6F_5)_4(\eta^5\text{-}C_5H_5)]$	2.367(1)	2.392(1)	2.399(1)	113.62(5)	122.28(5)	123.83(5)	37
$[Au(PCy_2Ph)_3]ClO_4$	2.421(3)			119.9(3)			32
$[AuI(MeTPA)_3]I_3$	2.339(2)	2.339(2)	2.343(3)	116.1(1)	116.1(1)	120.2(1)	77b
$[Au\{(PPh_2)_2C_2B_{10}H_{10}\}(PPh_3)]ClO_4$	2.318(1)	2.405(1)	2.417(1)	90.2(1)	135.6(1)	132.2(1)	60
$[Au(dppf)(PPh_3)]ClO_4$	2.343(29	2.357(2)	2.409(2)	109.5(1)	118.2(1)	132.0(1)	58
$[(\mu\text{-dppf})\{Au(dppf)\}_2](ClO_4)_2$	2.332(4)	2.377(3)	2.385(3)	108.8(1)	124.3(1)	126.3(1)	58
$[(\mu\text{-dcpe})\{Au(dcpe)\}_2][Au(CN)_2]_2$	2.318(1)	2.422(2)	2.440(2)	87.4(1)	135.3(1)	136.9(1)	79
$[Au_2(2,6\text{-}PPh_2C_6H_3NPPh_2)_3](ClO_4)_2$	2.357(4)	2.362(4)	2.384(4)	118.1(1)	118.6(1)	122.0(1)	82
	2.338(4)	2.355(4)	2.366(4)	115.8(1)	122.1(1)	122(1)	
$[Au(NP_3)]PF_6$	2.350(2)	2.352(2)	2.365(2)	116.4(1)	117.2(1)	117.3(1)	83
$[Au_2(NP_3)_2](BPh_4)_2$	2.364(4)	2.364(3)	2.399(2)	114.4(1)	116.5(1)	128.9(1)	83



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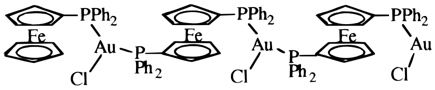
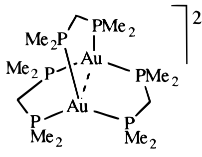


(14)

Addition of the diphosphine dppf to dichloromethane solutions of $[AuCl(SMe_2)]$ gives an intermediate complex $[AuCl(\mu\text{-dppf})]_x$ which readily polymerizes to give $[AuCl(\mu\text{-dppf})]_n$ (**14**). It comprises a polymeric chain structure involving bridging ferrocenylphosphine units linking trigonal Au−Cl groups.[79]

The cations of the complexes $[Au_2(P\text{-}P)_3]X_2$ (P-P = $PMe_2CH_2PMe_2$, X = Cl (**15**); P-P = 2,6-$PPh_2C_5H_3$-$NPPh_2$, X = ClO_4)[81,82] have a similar structure, in which two AuP_3 units are bridged by three diphosphines, but the measured intramolecular Au···Au separation is 3.040(1) and 4.866 Å, suggesting no metal−metal interaction in the derivative with 2,6-$PPh_2C_5H_3NPPh_2$. The geometry around the gold center is close to ideal trigonal planar (Table 5). The complex with 2,6-(diphenylphosphino)pyridine shows photoluminescence both in the solid state and in acetonitrile solution.[82]



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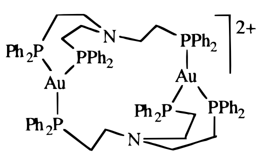

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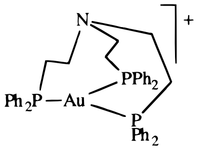


(17)

Reactions of the tetradentate "tripodlike" ligand tris{2-(diphenylphosphino)ethyl}amine (NP_3) with [AuX(tht)] produces three-coordinate complexes, with a trigonal planar AuP_3 coordination, such as the binuclear $[Au_2(NP_3)_2](BPh_4)_2$ (**16**) or the monomer $[Au(NP_3)]PF_6$ (**17**). The nitrogen atom on the ligand does not appear to participate in the coordination, but the three P atoms are coordinated to gold(I) at approximately the same distance (Table 5). The binuclear complex luminesces in the solid state at room temperature with λ_{max} = 470 nm. The luminescence of the mononuclear $[Au(NP_3)]X$ (X = BPh_4, PF_6, NO_3) depends on the nature of the anion. The BPh_4 and PF_6 salts exhibit a yellow luminescence, whereas the NO_3 salt gives a blue luminescence. This difference in luminescent properties of these three-coordinate complexes presumably arises from small changes in the coordination geometry around the Au(I) center.[83]

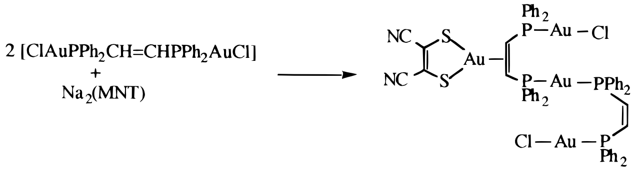
D. Other Complexes

Other three-coordinate gold(I) complexes without phosphine as ligands have also been reported. They include the ternary compounds $Au_7P_{10}I$[31] or $Au_2Tl_6I_{10}$[33] which contain almost regular three-coordinate gold(I) centers bonded to three phosphorus or iodine atoms, respectively (Table 2), and the more recently reported quaternary derivatives $A_2AuP_2Se_6$ (A = K, Rb).[84] The latter is an unusual mixed-valent compound which can be written as $A_6Au^{I}_{1.5}Au^{III}_{1.5}(P_2Se_6)_3$. The structure is formed by a chain with a complicated one-dimensional sinusoidal structure. The gold centers assigned in the oxidation state +1 show two coordination environments; one is linear and the other is a distorted trigonal-planar geometry, surrounded by two or three selenium atoms, respectively.

Other examples are the anionic complexes $(PPh_4)_2[MSe_4(AuCN)]$ or $(PPh_4)_2[MSe_4(AuCN)_2]$ (M = Mo, W), obtained by reaction of $(PPh_4)_2[MSe_4]$ with 1 or 2 equiv of AuCN, respectively,[44] which contain one or two AuCN fragments ligated across an edge of a tetrahedral $[MSe_4]$ moiety.

The displacement of tetrahydrothiophene (tht) in $[Au\{2,4,6\text{-}C_6H_2(NO_2)_3\}(tht)]$ by 2,9-dimethyl-1,10-phenanthroline (dmphen) leads to $[Au\{2,4,6\text{-}C_6H_2(NO_2)_3\}(dmphen)]$. This is another example of highly distorted three coordination, with C−Au−N angles of 168.4(1) and 120.0(1)°, but it is the first quasi-three-coordinate organogold(I) complex for which a crystal structure has been solved.[85a] The reaction of $[Au(2\text{-}C_6H_4NO_2)(tht)]$ with $SbPh_3$ or 1,10-phenanthroline leads to the neutral $[Au(2\text{-}C_6H_4NO_2)(SbPh_3)_2]$ or $[Au(2\text{-}C_6H_4NO_2)(phen)]$, respectively, which presumably are three coordinate.[85b] A trigonal-planar complexation of gold(I) centers by alkynes has been recently reported.[86] The reaction of [AuR(SMe$_2$)] (R = Me, 2,4,6-$C_6H_2(CF_3)_3$ or C≡CSiMe$_3$) with the 3-titanapenta-1,4-diyne [(η^5-$C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$] leads to [($\eta^5$-$C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2(AuR)$], in which the gold(I) center possesses a trigonal-planar environment formed by two η^2-coordinated alkyne units and a η^1-bonded organic group R.

A new situation occurs in the metal−olefin complex [AuCl(MNT)(dppee)] (MNT = 1,2-dicyanoethene-1,2-dithiloate-*S*,*S′*; dppee = *cis*-bis(diphenylphosphino)ethylene), obtained from the reaction of 1 equiv of Na$_2$MNT with 2 equiv of [(μ-dppee)(AuCl)$_2$] (eq 8).[87] One of the four gold centers is coordinated to two S atoms of the MNT ligand and to the olefinic center of one of the dppee ligands with a coplanar orientation of the olefin with respect to AuS$_2$.



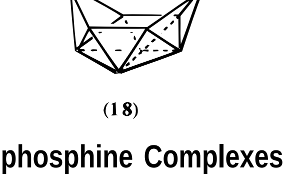
(8)

III. Four-Coordinate Complexes

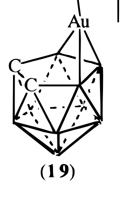
Most of the four-coordinate gold(I) complexes contain one, two, three, or four phosphines bound to the metal center.

A. Monophosphine complexes

Some gold−borane complexes contain one or two [AuPR$_3$]$^+$ units which act as bridging groups for three boron atoms. They can be considered as four-coordinate gold derivatives. Thus, the reaction of [AuCl(PCy$_3$)] with *arachno*-$B_{10}H_{12}(PPh_3)_2$ causes partial degradation of the B_{10} cluster and leads to [(AuPCy$_3$)$_2B_8H_{10}$] (**18**).[88] Its structure shows a distorted tetrahedral coordination for the gold center which is bound to three boron and one phosphorus atoms (Au−B distances of 2.225(13), 2.442(13), and 2.443(12) Å and P−Au−B angles of 164.2(4), 147.4(3), and 129.8(3)°). A similar environment for the gold atom is present in the carborane derivatives [N(CH$_2$Ph)Me$_3$][10-*endo*-(AuPPh$_3$)-7,8-*nido*-$C_2B_9H_{11}$] (**19**)[89] and [N(CH$_2$Ph)Et$_3$][11-*endo*-(AuPPh$_3$)-7,9-Me$_2$-*nido*-7,9-$C_2B_{10}H_{10}$],[90] obtained by reaction of equimolar amounts of [AuCl(PPh$_3$)] and Tl[TlC$_2B_9H_{11}$] or Na$_2$[7,9-Me$_2$-*nido*-7,9-$C_2B_{10}H_{10}$] in the presence of the corresponding ammonium salt. The *endo* attachment of the [AuPPh$_3$]$^+$ unit to three boron atoms in the open pentagonal or hexagonal face, respectively, of the carborane cage is similar in both complexes.



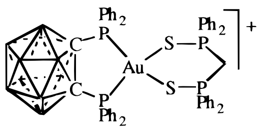
(**18**)



(**19**)

B. Bisphosphine Complexes

The displacement of tetrahydrothiophene from the three-coordinate derivative [Au{(PPh$_2$)$_2C_2B_{10}H_{10}$}tht]ClO$_4$ with diphosphine disulfides affords the mixed four-coordinate complexes [Au{(PPh$_2$)$_2C_2B_{10}H_{10}$}(S-S)]ClO$_4$ (S-S = SPPh$_2$NHPPh$_2$S or SPPh$_2$CH$_2$PPh$_2$S (**20**)).[91] The structure of the cation **20** shows the gold center chelated by the diphosphine and the diphosphine disulfide ligand, thus presenting a somewhat distorted tetrahedral geometry (P−Au−P and S−Au−S angles of 89.72(6) and 95.32(5)°, respectively). The gold center in [Au(S$_2$CPh)(PPh$_3$)$_2$] (**21**),[92] obtained by addition of PPh$_3$ to [Au(S$_2$CPh)]$_x$, is also pseudo-tetrahedrally coordinated by the two phosphines and the chelating aryl dithiocarboxylate anion (P−Au−P and S−Au−S angles of 136.5(1) and 64.5(1)°, respectively). The four-membered chelate ring shows remarkably long Au−S bonds (2.620(5) and 2.859(4) Å, compared with 2.485(2) and 2.661(2) Å in complex **20**). The derivatives [Au(S$_2$CR)(PPh$_3$)$_2$] (R = Ph, *o*-tolyl, *p*-tolyl) are stable in solution only below −30 °C. They are in equilibria with the monophosphino complexes [Au(S$_2$CR)(PPh$_3$)] and the intermolecular exchange of phosphine is fast.[92]



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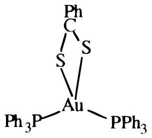
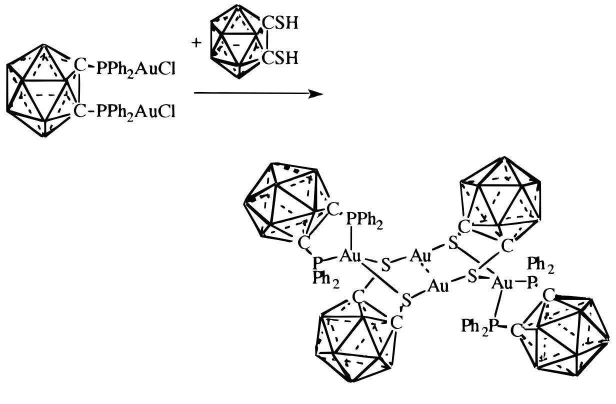


(**21**)

An analogous derivative can be obtained with the bidentate ligand PPh$_2$CH$_2$CH$_2$AsPh$_2$ (dadpe). Addition of dadpe to an aqueous acetone solution of Na[AuCl$_4$] leads to the binuclear [(AuCl)$_2$dadpe]. This complex is converted into [Au(dadpe)$_2$]Cl on titration with the ligand in CDCl$_3$ at an Au/ligand ratio of 1/2. At higher ratios there is exchange between the four-coordinate complex and the excess of dadpe.[93] The structure of the later shows a gold center in a distorted tetrahedral environment, but the P and As atoms are disordered. It is more toxic toward WS and V.79 cells *in vitro* than the free ligand and its toxicity is comparable to that of [Au(dppe)$_2$]Cl.[93]

Another interesting example is obtained in the reaction of the binuclear derivative [(AuCl)$_2${(PPh$_2$)$_2$-$C_2B_{10}H_{10}$}] with $B_{10}H_{10}C_2(SH)_2$ in the presence of Na$_2$CO$_3$, according to eq 9.[91b] The structure of the tetranuclear complex shows an eight-membered Au$_4$S$_4$ ring with a short transannular gold−gold interaction. The peripheral gold atoms display distorted tetrahedral geometry, with P−Au−P and S−Au−S angles of 95.52(8) and 82.85(7)°, respectively.



(9)

C. Trisphosphine Complexes

Compounds of the type $[AuX(PR_3)_3]$ [$PR_3 = PPh_3$, X = Cl, SCN; PR_3 = 1-phenyldibenzophosphole (DBP), X = Cl] can be obtained from reaction of the corresponding linear complexes with excess of the ligand. The coordination geometry for the chloro complexes $[AuCl(PPh_3)_3]$[94] and $[AuCl(DBP)_3]$[95] is only slightly distorted from a regular tetrahedron. The average of the three P−Au−P angles is 113.9° or 117.4°, respectively for the derivatives with $PR_3 = PPh_3$ or DBP. The smaller average Au−P bond lengths for the DBP complex (2.372 Å) compared with that PPh_3 suggest better donor properties of the DBP ligand. The Au−Cl distance is rather long in both complexes [2.710(2) (PPh_3) and 2.735(2) Å (DBP)]. The structures of two modifications of $[Au(SCN)(PPh_3)_3]$[96] show that the geometry about the gold atom differs only slightly from that of the analogous chloro complex. The gold is four coordinate with a rather long Au−S bond distance of 2.791(3) and 2.928(17) Å.

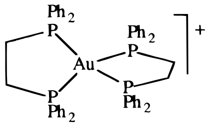
The reaction of $[AuCl(PPh_3)]$ with $[GeCl_2(diox)]$ (diox = 1,4-dioxane) leads to the 1:1 addition compound $[Au(GeCl_3)(PPh_3)]$. Analogous reactions in the presence of 1 or 2 equiv of PPh_3 give $[Au(GeCl_3)(PPh_3)_2]$ and $[Au(GeCl_3)(PPh_3)_3]$.[97] The molecule of the latter features a quasi-tetrahedrally coordinated gold atom with a rather long Au−Ge distance of 2.563(1) Å. $[Au(GeCl_3)(PPh_3)_3]$ is strongly luminescent both in the solid state and in solution, which is in agreement with a trigonal symmetry, as for the above discussed $[AuI(MeTPA)_3]I_3$.[77b]

D. Tetrakisphosphine Complexes

Four-coordinate gold(I) complexes with monodentate phosphines have been reported during the last two decades. As expected, the steric bulk of the phosphine plays a role. Thus, with the bulky phosphine PPh_3, none of three modifications of the compound $[Au(PPh_3)_4]BPh_4$ shows the expected simple tetrahedral geometry.[98] The chloroform solvate contains an almost trigonal-planar $Au(PPh_3)_3$ unit (the gold atom is displaced only 0.25 Å out of the plane formed by the three P atoms and the average Au−P distance is 2.40 Å), bound to the other phosphine with a very long Au···P contact (3.95 Å).

The use of phosphines with small cone angle favors the formation of tetrahedral complexes. Thus, $[Au(PMePh_2)_4]PF_6$, obtained by reaction of $K[AuBr_4]$ with an excess of $PMePh_2$,[99] shows a nearly regular tetrahedral geometry (the two independent P−Au−P angles are 105.24(4) and 118.32(4)°). A similar situation has been found with the 1,3,5-triaza-7-phosphaadamantane phosphine ligand (TPA) or its protonated or methylated derivatives, (HTPA)Cl or (MeTPA)I. They have a relatively small cone angle and a reduced steric hindrance. As a consequence, it has been possible to crystallize a series of stable four-coordinate complexes, such as $[Au(TPA)_4]X$ (X = Cl, PF_6), $[Au(TPA)(HTPA)_3](PF_6)_4$, or $[Au(MeTPA)_4](PF_6)_5$.[100] The central gold atom is coordinated by four P atoms in a nearly regular tetrahedral geometry, where the six tetrahedral angles range from 104.1 to 113.8° with an average value of 109.4°. The Au−P distances range from 2.371 to 2.423 Å, distances which are somewhat shorter than in $[Au(PMePh_2)_4]PF_6$ (2.449 Å).

Four-coordinate complexes containing two diphosphine chelated ligands, such as $[Au(L\text{-}L)_2]X$ (L-L = $PPh_2(CH_2)_2PPh_2$ (dppe) (**22**),[101−103] $PEt_2(CH_2)_2PEt_2$,[101] *cis*-$PPh_2CH{=}CHPPh_2$ (dppey),[104] 1,1′-bis(diphenylphosphino)ferrocene (dppf),[58] $(C_5Me_4)_2Fe(PPh_2)_2$,[59] 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane $[(PPh_2)_2C_2B_{10}H_{10}]$,[60] or $PPh_2CH_2AsPhCH_2PPh_2$ (dpma);[105] X = Cl^-, ClO_4^-, PF_6^-, SbF_6^-, 2-thiouracil, or $[Au(CN)_2]^-$), have been reported. The geometry of the cation $[Au(dppe)_2]^+$ is virtually identical for the salts with X = Cl, SbF_6, or 2-thiouracil.[101−103] The gold atom exists in a distorted tetrahedral environment, the distortion arising from the restricted bite distances of the dppe ligands which subtend angles at the Au atom of *ca.* 86°. As a consequence the remaining P−Au−P angles are opened up from the ideal tetrahedral angle. In $[Au(dppey)_2]PF_6$,[104] the AuP_4 coordination sphere exhibits a similar distortion, with intraligand P−Au−P angles of 86.87(5) and 86.90(5)°. Salts of $[Au(dppe)_2]^+$ or $[Au(dppey)_2]^+$ have been reported to have good cytotoxic and a broad spectrum of antitumor activity.[104,106]



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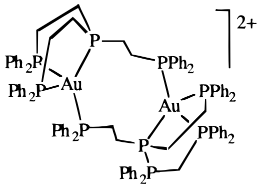


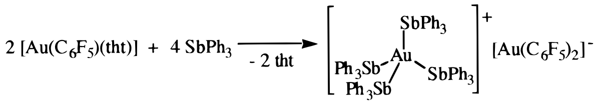
(23)

Dpma reacts with gold(I) cyanide to give $[Au(dpma)_2][Au(CN)_2]$.[105] The structure consists of tetrahedral cations with two six-membered chelate rings (the arsenic atom is not coordinated to the gold center) and nearly linear $[Au(CN)_2]$ ions. The P−Au−P angles are distorted from those of an ideal tetrahedron and range from 103.9(2) to 121.7(2)°.

Treatment of the tetradentate ligand $P(CH_2CH_2PPh_2)_3$ with $[AuCl(SMe_2)]$ produces the binuclear complex $[Au_2\{P(CH_2CH_2PPh_2)_3\}_2]Cl_2$ (**23**).[107] The cation consist of two gold atoms that are each coordinated by three phosphorus atoms of one ligand and by another phosphorus atom of the other ligand. The bridging arms of the ligands produce a ten-membered ring that incorporates the two golds which are widely separated by 6.199 Å. Each gold atom has roughly tetrahedral geometry. This complex reacts with $[AuCl(SMe_2)]$ to give the tetranuclear $[ClAuP\{CH_2CH_2PPh_2(AuCl)\}_3]$,[107] in which each phosphorus atom is involved in a nearly linear P−Au−Cl unit.

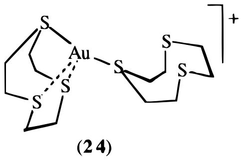
E. Other Complexes

Other four-coordinate gold(I) complexes without phosphines have also been reported. They include derivatives with the monodentate triphenylstibine, $[Au(SbPh_3)_4]X$ (X = ClO_4^-,[108] $[Au(C_6F_5)_2]^-$,[109] or $[Au\{2,4,6\text{-}C_6H_2(NO_2)_3\}_2]^-$,[85] or with the bidentate *o*-phenylenebis(dimethylarsine) (pdma), $[Au(pdma)_2][Au(C_6F_5)_2]$.[110] The stibine complexes can be obtained by addition of $SbPh_3$ to solutions of [AuR(tht)] (eq 10). In the solid state the cations show an almost tetrahedral coordination at the gold center, with Sb−Au−Sb bond angles in the range 107.8 to 111.0°. An equilibrium between the neutral three-coordinate $[AuR(SbPh_3)_2]$ and the ionic complex $[Au(SbPh_3)_4][AuR_2]$ has been proposed in solution.[85] Addition of pdma to solutions of $[Au(C_6F_5)(tht)]$ leads to $[Au(pdma)_2][Au(C_6F_5)_2]$.[110] The gold atom in the cation is coordinated by four arsenic atoms in a close approximation to D_{2d} symmetry, the bite of diarsine being too small to allow exact tetrahedral geometry.



(10)

Reaction of $K[AuCl_4]$ with 2 equiv of the trithia macrocyclic ligand $[9]aneS_3$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane) gives the gold(I) complex $[Au([9]aneS_3)_2]PF_6$ (**24**).[111] The structure of the cation shows distorted tetrahedral coordination at the gold center with one ligand bound in a unidentate manner and the other bound asymmetrically through three sulfur atoms. There are, therefore, two short (average 2.320 Å) and two long Au−S distances (average 2.791 Å). An analogous situation occurs in the mononuclear complexes $[AuL]PF_6$ (**25**) with the tetradentate ligand L = $Ph_2P(CH_2)_2S(CH_2)_nS(CH_2)_2PPh_2$ (n = 2 or 3), obtained by reaction of [AuCl(tht)] and L.[112] In the cation the two phosphorus atoms are coordinated to the gold center (Au−P distances of 2.284(7) and 2.303(7) Å; P−Au−P angle of 169.1(2)°) and additionally, both thioether donors are involved in long-range, weak interactions (Au−S distances of 2.889(6) and 3.190(7) Å).



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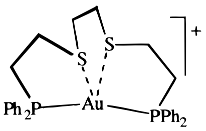
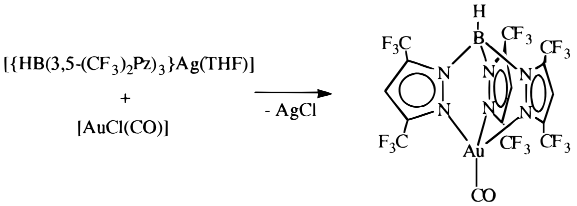


(**25**)

The reaction of $[\{HB(3,5-(CF_3)_2Pz)_3\}Ag(THF)]$ $[HB(3,5-(CF_3)_2Pz)_3$ = hydrotris(3,5-bis(trifluoromethyl)pyrazolyl)borate] with [AuCl(CO)] leads to the carbonyl gold(I) complex $[\{HB(3,5-(CF_3)_2Pz)_3\}Au(CO)]$, according to eq 11.[113] The gold atom adopts a distorted tetrahedral geometry with a Au−C distance of 1.862(9) Å and Au−N distances of 2.312(5), 2.317(5), and 2.384(6) Å. The carbon monoxide ligand can be replaced by *tert*-butyl isocyanide. The complex $[\{HB(3,5-(CF_3)_2Pz)_3\}Au(CNBu^t)]$ shows a different structure from that of the carbonyl analogue. The coordination geometry of the gold center can be best described as bent rather than pseudotetrahedral. The Au−N distances show notable differences in length with one short (2.077(6) Å) and two long separations (2.734 and 2.787 Å).[113]

IV. Outlook

Since the early 1980s gold chemistry has been continuously expanded into a rich field of research and the coordination chemistry of gold(I) in high coordination numbers is no exception. An important number of three- and four-coordinate complexes, with different structures showing variations from highly distorted ones to regular geometries and interesting properties, have been prepared during the last few years.



(11)

This field is presently attracting growing interest not only because of the novel structural situations that present these complexes, but also because of their potential applications for various techniques. A particularly interesting example is the fact that three-coordinate species generally have luminescent properties and they can be used as photocatalysts. Some three- or four-coordinate phosphine or thiolate complexes are effective therapeutic agents in the treatment of rheumatoid arthritis and in the therapy of cancer. Other potential uses are for influencing the behavior of "liquid gold" pastes and for the stabilization of mesogenic and dendrimeric phases. In conclusion, we shall see during the next few years a major expansion in the synthesis and applications of gold(I) compounds in high coordination numbers.

V. Acknowledgments

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VI. References

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