Bidentate Ligand Transfer Reactions between Gold(I) Complexes

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Reactions of the cationic derivative [Au$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)$_2$][ClO$_4$]$_2$ with [AuX$_2$]$^-$ (X = Cl or Br) in a 1 : 1 or a 1 : 2 molar ratio afforded tri- or di-nuclear derivatives, respectively. Neutral complexes [Au$_2$(μ-L-L)$_2$] [L-L = S$_2$CNR$_2$ (R = Me or CH$_2$Ph)] or [Au$_n$(μ-L-L)$_n$] [L-L = S$_2$COR (R = Me or Et) or C$_5$H$_4$NS] react with the cationic [Au(PPh$_3$)$_2$]ClO$_4$ in 1 : 2 molar ratio, to give open-ring complexes [{Au(PPh$_3$)}$_2$(μ-L-L)]ClO$_4$. Reactions of the neutral complexes [Au$_2$(μ-S$_2$CNR$_2$)$_2$] (R = Me or CH$_2$Ph) with cationic [Au$_2$(μ-P-P)$_2$][ClO$_4$]$_2$ (P-P = Ph$_2$PCH$_2$PPh$_2$ or Ph$_2$PCH$_2$CH$_2$PPh$_2$) led to the heterobridged dinuclear complexes [Au$_2$(μ-S$_2$CNR$_2$)(μ-P-P)]ClO$_4$. All these processes proceed *via* donor-acceptor intermediates, with bidentate ligand transfer.

Binuclear cyclic gold(I) complexes have been extensively synthesized in recent years.[1-2] The most studied diauracycles are the bis(ylide) derivatives [Au$_2${μ-(CH$_2$)$_2$PR$_2$}$_2$] (R = Me, Et, Bu or Ph), which undergo a two-[3,4] or four-electron[5,6] oxidative addition to form cyclic gold(II) or gold(III) complexes. In all these reactions the bridging ylide ligand does not participate, and it preserves the dimeric nature by holding the two gold centres close together. In fact, only a few reactions have been described in which the ylide is an active component and carbon-gold bonds are cleaved.[7-10]

In contrast, homoleptic gold(I) complexes containing diphosphines, S-S or S-N ligands have been less studied and only a few reactions involving the bridging ligands are known. For instance, the isomerization[11] of the gold(II) derivatives [Au$_2$(μ-S$_2$CNR$_2$)$_2$X$_2$] to a dinuclear mixed-valence gold(I)-gold(III) compound [Au$^{\rm III}$(S$_2$CNR$_2$)$_2$][Au$^{\rm I}$X$_2$] which takes place with partial dithiocarbamate transfer, or diphosphine migrations, which have been recently reported.[12,13]

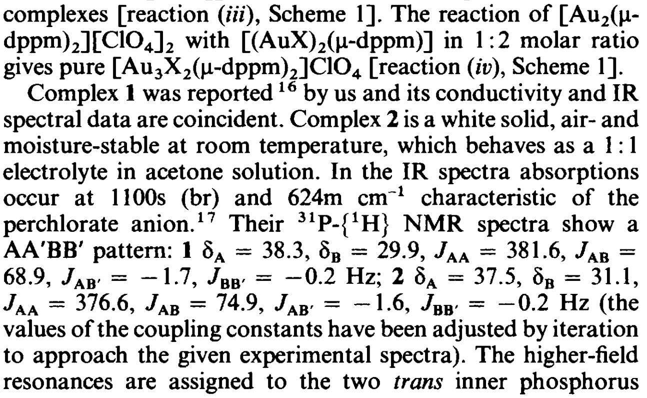
We have reported that bidentate ligand transfers between two homoleptic gold(I) dimers progress to produce heterobridged gold derivatives[12] and the synthesis of di- and tri-nuclear gold complexes[14] by ylide-transfer reactions. The mild conditions used in these processes led us to believe that this type of reaction, *via* donor-acceptor intermediates, is more general than expected. Therefore we have explored a series of processes between homoleptic di- or poly-nuclear gold(I) complexes containing diphosphine, dithiocarbamate, dithiocarbonate or pyridine-2-thiolate and the mononuclear gold(I) derivatives [AuX$_2$]$^-$ (X = Cl or Br) or [Au(PPh$_3$)$_2$]$^+$, which evolve to di- or tri-nuclear open-ring complexes *via* donor-acceptor intermediates. Reactions of [Au$_2$(μ-P-P)$_2$]$^{2+}$ [P-P = Ph$_2$PCH$_2$PPh$_2$(dppm) or Ph$_2$PCH$_2$CH$_2$PPh$_2$(dppe)] with [Au$_2$(μ-S$_2$CNR$_2$)$_2$] (R = Me, Et or CH$_2$Ph), the latter as donor and the former as acceptor, afford heterobridged dinuclear complexes [Au$_2$(μ-S$_2$CNR$_2$)(μ-P-P)]$^+$ (R = Me or CH$_2$Ph; P-P = dppm or dppe).

Results and Discussion

The reaction in dichloromethane of the cationic complex [Au$_2$(μ-dppm)$_2$][ClO$_4$]$_2$ with [AuX$_2$]$^-$ (X = Cl or Br) in a 1 : 1 molar ratio, leads to the trinuclear derivatives [Au$_3$X$_2$(μ-dppm)$_2$]ClO$_4$ (X = Cl **1** or Br **2**) according to reaction (*i*) (Scheme 1). When these reactions are performed in a 1 : 2 molar ratio, the previously known dinuclear derivatives [(AuX)$_2$(μ-dppm)][15] are obtained [reaction (*ii*), Scheme 1]. The former implies partial transfer of the diphosphine and the latter a total transfer. We can suppose that complexes **1** and **2** are intermediates in reaction (*ii*), which is supported by the reaction of **1** or **2** with [AuX$_2$]$^-$ in 1 : 1 molar ratio to give the dinuclear complexes [reaction (*iii*), Scheme 1]. The reaction of [Au$_2$(μ-dppm)$_2$][ClO$_4$]$_2$ with [(AuX)$_2$(μ-dppm)] in 1 : 2 molar ratio gives pure [Au$_3$X$_2$(μ-dppm)$_2$]ClO$_4$ [reaction (*iv*), Scheme 1].

Complex **1** was reported[16] by us and its conductivity and IR spectral data are coincident. Complex **2** is a white solid, air- and moisture-stable at room temperature, which behaves as a 1 : 1 electrolyte in acetone solution. In the IR spectra absorptions occur at 1100s (br) and 624m cm^{-1} characteristic of the perchlorate anion.[17] Their ^{31}P-{^{1}H} NMR spectra show a AA'BB' pattern: **1** δ_A = 38.3, δ_B = 29.9, $J_{AA'}$ = 381.6, J_{AB} = 68.9, $J_{AB'}$ = −1.7, $J_{BB'}$ = −0.2 Hz; **2** δ_A = 37.5, δ_B = 31.1, $J_{AA'}$ = 376.6, J_{AB} = 74.9, $J_{AB'}$ = −1.6, $J_{BB'}$ = −0.2 Hz (the values of the coupling constants have been adjusted by iteration to approach the given experimental spectra). The higher-field resonances are assigned to the two *trans* inner phosphorus atoms and the lower resonances to the outer phosphorus atoms, by comparison with the resonances of the complexes [Au$_2$(μ-dppm)$_2$][ClO$_4$]$_2$ and [(AuX)$_2$(μ-dppm)]. The positive-ion fast atom bombardment (FAB) mass spectra show the peaks due to [M − ClO$_4$]$^+$ at m/z 1429 (15) or 1519 (50%) respectively.

In a similar way, we have carried out the same type of reactions using dppe complexes. So the reactions between [Au$_2$(μ-dppe)$_2$][ClO$_4$]$_2$ and [AuX$_2$]$^-$ (X = Cl or Br) in a 1 : 1 molar ratio lead to a mixture of [Au$_3$X$_2$(μ-dppe)$_2$]ClO$_4$,



Scheme 1 (*i*) Q[AuX$_2$], −Q[ClO$_4$]; (*ii*) 2Q[AuX$_2$], −2Q[ClO$_4$]; (*iii*) Q[AuX$_2$], −Q[ClO$_4$]; Q = N(PPh$_3$)$_2$ and X = Cl or Q = NBu$_4$ and X = Br

Table 1 Analytical and spectroscopic data for complexes **1**–**11**

Complex	Yield (%)	Analysis[a] (%) C	H	N	^{31}P-{^{1}H} NMR[b]	Λ_M[c]	M.p.
1 $[Au_3Cl_2(\mu\text{-dppm})_2]ClO_4$	67	39.65 (39.25)	2.9 (2.85)	— —	*d*	140	270 (decomp.)
2 $[Au_3Br_2(\mu\text{-dppm})_2]ClO_4$	74	38.0 (38.0)	2.85 (2.85)	— —	*d*	131	260 (decomp.)
3 $[\{Au(PPh_3)\}_2(\mu\text{-}S_2CNMe_2)]ClO_4$	84	40.9 (41.15)	3.1 (3.2)	1.2 (1.25)	36.7 (s)	140	172
4 $[\{Au(PPh_3)\}_2\{\mu\text{-}S_2CN(CH_2Ph)_2\}]ClO_4$	84	47.1 (47.45)	3.35 (3.45)	1.15 (1.1)	36.6 (s)	134	114
5 $[\{Au(PPh_3)\}_2(\mu\text{-}S_2COMe)]ClO_4$	65	41.0 (40.55)	3.2 (2.95)	— —	36.7 (s)	136	100 (decomp.)
6 $[\{Au(PPh_3)\}_2(\mu\text{-}S_2COEt)]ClO_4$	78	41.3 (41.1)	3.1 (3.1)	— —	36.9 (s)	143	100 (decomp.)
7 $[\{Au(PPh_3)\}_2(\mu\text{-}C_5H_4NS)]ClO_4$	75	43.8 (43.65)	3.15 (3.05)	1.3 (1.25)	33.8 (s)	138	110 (decomp.)
8 $[Au_2(\mu\text{-}S_2CNMe_2)(\mu\text{-dppm})]ClO_4$	76	33.75 (33.7)	2.75 (2.85)	1.3 (1.4)	35.3 (s)	139	168
9 $[Au_2\{\mu\text{-}S_2CN(CH_2Ph)_2\}(\mu\text{-dppm})]ClO_4$	65	41.4 (41.75)	3.1 (3.15)	0.95 (1.2)	36.2 (s)	122	136
10 $[Au_2(\mu\text{-}S_2CNMe_2)(\mu\text{-dppe})]ClO_4$	78	34.55 (34.4)	2.75 (3.00)	1.15 (1.4)	34.4 (s)	128	188 (decomp.)
11 $[Au_2\{\mu\text{-}S_2CN(CH_2Ph)_2\}(\mu\text{-dppe})]ClO_4$	77	42.15 (42.3)	3.35 (3.3)	1.25 (1.2)	34.7 (s)	143	148 (decomp.)

[a] Calculated values in parentheses. [b] Recorded in $CDCl_3$, referenced to external H_3PO_4; s = singlet. [c] In acetone, ohm^{-1} cm^2 mol^{-1}. [d] See text.

$[(AuX)_2(\mu\text{-dppe})]$ and starting material whereas a 1:2 molar ratio afforded $[(AuX)_2(\mu\text{-dppe})]$.

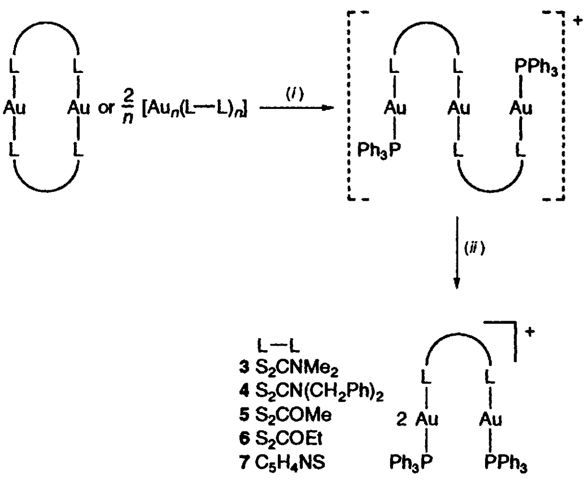
Reaction (*i*) of Scheme 1 can be interpreted as a nucleophilic attack of $[AuX_2]^-$ at one gold centre of the starting diauracycle which could evolve with partial transfer of the diphosphine ligand to give the trinuclear complex, which reacts further with a new molecule of $[AuX_2]^-$ through the inner gold atom (which is probably more susceptible to attack by a nucleophile) to afford the dinuclear derivatives $[(AuX)_2(\mu\text{-dppm})]$. It is noteworthy that although the process (*iv*) (Scheme 1) is very close to equation (1) (but using ClO_4^- instead of Cl^-) the results are different: equation (1) is an equilibrium while

$$[Au_2(\mu\text{-dppm})_2Cl_2] + 2[(AuCl)_2(\mu\text{-dppm})] \rightleftharpoons 2[Au_3Cl_2(\mu\text{-dppm})_2]Cl \quad (1)$$

reaction (*iv*) affords pure trinuclear complexes as shown by the ^{31}P-{^{1}H} NMR spectra of the reaction mixture. Similar intermediates have been recently proposed in the equilibrium[13] of $[Au_2(\mu\text{-dppm})_2Cl_2]$ with $[(AuCl)_2(\mu\text{-dppm})]$ [equation (1)] and in the ylide and/or dppm transfer reaction.[12] It is also supported by the crystal structures of $[Au_2(\mu\text{-dppm})_2X_2]$ (X = Cl,[18] Br[19] or NO_3[20]) and $[Au_2(\mu\text{-dppm})_2X]X'$ (X = X' = I;[19] X = S_2CNEt_2, X' = BH_3CN;[21] X = S_2CPh, X' = Cl[22]) that show the approach of X to the gold atoms.

The reactions of the neutral complexes $[Au_2(\mu\text{-}S_2CNR_2)_2]$ (R = Me or CH_2Ph) or $[Au_n(\mu\text{-L–L})_n]$ [L–L = S_2COR (R = Me or Et) or C_5H_4NS] with the cationic $[Au(PPh_3)_2]ClO_4$ in dichloromethane, in 1:2 molar ratio, led to the dinuclear complexes $[\{Au(PPh_3)\}_2(\mu\text{-L–L})]ClO_4$ [L–L = S_2CNMe_2 **3**, $S_2CN(CH_2Ph)_2$ **4**, S_2COMe **5**, S_2COEt **6** or C_5H_4NS **7**], according to Scheme 2.

Complexes **3**–**7** are air- and moisture-stable white solids at room temperature. They behave as 1:1 electrolytes in acetone solution and their IR spectra show absorptions at 1090s (br) and 623m cm^{-1} due to the perchlorate anion. The ^{31}P-{^{1}H} NMR spectra show a singlet for the phosphorus atom of the phosphine even for complex **7** with pyridin-2-thiolate that does not split at −85 °C in deuterioacetone (Table 1). That is why we cannot decide between a μ-S,N or a μ-S co-ordination mode for this ligand. In the ^{1}H NMR spectra the resonances are as expected. The positive-ion FAB mass spectra show the peaks corresponding to the cations $[M - ClO_4]^+$ at *m*/*z* (abundance, complex): 1038 (35, **3**), 1190 (54, **4**), 1025 (87, **5**), 1039 (100, **6**) and 1028 (55, **7**).

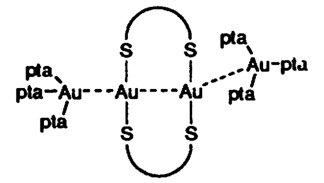


Scheme 2 (*i*) $[Au(PPh_3)_2]ClO_4$; (*ii*) $[Au(PPh_3)_2]ClO_4$

The trinuclear derivatives, likely intermediates of these reactions, cannot be obtained when these processes are carried out in a 1:1 molar ratio although in the ^{31}P-{^{1}H} and ^{1}H NMR spectra of reaction mixtures with L–L = S_2CNMe_2 or $S_2CN(CH_2Ph)_2$ resonances that can be assigned to these trinuclear intermediates are evident. Their ^{31}P-{^{1}H} NMR spectra show a singlet at δ 37.4 and δ 37.5, respectively, whilst their ^{1}H NMR spectra show broad resonances at δ 3.22 (CH_3N) for L–L = S_2CNMe_2 and δ 4.78 (CH_2N) for L–L = $S_2CN(CH_2Ph)_2$. In all cases, a mixture of dinuclear starting materials and complexes **3**–**7** is obtained.

These processes can occur in a similar way by nucleophilic attack of $[Au_n(\mu\text{-L–L})_n]$ on $[Au(PPh_3)_2]^+$. This is also supported by the recent preparation[23] of $[\{Au(pta)_3\}_2Au_2\{S_2C_2(CN)_2\}_2]$ (pta = phosphatriazaadamantane), a tetranuclear chain with unsupported gold(I)–gold(I) interactions.

In accordance with the proposed donor–acceptor interaction, the reaction of $[Au_2(\mu\text{-dppm})_2]^{2+}$ with $[Au(PPh_3)_2]^+$ does not



progress and the starting materials are recovered, as well as in the reaction of $[Au_n(\mu\text{-L–L})_n]$ [L–L = C_5H_4NS; $n = 2$, L–L = S_2CNMe_2 or $S_2CN(CH_2Ph)_2$] with $[AuCl_2]^-$.

After investigating the reactions of cationic or neutral dinuclear derivatives with the appropriate mononuclear gold complexes, the following step was to study the processes between dinuclear acceptors and dinuclear donors. Therefore we have carried out reactions of the neutral complexes $[Au_2(\mu\text{-}S_2CNR_2)_2]$ (R = Me or CH_2Ph) with the cationic complexes $[Au_2(\mu\text{-P–P})_2][ClO_4]_2$ (P–P = dppm or dppe) in a 1 : 1 molar ratio, which afforded the heterobridged dinuclear derivatives $[Au_2(\mu\text{-}S_2CNR_2)(\mu\text{-P–P})]ClO_4$ (P–P = dppm, R = Me **8** or CH_2Ph **9**; P–P = dppe, R = Me **10** or CH_2Ph **11**).

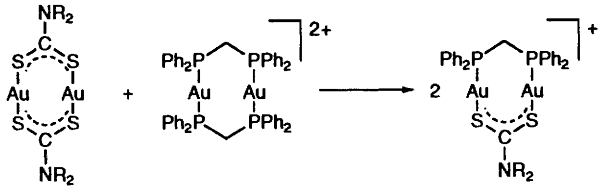
Complexes **8**–**11** were obtained as air- and moisture-stable yellow solids at room temperature. Their acetone solutions behave as 1 : 1 electrolytes and their IR spectra show bands at 1100s (br) and 623m cm^{-1} due to the perchlorate anion. The $^{31}P\text{-}\{^1H\}$ NMR spectra show a singlet at *ca.* δ 36 (**8**, **9**) or 34 (**10**, **11**) for the phosphorus atoms of the dppm or dppe, respectively (Table 1). Their ^1H NMR spectra show the expected resonances due to the dithiocarbamate and the methylene protons as triplets (**8**, **9**) or pseudo doublets (**10**, **11**). The simplicity of the $^{31}P\text{-}\{^1H\}$ NMR spectra compared with those of complexes **1**, **2**, or that reported for the tetranuclear complexes $[Au_4(\mu\text{-}C_3S_5)_2(\mu\text{-dppm})_2]$[24] [which also shows an AA'BB' pattern; $C_3S_5^{2-}$ = 4,5-disulfanyl-1,3-dithiole-2-thionate(2−)] or $[Au_4\{SC(CN)C(CN)S\}(Ph_2PCHCHPPh_2)_2Cl_2]$[25] points to a dinuclear structure rather than a larger nuclearity, as was shown for the $[Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNR_2)]$[12] derivatives. Their dinuclear structure is also supported by their positive-ion FAB mass spectra which show in all cases the parent ion $[Au_2(S_2CNR_2)(P\text{–}P)]^+$ as the base peak at *m*/*z* 898 (**8**), 1050 (**9**), 912 (**10**) and 1064 (**11**).

Experimental

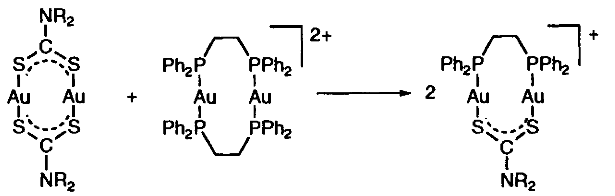
Infrared spectra were recorded on a Perkin-Elmer 559 or 883 spectrophotometer, over the range 4000–200 cm^{-1}, by using Nujol mulls between polyethylene sheets and ^1H and ^{31}P NMR spectra on a Varian UNITY 300 (VNMR Software Version 4.1) in $CDCl_3$ solutions; chemical shifts are quoted relative to $SiMe_4$ (external, ^1H) and H_3PO_4 (external, ^{31}P). Carbon, H and N analyses were performed with a Perkin-Elmer 2400 microanalyser. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Melting points were measured on a Büchi apparatus and are uncorrected. Mass spectra were recorded on a VG Autospec using positive-ion fast atom bombardment techniques.

The yields, C, H and N analyses, conductivities, melting points and $^{31}P\text{-}\{^1H\}$ NMR data are listed in Table 1. All reactions were carried out at room temperature.

Syntheses.—$[Au_3X_2(\mu\text{-dppm})_2]ClO_4$ (X = Cl **1** *or* Br **2**). To a suspension of $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$[26] (0.068 g, 0.05 mmol) in dichloromethane (40 cm^3) was added $Q[AuX_2]$[27] [0.05 mmol; Q = $N(PPh_3)_2$, X = Cl, 0.040 g; Q = NBu_4, X = Br, 0.030 g]. After stirring the suspension for about 4 h, the clear solution was evaporated to *ca.* 5 cm^3. Addition of diethyl ether (15 cm^3) led to precipitation of complex **1** or **2**. The former was washed three times with MeOH–Et_2O (5 cm^3, 1 : 1), to remove $[N(PPh_3)_2]ClO_4$.



R = Me **8** or CH_2Ph **9**



R = Me **10** or CH_2Ph **11**

$[(AuX)_2(\mu\text{-dppm})]$ (X = Cl *or* Br). These complexes were obtained in two different ways. (*a*) To a suspension of $[Au_2(\mu\text{-dppm})_2][ClO_4]_2$ (0.068 g, 0.05 mmol) in dichloromethane (40 cm^3) was added $Q[AuX_2]$ [0.1 mmol; Q = $N(PPh_3)_2$, X = Cl, 0.081 g; Q = NBu_4, X = Br, 0.060 g]. The mixture was stirred for 3 h and then was evaporated to *ca.* 5 cm^3. Addition of diethyl ether (20 cm^3) led to precipitation of the complexes. The compound with X = Cl was washed three times with MeOH–Et_2O (5 cm^3, 1 : 1), to remove $[N(PPh_3)_2]ClO_4$. Yield: 53 (Cl), 80% (Br).

(*b*) To a solution of complex **1** (0.05 mmol, 0.076 g) or **2** (0.05 mmol, 0.081 g) in dichloromethane (30 cm^3) was added $Q[AuX_2]$ [0.05 mmol; Q = $N(PPh_3)_2$, X = Cl, 0.040 g; Q = NBu_4, X = Br, 0.030 g]. After stirring for about 2 h, the solution was evaporated to *ca.* 5 cm^3. Addition of diethyl ether (20 cm^3), led to precipitation of the complexes. The chloride compound was washed three times with MeOH–Et_2O (5 cm^3, 1 : 1), to remove $[N(PPh_3)_2]ClO_4$. Yield 45 (Cl), 75% (Br).

$[\{Au(PPh_3)\}_2(\mu\text{-L–L})][ClO_4]$ [L–L = S_2CNMe_2 **3**, $S_2CN(CH_2Ph)_2$ **4**, S_2COMe **5**, S_2COEt **6** *or* C_5H_4NS **7**]. To a solution of $[Au_2\{\mu\text{-}S_2CN(CH_2Ph)_2\}_2]$[12] (0.047 g, 0.05 mmol) or a suspension of $[Au_2(\mu\text{-}S_2CNMe_2)_2]$[12] (0.032 g, 0.05 mmol) or $[Au_n(\mu\text{-L–L})_n]$[28,29] (0.05 mmol if $n = 2$; L–L = S_2COMe, 0.030 g; S_2COEt, 0.032 g; or C_5H_4NS, 0.031 g) in dichloromethane (40 cm^3) was added $[Au(PPh_3)_2]ClO_4$[30] (0.1 mmol, 0.082 g). The mixture was stirred for 90 min, and evaporated to *ca.* 5 cm^3. Addition of diethyl ether (20 cm^3) afforded complexes **3**–**7**. Solids were washed with diethyl ether (2 × 5 cm^3). ^1H NMR: **3**, δ 7.45–7.30 (m, Ph) and 3.73 (s, MeN); **4**, δ 7.60–7.24 (m, Ph) and 5.25 (s, CH_2N); **5**, δ 7.53 (br, Ph), 4.43 (s, MeO); **6**, δ 7.65–7.45 (m, Ph), 4.73 [q, *J*(HH) = 7.1, CH_2O] and 1.47 (t, CH_3); **7**, δ 8.39 [d, *J*(HH) = 5.7], 7.78 [d, *J*(HH) = 7.9], 7.67 [t, *J*(HH) = 7.3 Hz] and 7.50–7.40 (m).

$[Au_2(\mu\text{-}S_2CNR_2)(\mu\text{-P–P})]ClO_4$ (P–P = dppm, R = Me **8** *or* CH_2Ph **9**; P–P = dppe, R = Me **10** *or* CH_2Ph **11**). To a solution of $[Au_2\{\mu\text{-}S_2CN(CH_2Ph)_2\}_2]$ (0.047 g, 0.05 mmol) or a suspension of $[Au_2(\mu\text{-}S_2CNMe_2)_2]$ (0.032 g, 0.05 mmol) in dichloromethane (40 cm^3) was added $[Au_2(\mu\text{-P–P})_2][ClO_4]_2$[26] (0.05 mmol; P–P = dppm 0.068 g or dppe 0.069 g). After stirring for 1 d (**8**), 10 h (**10**) or 2 h (**9**, **11**) the unreacted starting material was filtered off. The clear solution was evaporated to *ca.* 5 cm^3 and addition of diethyl ether led to precipitation of complexes **8**–**11**. ^1H NMR: **8**, δ 7.80–7.30 (m, Ph), 4.14 [t, *J*(HP) = 13.0, PCH_2P] and 3.57 (s, MeN); **9**, δ 7.90–7.25 (m, Ph), 5.25 (s, CH_2N) and 4.24 [t, *J*(HP) = 12.2, PCH_2P]; **10**, δ 7.83–7.37 (m, Ph), 3.64 (s, MeN) and 3.05 ['d', *J*(HP) = 12.6, $P(CH_2)_2P$]; **11**, δ 7.87–7.40 (m, Ph), 5.25 (s, CH_2N) and 3.09 ['d', *J*(HP) = 12.6 Hz, $P(CH_2)_2P$].

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