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GOLD(I) AND GOLD(III) COMPLEXES CONTAINING BIS(DIPHENYLPHOSPHINE)METHANE DISULFIDE OR BIS(DIPHENYLPHOSPHINE)AMINE DISULFIDE LIGANDS *

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Summary

The reaction of $SPPh_2CH_2PPh_2S$ with gold(I) or gold(III) complexes containing weakly coordinated ligands leads to the formation of the binuclear complexes $RAuSPPh_2CH_2PPh_2SAuR$ ($R = C_6F_5$), or $[Au_2\{SPPh_2\underline{CH_2PPh_2S\}_2](ClO_4})_2$, the mononuclear complexes, $R_3AuSPPh_2CH_2PPh_2S$, or, $[R_2\overline{AuSPPh_2CH_2PPh_2S}]ClO_4$. The last complex reacts with NaH to give $R_2\overline{AuSPPh_2C}HPPh_2S$ which reacts with gold(I) or silver(I) derivatives to give binuclear, $R_2\overline{AuSPPh_2C}HPPh_2SAuR$, or trinuclear complexes, $[\{R_2\overline{AuSPPh_2C}HPPh_2S\}_2M]ClO_4$ ($M = Au$ or Ag).

Reaction of $SPPh_2NHPPh_2S$ with RAuTHT, ClAuTHT (THT = tetrahydrothiophen) or $[R_2AuCl]_2$ gives $[AuSPPh_2NPPh_2S]_2$ or $R_2\overline{AuSPPh_2NPPh_2)S}$, containing the deprotonated ligand.

Introduction

A number of interesting gold derivatives with bis(diphenylphosphino)methane $[(Ph_2P)_2CH_2]$ [1–3], bis(diphenylphosphino)methanide $[(Ph_2P)_2CH]^-$ [4] or bis(diphenylphosphino)amine $[(Ph_2P)_2NH]$ [5] as ligands have been described, but there is no information on the donor properties and reactivity of the disulfide derivatives of these ligands in gold chemistry.

We describe here the preparation of mono- and bi-nuclear gold(I) and gold(III) complexes containing (a) $SPPh_2CH_2PPh_2S$ as a uni- or S,S-bidentate ligand; (b) $[SPPh_2CHPPh_2S]^-$ as an S,C-chelating or tridentate ligand; and (c) $[SPPh_2NPPh_2S]^-$ as a bridging or S,S-chelating ligand.

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* Dedicated to Professor Rafael Usón on the occasion of his 60th birthday.

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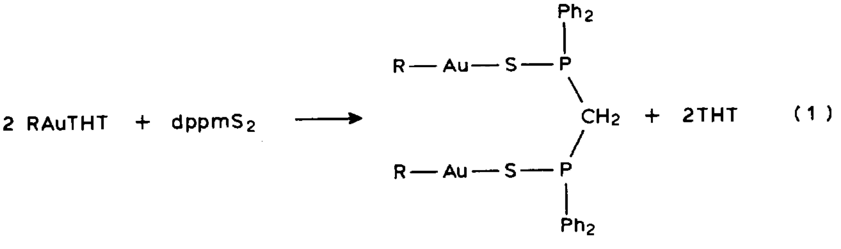
Results and discussion

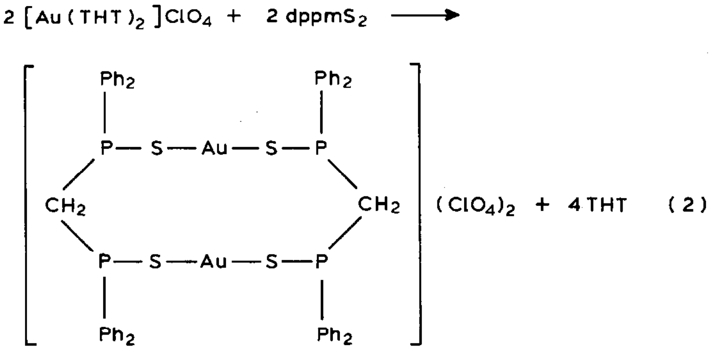
(a) Complexes with $SPPh_2CH_2PPh_2S$

Tetrahydrothiophen (THT) is readily displaced by $SPPh_2CH_2PPh_2S$ ($dppmS_2$) from gold(I) complexes to give binuclear derivatives (eq. 1 and 2), in which the disulfide acts as a bidentate bridging ligand, even when an excess (e.g. an 1/1.2 ratio in eq. 1) is used. To the best of our knowledge these are the first reported complexes containing $dppmS_2$ as bridging ligands.



(I)

$(R = C_6F_5)$



(II)

Complexes I and II are white solids, stable to air and moisture at room temperature. Acetone solutions of I are non-conducting, while solutions of II behave as 2/1 electrolytes (see Table 1). In their IR spectra the band due to $\nu(PS)$ (590(m) and 560(m) cm^{-1} for I and II, respectively) is shifted to lower frequencies relative to the free ligand (620 cm^{-1}), as expected [6]. The bands at 1100(s, br) and 625(m) cm^{-1}) in the spectrum of II are due to the ClO_4^- anion [7]. The ^1H NMR spectra each show a triplet (4.55 ppm ($J(PH)$ 13.5 Hz) and 3.88 ppm ($J(PH)$, 13.2 Hz) for I and II, respectively) corresponding to PCH_2P. ^{31}P NMR (^1H decoupled) spectra consist of a singlet at δ 38.5 and 39.0 ppm (for I and II), respectively).

Addition of $dppmS_2$ to dichloromethane solutions of $(C_6F_5)_3AuTHT$ gives a mixture of $(C_6F_5)_3AuSPPh_2CH_2PPh_2S$ (III) and the starting products, but the disulfide readily displaces diethyl ether in $(C_6F_5)_3AuOEt_2$ to give the mononuclear complex III, according to eq. 3.

$$R_3AuOEt_2 + dppmS_2 \rightarrow R_3AuSPPh_2CH_2PPh_2S + OEt_2 \qquad (3)$$

TABLE 1

ANALYTICAL DATA FOR COMPLEXES

Complex [a]	Yield (%)	Analysis Found (calcd.)(%)) C	H	N	Au	Λ_M [b]	Mol. wt [c] (Found (calcd.))	M.p. (°C)
I $RAuSP(Ph_2)CH_2P(Ph_2)SAuR$	95	37.75 (37.75)	1.95 (1.88)	–	33.05 (33.5)	2	1189 (1177)	185
II $[Au_2\{SP(Ph_2)CH_2P(Ph_2)S\}_2](ClO_4)$	50	40.6 (40.3)	3.6 (2.95)	–	26.15 (26.45)	200	–	191
III $R_3AuSP(Ph_2)CH_2P(Ph_2)S$	64	44.9 (45.0)	1.85 (1.95)	–	16.9 (17.2)	1	1100 (1147)	169
IV $[R_2AuSP(Ph_2)CH_2P(Ph_2)S]ClO_4$	83	41.2 (41.2)	2.1 (2.05)	–	18.2 (18.25)	139	–	232
V $R_2AuSP(Ph_2)CHP(Ph_2)S$	78	45.4 (45.45)	2.3 (2.2)	–	20.1 (20.15)	2	1006 (980)	208
VI $R_2AuSP(Ph_2)CHP(Ph_2)SAuR$	79	39.0 (38.5)	2.15 (1.6)	–	28.9 (29.3)	1	1335 (1343)	190
VII $[\{R_2AuSP(Ph_2)CHP(Ph_2)S\}_2Au]ClO_4$	67	39.25 (39.45)	1.9 (1.9)	–	26.5 (26.2)	155	–	228
VIII $[\{R_2AuSP(Ph_2)CHP(Ph_2)S\}_2Ag]ClO_4$	53	41.0 (41.0)	2.0 (1.95)	–	23.75 (23.2)	168	–	176
IX $[AuSP(Ph_2)NP(Ph_2)S]_2$	95	44.55 (44.65)	3.25 (3.1)	2.9 (2.2)	30.1 (30.5)	–	–	230(d)
X $R_2AuSP(Ph_2)NP(Ph_2)S$	75	44.15 (44.15)	1.9 (2.05)	2.05 (1.45)	19.9 (20.1)	6	1044 (980)	222(d)

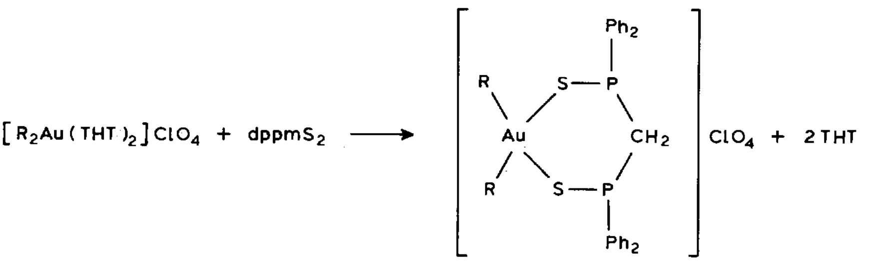
[a] $R = C_6F_5$. [b] In acetone, $ohm^{-1}\ cm^2\ mol^{-1}$. [c] In chloroform.

Complex III is a white solid, showing two IR bands at 620(m) and 595(s) cm^{-1} which are assignable to the vibration ν(P–S), indicating that only one of the two sulfur atoms of the ligand is coordinated to the central metal ion. The ^{31}P NMR spectrum confirms this structure, and shows two doublets at 43.78 and 33.49 ppm (J(PP) 15.2 Hz), corresponding to the phosphorus atom linked to the sulfur bonded to gold, and to the un-coordinated P–S end [8]. In the ^{1}H NMR spectrum the CH_2 protons appear as a distorted triplet at 4.43 ppm ($J(P_AH) \approx J(P_xH) = 13.9$ Hz). The complex is non-conducting in acetone and monomeric in chloroform (see Table 1). This is also a new type of coordination for this ligand.

Ligand interchange occurs between complex III and $[Au(THT)_2]ClO_4$ according to eq. 4.

$$2\ R_3AuSPPh_2CH_2PPh_2S + 2\ [Au(THT)_2]ClO_4 \rightarrow II + 2\ R_3AuTHT + 2\ THT \quad (4)$$

A new mononuclear derivative is obtained by displacement of THT from $[(C_6F_5)_2Au(THT)_2]ClO_4$ (eq. 5).



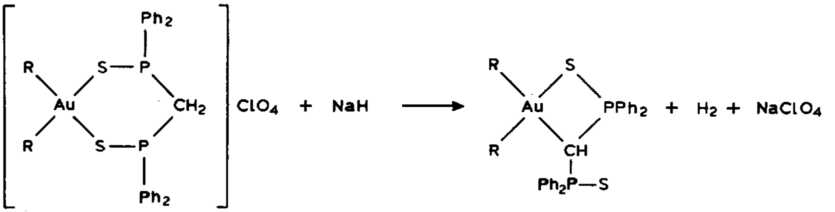
(5)

(IV)

Complex IV is a white solid, showing two IR bands at 1100(s, br) and 625(m) cm^{-1} characteristic [7] of the ClO_4^- anion, two bands at 810(s) and 795(s) cm^{-1} from the mutually *cis*-C_6F_5 groups [9,10], and only one ν(PS) vibration at 570(s) cm^{-1}, which suggests an S,S-chelate coordination of the ligand. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ 38.2 ppm and the ^1H NMR spectrum shows a triplet at δ 5.18 ppm (P–CH_2–P, J(PH) 12.5 Hz). The complex is a 1/1 electrolyte in acetone.

(b) Complexes with $[SPPh_2CHPPh_2S]^-$

Complex IV reacts with NaH by deprotonation of the methylene group and abstraction of ClO_4^-, leading to the neutral methanide complex (eq. 6).



(6)

(V)

The structure of the product must be similar to that of $(Et_3P)Cl\overline{PtSPPh_2C}HPPh_2S$ [11], in which bonding of the metal to the methanide carbon and to one sulfur atom creates a four-membered ring. The following observations are in accord with this: (a) The ^{31}P NMR spectrum shows two resonances at δ 38.65 and 69.56 ppm. There is no coupling between the two phosphorus atoms, such as observed for the platinum complex [11] and no exchange occurs at room temperature. In the ^{1}H NMR spectrum, the methanide group gives a doublet of doublets at 3.38 ppm (J(PH), 9.2 and 12.7 Hz). The $^{19}F\{^{1}H\}$ NMR spectrum shows two triplets at −158.38 and −158.87 ppm ($J(F^4F^3)$ 19.9 Hz), arising from the *para*-fluorine atoms of two different C_6F_5 groups, which are therefore mutually *cis*.

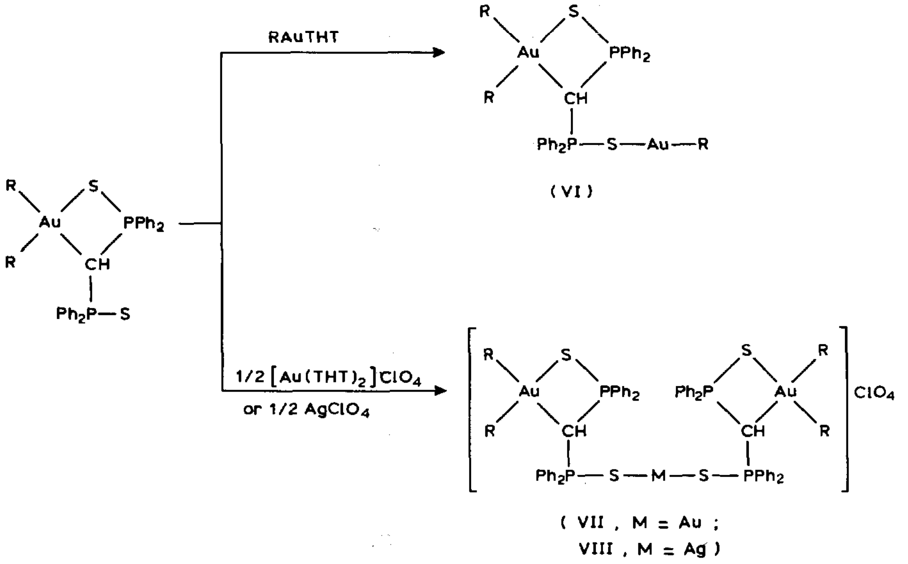
(b) The IR spectrum shows no band due to the ClO_4^- anion; two bands at 630(m) and 585(m) cm^{-1} are assignable to ν(PS) of the free and coordinated end of the disulfide, respectively, and the presence of two bands at 805(s) and 790(s) cm^{-1} confirms the *cis* position of the C_6F_5 groups.

(c) The molecular weight in chloroform is that expected for a mononuclear species, and it is non-conducting in acetone.

Complex V showed no reaction with $[(Bu_4N)Br]$, 1,10-phenanthroline, or triphenylphosphine. Complex V was recovered unchanged after a dichloromethane solution was refluxed for 1 day with an excess (1/1.2) of any of these ligands.

Since the disulfide ligand in V has one uncoordinated sulfur atom, the complex is capable of displacing poorly coordinated neutral (THT) or anionic $(OClO_3)^-$ ligands from other derivatives (Scheme 1) to give bi- or tri-nuclear compounds as shown in Scheme 1.

Complexes VI–VIII are light yellow solids, stable to air and moisture at room temperature. Acetone solutions of VI are non-conducting, whereas VII and VIII behave as 1/1 electrolytes. The IR spectra of VII and VIII show two bands, at 1100(s, br) and 620(m) cm^{-1}, due to the ClO_4^- anion, and the *cis* disposition of the two C_6F_5 groups is confirmed by the presence of two bands at 805(s) and 795(s) cm^{-1}. The ν(PS) vibrations appear at ca. 595 cm^{-1} as a broad asymmetric band. In the ^{1}H NMR spectra, the PCHP group gives a doublet of doublets at δ 3.92

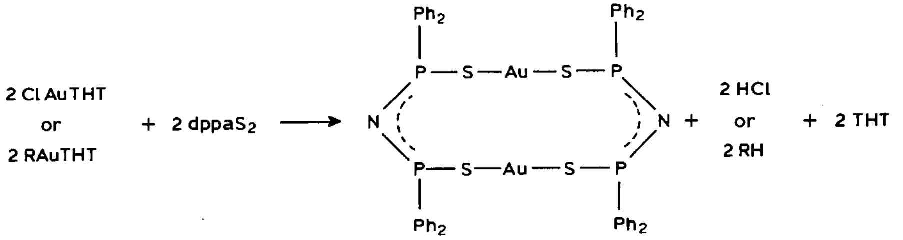


SCHEME 1

ppm (J(PH) 8.0 and 14.1 Hz) for VI; 3.61 ppm (J(PH) 8.7 and 11.9 Hz) for VII and 3.60 ppm (J(PH) 8.9 and 12.1 Hz) for VIII, respectively. The ^{31}P NMR spectra each show two doublets, at δ 66.68 and 47.34 ppm (J(PP) 10.7 Hz) for VI, 69.54 and 48.04 (J(PP) 9.0 Hz) for VII, and 69.05 and 48.19 ppm (J(PP) 8.9 Hz) for VIII.

(c) Complexes with [$SPPh_2NPPH_2S$]$^-$

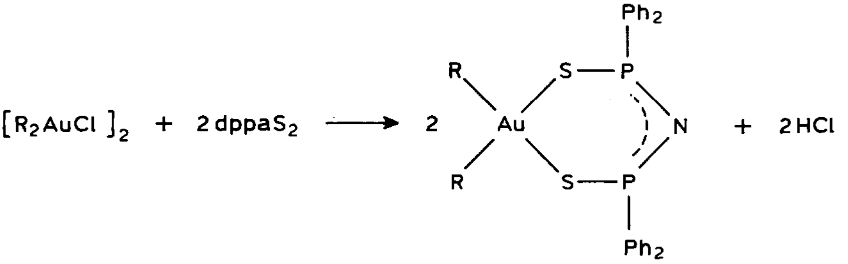
The disulfide $SPPh_2NHPPh_2S$ (dppaS_2) (dppa = diphenylphosphino-amino) is acidic [12] and so can be easily deprotonated [13–16]. Thus, dppaS_2 reacts with ClAuTHT or C_6F_5AuTHT to give the neutral binuclear complex IX (eq. 7).



(7)

(IX)

When the dinuclear [R_2AuCl]$_2$ is used the neutral mononuclear X is obtained (eq. 8).



(8)

(X)

Complexes IX and X are white solids, stable to air and moisture. Complex IX is insoluble in organic solvents. Complex X is monomeric in chloroform. The ^{31}P NMR spectrum of complex X consists of a singlet at δ 36.6 ppm, which indicates the equivalence of the phosphorus atoms, and the ^{19}F NMR spectrum reveals that the two C_6F_5 groups are magnetically equivalent, showing three multiplets at δ −162.0, −157.7 (*ortho*- and *meta*-F) and −122.8 ppm (*para*-F).

No reaction was observed between complexes IX or X and RAu(THT) or $HClO_4$; the unchanged starting materials were recovered after two days at room temperature.

Experimental

The instrumentation employed and general experimental techniques were as described earlier [3,4]. The yields, melting points, C, H, N and Au analyses, conductivities and molecular weights of the novel complexes are listed in Table 1.

Preparation of the complexes

All reactions were carried out at room temperature.

$C_6F_5AuSP(Ph_2)CH_2P(Ph_2)SAuC_6F_5$ *(I)*, $[Au_2\{SP(Ph_2)CH_2P(Ph_2)S\}_2](ClO_4)_2$ *(II), and* $[(C_6F_5)_2\overline{AuSP(Ph_2)CH_2P(Ph_2)S}]ClO_4$ *(IV).* A solution of $C_6F_5Au(THT)$ [17] (0.091 g, 0.2 mmol), $[Au(THT)_2]ClO_4$ [18] (0.047 g, 0.1 mmol) or $[(C_6F_5)_2Au(THT)_2]ClO_4$ [19] (0.0807 g, 0.1 mmol) and dppmS$_2$ [13] (0.045 g, 0.1 mmol) in 30 ml of dichloromethane was stirred for 1 h. Concentration to ca. 5 ml and addition of hexane (20 ml), in the case of I or II, or diethyl ether (20 ml) in the case of IV gave white crystals of I, II or IV.

$(C_6F_5)_3AuSP(Ph_2)CH_2P(Ph_2)S$ *(III).* To a solution of $(Bu_4N)[(C_6F_5)_3AuBr]$ [20] (0.102 g, 0.1 mmol) in 50 ml of diethyl-ether was added $AgClO_4$ (0.021 g, 0.1 mmol). The mixture was stirred for 90 min with exclusion of light, then the precipitated AgBr and $[Bu_4N]ClO_4$ were removed by filtration, and dppmS$_2$ [13] (0.045 g, 0.1 mmol) was added to the filtrate. The solution was stirred for 1 h, then evaporated to ca. 5 ml. Addition of hexane (15 ml) gave a white solid (III).

$(C_6F_5)_2\overline{AuS(Ph_2)C}HP(Ph_2)S$ *(V).* Complex IV (0.108 g, 0.1 mmol) was added to a suspension of NaH (0.3 g, 12.4 mmol) in diethyl ether (50 ml).The mixture was stirred for 1 h, then the excess of NaH and the precipitated $NaClO_4$ were removed by filtration. Evaporation of the filtrate to ca. 5 ml and addition of hexane (20 ml) gave light-yellow crystals of complex V.

$(C_6F_5)_2\overline{AuSP(Ph_2)C}HP(Ph_2)SAuC_6F_5$ *(VI) and* $[\{(C_6F_5)_2\overline{AuSP(Ph_2)C}HP(Ph_2)S\}_2Au]ClO_4$ *(VII).* To a solution of complex V (0.196 g, 0.2 mmol) in 30 ml of diethyl ether or dichloromethane was added C_6F_5AuTHT (0.091 g, 0.2 mmol) or $[Au(THT)_2]ClO_4$ (0.047 g, 0.1 mmol). The mixture was stirred for 1 h then filtered, and the filtrate was evaporated to ca. 5 ml. Slow addition of hexane (20 ml) for VI or diethyl ether (20 ml) for VII produced crystals of complex VI or VII.

$[\{(C_6F_5)_2\overline{AuSP(Ph_2)C}HP(Ph_2)S\}_2Ag]ClO_4$ *(VIII).* Silver perchlorate (0.021 g, 0.1 mmol) was added to a suspension of complex V (0.196 g, 0.2 mmol) in 20 ml of diethyl ether and the mixture was stirred for 45 min with exclusion of light. The light-yellow crystals of complex VIII were filtered off.

$[AuSP(Ph_2)NP(Ph_2)S]_2$ *(IX).* A solution of C_6F_5AuTHT [17] (0.452 g, 1 mmol) or ClAuTHT [17] (0.321 g, 1 mmol) and dppaS$_2$ (0.449 g, 1 mmol) in 100 ml of diethyl ether was stirred for 5 h. The white precipitate of IX was filtered off and washed with 2 × 5 ml of diethyl ether.

$(C_6F_5)_2\overline{AuSP(Ph_2)NP(Ph_2)S}$ *(X).* To a solution of $[(C_6F_5)_2AuCl]_2$ [9] (0.113 g, 0.1 mmol) in 50 ml of diethyl ether was added dppaS$_2$ (0.0898 g, 0.2 mmol). The mixture was stirred for 1 h then concentrated to ca. 5 ml. Addition of hexane (20 ml) gave white crystals of X.

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