

Synthesis of dinuclear dicationic heterobridged gold(I) ring derivatives with bis(diphenylphosphines) and bihapto symmetric or asymmetric ligands containing heterocycles: ^{31}P NMR investigations

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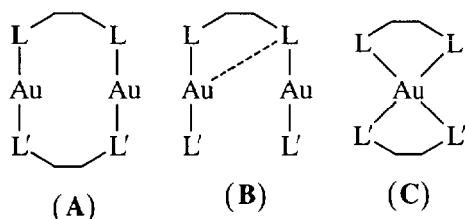
Abstract

The reactions of $[\text{Au}_2 \mu\text{-bis(diphosphine)}]^{2+}$ with 1,3-asymmetric bihapto or 1,5-symmetric bihapto ligands yield the heterobridged complexes $[\text{Au}_2 \mu\text{-bis(diphosphine)} \mu\text{-(L'-L')}]^{2+}$ (**I–VIII**) where the bis(diphosphine) can be: dpmm = bis(diphenylphosphinomethane), dppe = bis(diphenylphosphino)ethane, or dppp = bis(diphenylphosphino)propane; L'-L' can be: (1-benzyl-2-imidazolyl)diphenylphosphine, 2-mercapto-1-methylimidazole, or 1,1'-methylene-dipyrazole. The gold(I) complexes were characterized especially by ^{31}P NMR spectroscopy, and in two cases equilibrium reactions were also detected. Moreover, a ^{31}P NMR data correlation between the chemical shifts and the increase of the number of methylene groups in the bisphosphine ligands is also reported.

Keywords: Gold; Dinuclear complexes; Synthesis; Phosphine complexes; Heterocycles complexes; ^{31}P NMR spectroscopy

1. Introduction

The synthesis of gold(I) complexes with bridging ligands could produce more complicated results than expected. The bihapto ligands could be coordinated to the gold(I) to form at least cyclic (**A**), 'open ring' (**B**) or chelate (**C**) complexes.



L = L' or L ≠ L': neutral or anionic donor atom of the ligand

A large number of X-ray crystal structures were reported for compounds of the type (**A**) [1]. In these derivatives, the gold(I) atoms usually are bicoordinated linearly and a weak gold-gold interaction is present to stabilize the dinuclear ring. It has been established that

the closed-shell d^{10} interactions are due to relativistic effects [2]; moreover, dinuclear gold(I) ring systems frequently can be luminescent [3].

Examples of (**B**) in which both dithiolate and phosphine ligands are coordinated to metal centres have been reported [4]. The structures of these compounds show that one of the gold atoms is three-coordinated and the intramolecular distances Au---Au in the range 3.096–3.148 Å are indicative of a metal-metal contact.

Lastly, the bihapto ligands can chelate the gold atom giving derivatives of type (**C**). Even if the four-coordination is not common in gold(I) chemistry, some examples have been structurally characterized [5].

The cyclic dinuclear gold(I) systems (**A**) can be classified as homobridged or heterobridged complexes and they can be neutral or dicationic, according to the charge of the bidentate ligands coordinated to the gold(I) atoms [6].

Here we report the synthesis and characterization of dinuclear dicationic gold(I) ring complexes (type **A**) where L-L is a bis(diphosphine) and L'-L' is a neutral symmetric or asymmetric ligand containing heterocycles.

This study contributes additionally to our understanding of the interactions in solution between neutral lig-

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ands and $[(PPh_2(CH_2)_n)PPh_2]Au_2]^{2+}$ as related to their use in antitumor gold drugs [7].

2. Results and discussion

Recently, we reported the ability of a new phosphine, namely (1-benzyl-2-imidazolyl)diphenylphosphine $[(Bzim)Ph_2P]$, to coordinate a metal centre (Au(I), Ag(I)); mononuclear or homobridged dinuclear derivatives were also isolated and characterized [8].

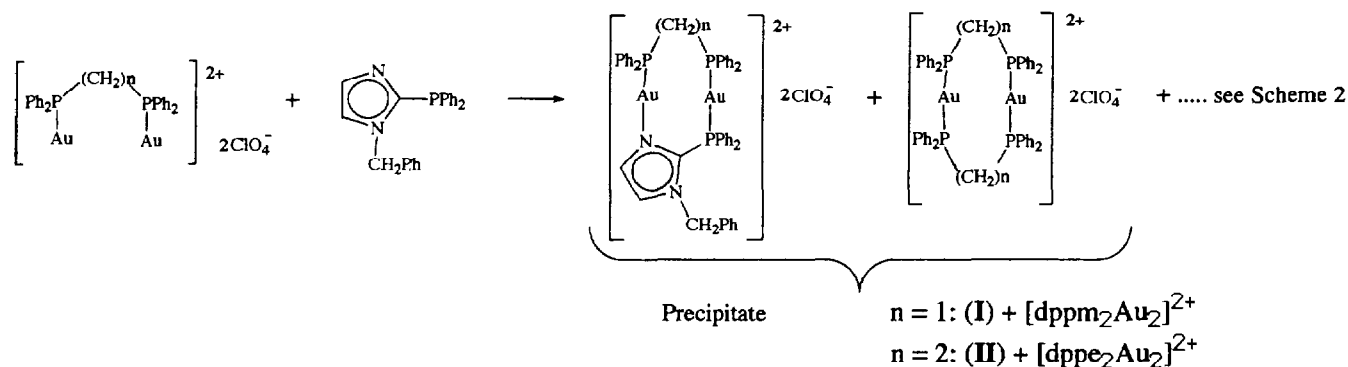
Now, we extend the use of $(Bzim)Ph_2P$ to obtain asymmetric heterobridged dinuclear complexes of gold(I).

When we react the fragment $[(PPh_2(CH_2)_n)PPh_2]Au_2]^{2+}$ ($n = 1; 2$) with $[(Bzim)Ph_2P]$ in THF solution (Scheme 1), white precipitates were isolated and characterized by 1H and ^{31}P NMR spectra. The precipitates resulted in a mixture of two compounds in the ratio $(I)/[dppm_2Au_2]^{2+} = 9:1$ and $(II)/[dppe_2Au_2]^{2+} = 4:1$; the respective amounts of the compounds were calculated by the integrals of the signals in the 1H NMR spectra.

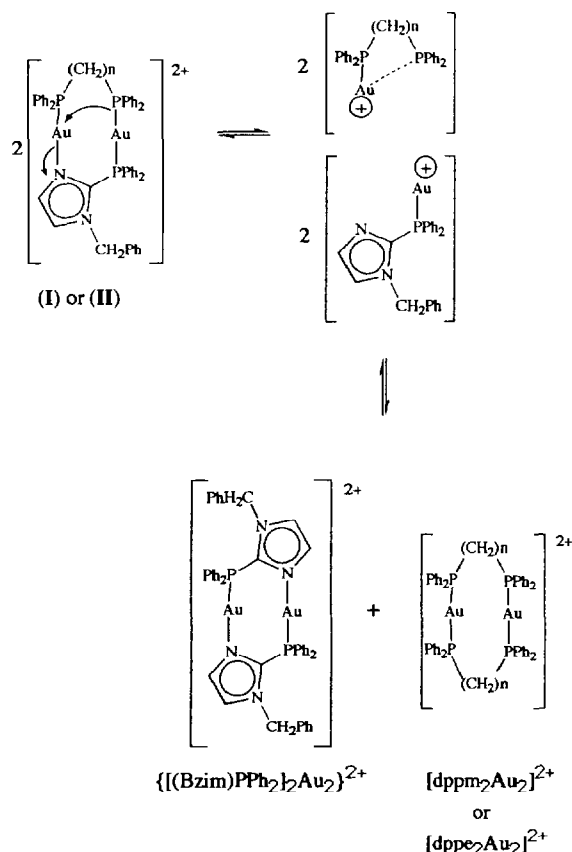
Different reaction conditions and various crystallization procedures were attempted to obtain pure (I) and (II), but we always obtained the mixed products. This failure left us to assume the possibility of equilibrium reactions.

When the reactions reported in the Scheme 1 were carried out in an NMR tube, using deuterated THF as a solvent, we observed in the ^{31}P NMR spectra the signals of the mixtures reported above and also a singlet at 19 ppm attributed to the homobridged dinuclear complex $[(Bzim)PPh_2]_2Au_2]^{2+}$ previously reported [8]. These results suggested the mechanism shown in Scheme 2.

Subsequently, the mechanism and the equilibrium reactions were confirmed by interchange reactions of $[dppm_2Au_2]^{2+}$ or $[dppe_2Au_2]^{2+}$ with $[(Bzim)PPh_2]_2Au_2]^{2+}$. When we reacted the $[dppm_2Au_2]^{2+}$ with $(Bzim)Ph_2P$ a precipitate was obtained; the ^{31}P NMR spectrum showed the formation of a large number of products that were impossible to separate.



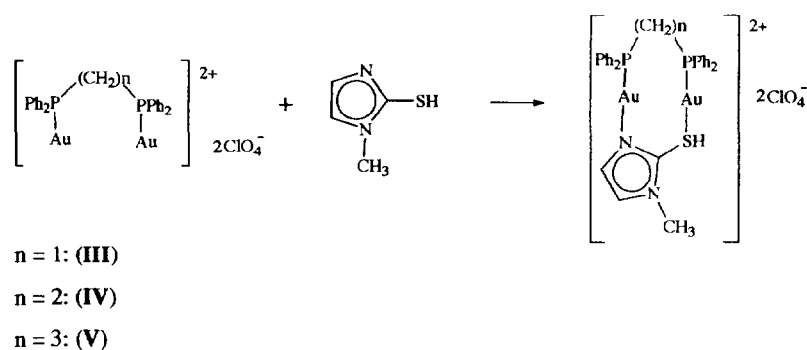
Scheme 1.



To verify if the scheme reaction reported above could be of general validity, we extended our investigation to another asymmetric 1,3 bihapto ligand containing heterocycle, namely 2-mercapto-1-methylimidazole (Scheme 3).

The precipitates isolated in quantitative yields were shown to be pure compounds (III–V); they are light sensitive both in the solid-state and in solution.

In order to obtain more-stable derivatives, we used a symmetric 1,5 bihapto ligand, namely 1,1'-methylene-dipyrazole, to coordinate the $[bis(diphenylphosphine)digold(I)]^{2+}$ fragments (Scheme 4).



Scheme 3.

From these reactions, pure white precipitates were obtained; the complexes (VI–VIII) are stable cyclic compounds, in spite of the large ring size ranging from ten to twelve atoms. From these results, we may infer that the low lability of some of our dicationic gold(I) cyclic complexes mainly depends on the strength of the trans effect. In compounds (I) and (II), the trans effect of the phosphorus atom bound to the imidazole ring is high and cleavage of the dinuclear gold(I) ring complexes occurs, bringing about the equilibrium reactions reported in Scheme 2.

When sulphur or nitrogen atoms with a trans effect lower than the phosphorus atom of a tertiary phosphine are coordinated to the gold centres, cyclic compounds were obtained (III–VIII) and large ring size derivatives were isolated without any cleavage of the cycles.

2.1. ^{31}P NMR investigation

In the absence of X-ray crystal structures, other spectroscopic techniques may be a valuable aid to elucidate the nature of the metal complexes. In our study, ^{31}P NMR spectroscopy [9] was a powerful and diagnostic tool. Elegant applications in gold chemistry of this technique have been reported [10], and recently the equilibrium in solution among three gold(I) species with dppm as bridging ligands was investigated [11].

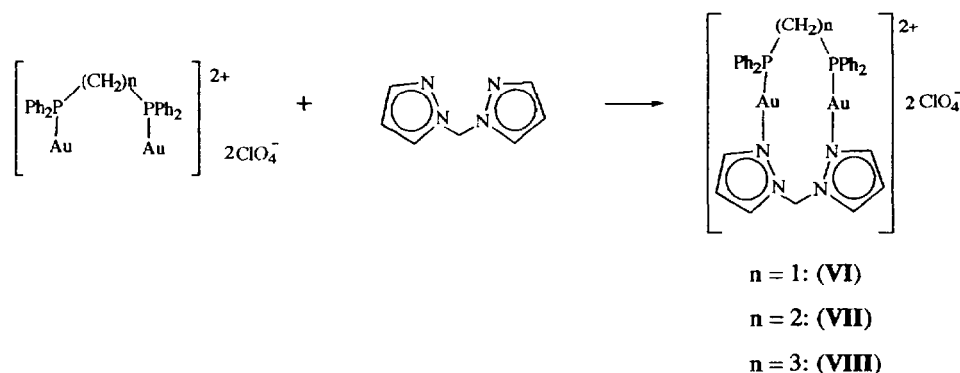
The ^{31}P NMR spectrum of the reaction products (I)

in deuterated acetone at 295 K is shown in Fig. 1. The doublet centred at 29.41 ppm was assigned at the phosphorus *Pa* of the tertiary phosphine containing an imidazole ring, the large coupling constant $^2J_{(Pa-Pb)} = 316.78$ Hz is indicative of two non-equivalent phosphorus atoms in trans to the gold centre. The signal centred at 39.44 ppm is a double doublet and was assigned to *Pb* of the dppm ligand. In fact the doublet due to the coupling with *Pa* is split by the coupling of *Pb* with *Pc* $^2J_{(Pb-Pc)} = 50.02$ Hz. The last doublet, centred at 28.87 ppm, is indicative of a phosphorus atom in trans to a nitrogen atom [12] and, considering the coupling constant, it was unequivocally assigned to *Pc* of the dppm ligand. The three signals discussed above are of equal intensity, as required.

The sharp singlet at 37.81 ppm was assigned by comparison with the published data [11] to the dinuclear complex $[\text{dppm}_2\text{Au}_2]^{2+}$, and its intensity takes into account four equivalent phosphorus atoms.

It is noteworthy to underline that, in the compound (I) the signals of the similar phosphorus atoms *Pb* and *Pc* fall at 39.44 and 28.87 ppm respectively. This difference is in agreement with the direct proportionality between the increase of the chemical shift and the number of the phosphines coordinated to the gold atom; in fact the signal of *Pb* falls in the same range as that found in the dimeric compound $[\text{dppm}_2\text{Au}_2]^{2+}$.

A similar spectrum was recorded in the mixture



Scheme 4.

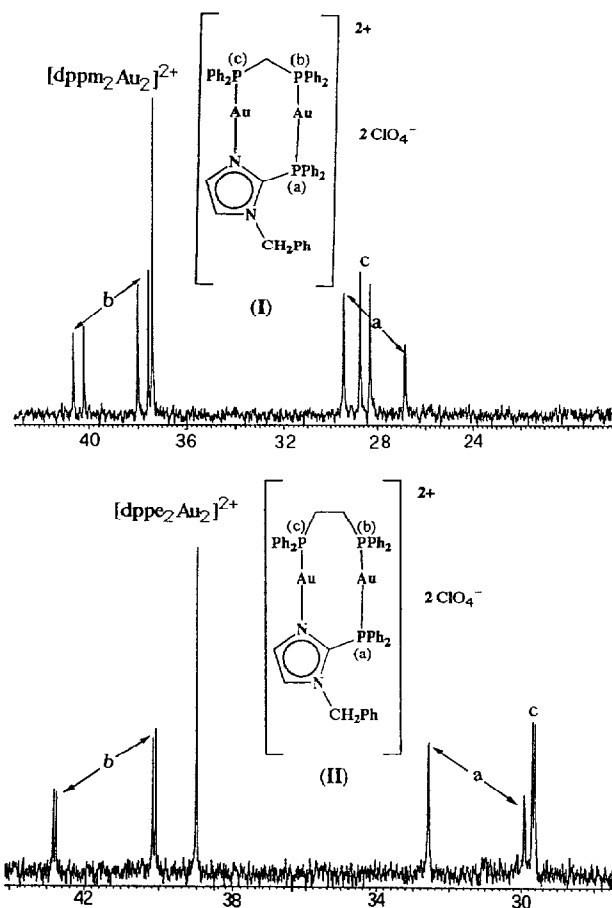


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of (I) (top) and (II) (bottom) at 295 K.

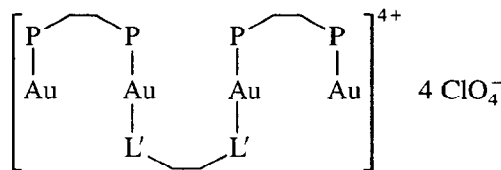
containing the compound (II) (Fig. 1); the chemical shifts and the coupling constants are reported in the experimental part.

The ^{31}P NMR spectrum of the compound (III) shows two doublets (Fig. 2). The first, centred at 27.34 ppm $^2J = 52.14$ Hz, was assigned to the phosphorus in trans to the nitrogen atom by analogy with the chemical shift of the signal of the similar phosphorus of the compound (I); the second, centred at 33.87 ppm, was assigned to the phosphorus in trans to the sulphur atom [13]. The compound (IV) shows a similar ^{31}P NMR spectrum, while only two singlets at 31.27 and 38.15 ppm were recorded in the spectrum of (V); the absence of coupling has to be attributed to the distance between the phosphorus atoms of the dppp ligand.

The complexes (VI–VIII) show only a singlet in the ^{31}P NMR spectra (Fig. 2), as expected for symmetric derivatives containing bridging bis(diphosphine) ligands.

In the ^{31}P NMR spectra discussed above, the number of the signals, the chemical shifts, and the coupling

constants suggest that the compounds (I–VIII) are cyclic dimeric gold(I) derivatives and chain structures like



any other structure can be ruled out.

A study of the ^{31}P NMR chemical shifts is reported in Fig. 3. We observed that the increase in the number of the methylene groups in the phosphine ligand brings an almost regular variation in the ^{31}P NMR chemical shifts of the complexes (I–VIII). The general trend within each series of signals is that the ^{31}P NMR chemical shifts become more positive when the aliphatic chain of the ligand is increased. The exception occurs in the complexes (VI–VIII) for which the trend is opposite. In these latter complexes, the ring sizes are very large and perhaps the ^{31}P NMR chemical shifts are not influenced by the ring effect, so they have the same

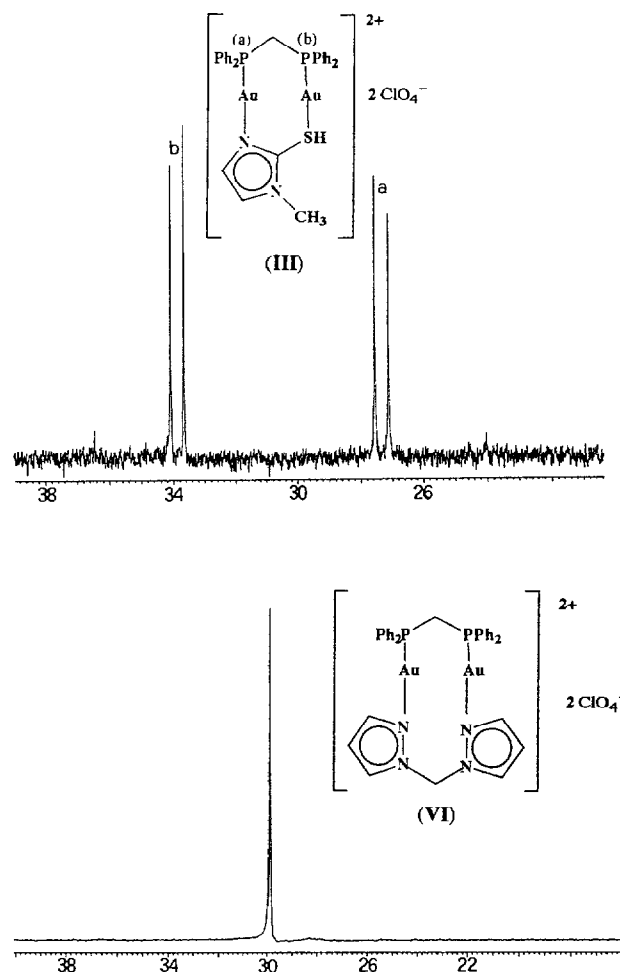
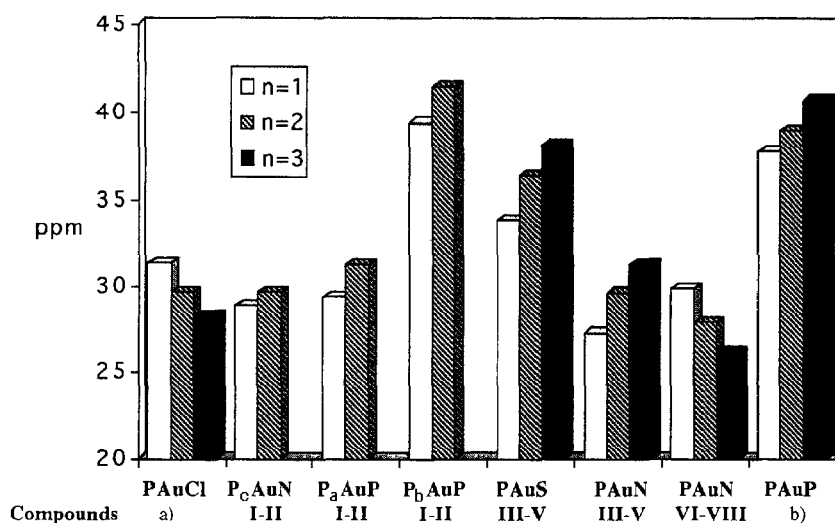


Fig. 2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of (III) (top) and (VI) (bottom) at 295 K.



a) Starting open chain gold complexes $\text{dpp}(\text{CH}_2)_n\text{Au}_2\text{Cl}_2$
 b) Dinuclear dicationic gold complexes $[(\text{dpp}(\text{CH}_2)_n)_2\text{Au}_2]^{2+}$

Fig. 3. Histogram showing the trend of the ³¹P NMR chemical shifts of the compounds (I–VIII).

trend as the starting dinuclear open-chain gold complexes $[(\text{dpp}(\text{CH}_2)_n)_2\text{Au}_2\text{Cl}_2]$.

From the analysis of the data, we observed that the complexes with the same ring size have almost the same chemical shift: for example, the chemical shift of complex (VI) (P–Au–N) differs by only 1.39 ppm from that of complex (V) (P–Au–N), and they are both ten-membered. Also, in comparing complex (I) (eight-membered, P–Au–N) and (III) (eight-membered, P–Au–N) we noticed a difference of only 1.5 ppm. In the case of complex (II) (nine-membered, P–Au–N) and complex (IV) (nine-membered, P–Au–N) the chemical shifts are practically equal. Moreover, from the analysis of the coordination chemical shift Δ ($\Delta = \delta_{\text{complexes}} - \delta_{\text{free ligand}}$), which contributes to the understanding of the ring effects [14], this led us to conclude that in the studied complexes the ³¹P NMR chemical shifts of the phosphorus atoms with the same environment are strongly affected by the ring effect.

2.2. Other analytical and spectroscopic data

In compounds (III–V) the S–H protons were not observed by either IR or ¹H NMR spectroscopy. How-

ever, in the IR spectra, weak peaks of the ν (S–H) stretching were reported [14]. In the ¹H NMR spectra the S–H proton was sought unsuccessfully from –8 to 15 ppm, but the signal could have fallen in the crowded aromatic region, in which the presence or absence of a proton in the integral could only be a speculation. A proof in favour of its presence came from the analysis of the signals in the ³¹P NMR of the products obtained reacting (III) with Na₂CO₃ in THF solution for 24 h; after this time the ³¹P NMR spectrum showed two sets of signals; one corresponded to unreacted (III), the other consisted of two doublets centred at δ 29.51 and δ 36.98 ($^2J_{(Pa-Pb)} = 64.13$ Hz) assigned to the deprotonated derivative.

In the solid state, the perchlorate anion of the gold(I) derivatives studied were found to be uncoordinated to the metal; in fact, the IR spectra of the compounds (III–VIII) and of the mixtures (I–II) show peaks characteristic of a ClO₄[–] group with a T_d symmetry [15]. Acetone solutions of (VI–VIII) gave conductivity values within the range expected for 1:2 electrolytes, confirming their dicationic nature.

The elemental analyses of the compounds (III–VIII) are in agreement with the proposed structures.

Table 1^{a,b}

Correlation between the coordination chemical shifts (Δ) and the number of the methylene groups–of the phosphine ligand

	I–II Pc–Au–N	I–II Pb–Au–P	I–II Pa–Au–P	III–V P–Au–S	III–V P–Au–N	VI–VIII P–Au–N	$[(\text{dpp}_2(\text{CH}_2)_n)_2\text{Au}_2]^{2+}$ P–Au–P
$n = 1$	52.47{8}	63.01{8}	53.01{8}	57.46{8}	50.94{8}	53.48{10}	61.41{8}
$n = 2$	42.16{9}	54.01{9}	43.75{9}	48.89{9}	42.18{9}	40.42{11}	51.49{10}
$n = 3$	—	—	—	54.99{10}	48.13{10}	43.5{12}	58.53{12}

^a The chemical shift values of the free ligands have been collected from the literature data [9]. ^b Ring sizes of the complexes in brackets.

3. Experimental

Elemental analyses were carried out with a Carlo Erba 1106 elemental microanalyser. ^1H , and $^{31}\text{P}\{\text{H}\}$ NMR spectra were recorded in deuterated DMSO solution on a Varian VXR-300 instrument at 300 MHz or on Varian Gemini 200 instrument at 200 MHz, using SiMe_4 or H_3PO_4 85% as internal standard. Chemical shifts are reported as δ (ppm), coupling constants are reported in hertz. The following abbreviations were used: s, singlet; t, triplet; d, doublet; dd, double doublet; dt double triplet; m, multiplet; br, broad. IR spectra were recorded in the range $4000\text{--}200\text{ cm}^{-1}$ on a Perkin-Elmer 1310 spectrophotometer using Nujol mulls in sodium chloride or polyethylene windows (vs, very strong; m, medium; br, broad). Conductivities were measured at 25°C with a Crison conductimeter 522 using $1 \times 10^{-3}\text{ M}$ $(\text{CH}_3)_2\text{CO}$ solutions.

Dinitrogen atmosphere was always used; moreover, the products (III–VI) were obtained by carrying out the reactions in the dark. THF was degassed prior to use.

The $\text{dppmAu}_2\text{Cl}_2$ [11], $\text{dppeAu}_2\text{Cl}_2$ [6b], and $\text{dppAu}_2\text{Cl}_2$ [6b] were prepared as described.

3.1. Formation of $[\text{dppmAu}_2]^{2+} 2\text{ClO}_4^-$

To a suspension of $[\text{dppmAu}_2\text{Cl}_2]$ (0.080 g, 9.4×10^{-2} mmol) in THF (20 ml), $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ (0.042 g, 0.19 mmol) was added. After half an hour, the suspension containing AgCl was transferred by cannula over a celite bed (ca. 2 cm). The filtered solution was collected on the reaction vessel and used immediately.

The $[\text{dppeAu}_2]^{2+} 2\text{ClO}_4^-$ and $[\text{dpppAu}_2]^{2+} 2\text{ClO}_4^-$ were prepared in a similar way.

3.2. Reaction of $[\text{dppmAu}_2]^{2+} 2\text{ClO}_4^-$ with $(\text{Bzim})\text{Ph}_2\text{P}$; formation of the compound (I)

To a solution of $[\text{dppmAu}_2]^{2+} 2\text{ClO}_4^-$ (0.092 g, 9.4×10^{-2} mmol) a stoichiometric amount of $(\text{Bzim})\text{Ph}_2\text{P}$ (0.032 g, 9.4×10^{-2} mmol) was added. A white precipitate formed immediately; the suspension was stirred at room temperature for 1 h and then the reaction mixture was evaporated to dryness. The crude compound was washed with ethyl ether to give 0.12 g of a white solid containing (I) and $[\text{dppm}_2\text{Au}_2]^{2+} 2\text{ClO}_4^-$ in the ratio 9:1.

(I). ^1H NMR (CD_3) $_2\text{CO}$: δ 4.76 (dt, 2H, $^2J_{(\text{H}-\text{P})} = 12.98\text{ Hz}$, $^4J_{(\text{H}-\text{P})} = 2.56\text{ Hz}$); 5.35 (s, 2H); 6.65 (d, 2H); 7.10–7.25 (m, 3H); 7.40–8.0 (m, 31H); 8.21 (s, 1H). ^{31}P NMR (CD_3) $_2\text{CO}$: δ 29.41 (d, $^2J_{(\text{P}a-\text{P}b)} = 318.61\text{ Hz}$); 39.44 (dd, $^2J_{(\text{P}b-\text{P}a)} = 318.61\text{ Hz}$, $^2J_{(\text{P}b-\text{P}c)} = 51.24\text{ Hz}$); 28.87 (d, $^2J_{(\text{P}c-\text{P}b)} = 51.24\text{ Hz}$).

$[\text{dppm}_2\text{Au}_2]^{2+}$. ^1H NMR (CD_3) $_2\text{CO}$: δ 4.91 (dt); 7.40–8.0 (m); ^{31}P NMR: δ 37.81 (s).

3.3. Reaction of $[\text{dppeAu}_2]^{2+} 2\text{ClO}_4^-$ with $(\text{Bzim})\text{Ph}_2\text{P}$; formation of the compound (II)

The product containing (II) and $[\text{dppe}_2\text{Au}_2]^{2+} 2\text{ClO}_4^-$ in the ratio 4:1 was obtained as reported for (I) using the appropriate starting materials.

(II). ^1H NMR: δ 3.0–3.33 (m, 4H); 5.15 (s, 2H); 6.5 (d, 2H); 7.11–7.30 (m, 3H); 7.40–8.0 (m, 30H); 8.16 (s, 1H); 8.40 (s, 1H). ^{31}P NMR: δ 31.25 (d, $^2J_{(\text{P}a-\text{P}b)} = 323.50\text{ Hz}$); 41.51 (dd, $^2J_{(\text{P}b-\text{P}a)} = 323.50\text{ Hz}$, $^2J_{(\text{P}b-\text{P}c)} = 9.1\text{ Hz}$); 29.66 (d, $^3J_{(\text{P}c-\text{P}b)} = 9.1\text{ Hz}$).

$[\text{dppe}_2\text{Au}_2]^{2+}$. ^1H NMR: δ 3.51 (m, br); 7.40–8.0 (m); ^{31}P NMR: δ 38.99 (s).

3.4. Synthesis of the compounds (III–V)

To a stirred THF solution of $[\text{dppmAu}_2]^{2+} 2\text{ClO}_4^-$ (0.090 g, 9.16×10^{-2} mmol) the solid 2-mercapto-1-methylimidazole (0.010 g, 9.16×10^{-2} mmol) was added. After half an hour the white precipitate obtained was centrifuged; this resulted in compound (III). A second portion of (III) was recovered from the supernatant, by washing the oily compound obtained after distillation of the THF with diethyl ether.

The compounds (IV) and (V) were obtained in a similar way using the appropriate starting materials.

(III). Yield 98%. Anal. Found: C, 31.45; H, 2.39; N, 2.71; S, 3.10. $\text{C}_{29}\text{H}_{28}\text{Au}_2\text{Cl}_2\text{N}_2\text{O}_8\text{P}_2\text{S}$. Calc.: C, 31.91; H, 2.59; N, 2.57; S, 2.94%.

^1H NMR: δ 3.48 (s, 3H); 4.68 (t, 2H, $^2J_{(\text{H}-\text{P})} = 10.76\text{ Hz}$); 7.22 (s, 1H); 7.30–7.50 (m, 13H); 7.65–7.84 (m, 8H); S–H not observed. ^{31}P NMR: δ 27.34 (d, $^2J_{(\text{P}a-\text{P}b)} = 52.1\text{ Hz}$); 33.87 (d, $^2J_{(\text{P}b-\text{P}a)} = 52.1\text{ Hz}$). IR: (uncoordinated ClO_4^-) 1082 vs, br; 623 m.

(IV). Yield 90%. Anal. Found: C, 32.01; H, 2.51; N, 2.93; S, 2.52. $\text{C}_{30}\text{H}_{30}\text{Au}_2\text{Cl}_2\text{N}_2\text{O}_8\text{P}_2\text{S}$. Calc.: C, 32.60; H, 2.74; N, 2.53; S, 2.90%.

^1H NMR: δ 2.90–3.15 (m, 4H); 3.61 (s, 3H); 7.28 (s, 1H); 7.40 (s, 1H); 7.42–7.61 (m, 12H); 7.64–8.0 (m, 8H); S–H not observed. ^{31}P NMR: δ 29.64 (d, $^3J_{(\text{P}a-\text{P}b)} = 7.89\text{ Hz}$); 36.41 (d, $^3J_{(\text{P}b-\text{P}a)} = 7.89\text{ Hz}$). IR: (uncoordinated ClO_4^-) 1100 vs, br; 623 m.

(V). Yield 88%. Anal. Found: C, 32.85; H, 2.94; N, 2.36; S, 2.84. $\text{C}_{31}\text{H}_{32}\text{Au}_2\text{Cl}_2\text{N}_2\text{O}_8\text{P}_2\text{S}$. Calc.: C, 33.26; H, 2.88; N, 2.50; S, 2.86%.

^1H NMR: δ 2.0–2.15 (m, 2H); 2.75–3.08 (m, 4H); 3.68 (s, 3H); 7.21 (s, 1H); 7.42 (s, 1H); 7.50–7.96 (m, 21H), S–H not observed. ^{31}P NMR: δ 31.27 (s); 38.15 (s). IR: (uncoordinated ClO_4^-) 1100 vs, br; 623 m.

3.5. Synthesis of the compounds (VI–VIII)

To a suspension of [dppmAu₂Cl₂] (0.091 g, 1.1 × 10⁻¹ mmol) in THF (12 ml), AgClO₄ · H₂O (0.024 g, 1.1 × 10⁻¹ mmol) and, after 15 min of stirring at room temperature, the solid 1,1'-metylenedipyrazole (0.0158 g, 1.1 × 10⁻¹ mmol) were added. After a further 15 min, a second portion of AgClO₄ · H₂O (0.024 g, 1.1 × 10⁻¹ mmol) was added to the reaction mixture that was stirred for another half an hour. The suspension obtained was filtered through celite and the white precipitate deposited was extracted with acetone (200 ml). The acetone and the THF solutions were brought together and evaporated to dryness. The crude compound was washed with ethyl ether to give the analytical sample of (VI) (0.120 g).

The compounds (VII) and (VIII) were synthesized in a similar way using the appropriate starting materials.

(VI). Yield 97%. Anal. Found: C, 34.55; H, 2.84; N, 4.70. C₃₂H₃₀Au₂Cl₂N₄O₈P₂. Calc.: C, 34.15; H, 2.69; N, 4.98%.

¹H NMR: δ 4.71 (t, 2H, ²J_(H-P)); 6.91 (s, 2H); 7.30 (s, 2H); 7.36–7.67 (m, 12H); 7.80–8.10 (m, 8H); 8.48 (s, 2H); 8.85 (s, 2H). ³¹P NMR: δ 29.88 (s). IR: (uncoordinated ClO₄⁻) 1082 vs, br; 623 m. Conductivity: 155 Ω⁻¹ cm² mol⁻¹.

(VII). Yield 98%. Anal. Found: C, 35.06; H, 2.84; N, 5.27. C₃₃H₃₂Au₂Cl₂N₄O₈P₂. Calc.: C, 34.79; H, 2.83; N, 4.92%.

¹H NMR: δ 3.15–3.42 (m, 4H); 6.76 (s, br, 2H); 7.12 (s, br, 2H); 7.42–7.71 (m, 12H); 7.75–7.98 (m, 8H); 8.20 (s, br, 2H); 8.60 (s, br, 2H). ³¹P NMR: δ 27.92 (s). IR: (uncoordinated ClO₄⁻) 1082 vs, br; 623 m. Conductivity: 161 Ω⁻¹ cm² mol⁻¹.

(VIII). Yield 97%. Anal. Found: C, 35.86; H, 3.20; N, 4.54. C₃₄H₃₄Au₂Cl₂N₄O₈P₂. Calc.: C, 35.40; H, 2.97; N, 4.86%.

¹H NMR: δ 1.75–2.17 (m, 2H); 3.09–3.32 (m, 4H); 6.75 (s, br, 2H); 7.08 (s, br, 2H); 7.45–7.70 (m, 12H); 7.25–7.83 (m, 8H); 8.20 (s, br, 2H); 8.55 (s, br, 2H). ³¹P NMR: δ 26.20 (s). IR: (uncoordinated ClO₄⁻) 1082 vs, br; 623 m. Conductivity: 160 Ω⁻¹ cm² mol⁻¹.

Acknowledgement

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