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Ylide–gold(I) complexes of the types $[Au(ylide)L]^+$, $[Au(ylide)(C{\equiv}CR)]$ and $[Au(ylide)\{Co(CO)_4\}]$

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Abstract

Displacement of tetrahydrothiophene (tht) from $[Au(ylide)(tht)]ClO_4$ (ylide = CH_2PPh_3, CH_2PPh_2Me, CH_2PPhMe_2, $CHPhPPh_3$, $CHMePPh_3$ or CH_2AsPh_3) by other neutral or anionic ligands leads to the mono- and dinuclear cationic complexes $[Au(ylide)L]ClO_4$ (L = $SbPh_3$ or phen) or $[\{Au(ylide)\}_2(L\text{-}L)]ClO_4$ (L-L = dppm or dpam), complexes with tetracarbonylcobaltate as ligand $[Au(ylide)\{Co(CO)_4\}]$ or acetylide complexes $[Au(ylide)(C{\equiv}CR)]$ (R = Ph or ^tBu). The structure of $[Au(CH_2PPhMe_2)(phen)]ClO_4$ was established by single-crystal X-ray diffraction studies.

Introduction

Many neutral or cationic ylide–gold complexes are known [1–4], although some types are unrepresented or poorly represented. For instance, no derivatives with metallic carbonylates, such as $[Au(ylide)\{Co(CO)_4\}]$, or with acetylides, such as $[Au(ylide)(C{\equiv}CR)]$, have been reported, and only a few compounds of the type $[Au(ylide)L]ClO_4$ are known [3, 5].

In the present paper we describe the synthesis of several types of mono- and dinuclear derivatives of gold(I) obtained by displacement of tetrahydrothiophene (tht) from $[Au(ylide)(tht)]ClO_4$ with neutral or anionic ligands.

Experimental

Instrumentation and general experimental techniques were as described earlier [4]. Nuclear magnetic resonance spectra were recorded on a Varian XL 200 spectrometer in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (external, ^{31}P). The yields and C, H, N and Au analyses, and some ^1H NMR data are listed in Table 1. All the reactions were performed at room temperature.

Preparation of the complexes

$[Au(ylide)(tht)]ClO_4$ (tht = tetrahydrothiophene; ylide = CH_2PPh_3 (1), CH_2PPh_2Me (2), CH_2PPhMe_2 (3), $CHPhPPh_3$ (4), $CHMePPh_3$ (5) or CH_2AsPh_3 (6)

To a suspension of $[Ag(OClO_3)(tht)]$ [6] (0.148 g, 0.5 mmol) in 20 ml of dichloromethane was added $[Au(ylide)Cl]$ [4] (0.5 mmol) and the mixture was stirred for 1 h. The AgCl precipitated was filtered off and the solution was concentrated to 5 ml. Addition of diethyl ether (20 ml) gave complexes **1–6** as white solids. NMR: **1**, ^1H, δ 7.9–7.4 (m, Ph), 2.25 [d, J(PH) 13.3 Hz, CH_2]; ^{31}P, δ 31.4 (s); **2**, ^1H, δ 7.9–6.9 (m, Ph), 2.40 [d, J(PH) 13.1 Hz, Me], 2.04 [d, J(PH) 9.0 Hz, CH_2]; ^{31}P, δ 29.15 (s); **3**, ^1H, δ 7.9–7.2 (m, Ph), 2.04 [d, J(PH) 13.2 Hz, Me], 1.77 [d, J(PH) 12.9 Hz, CH_2]; ^{31}P, δ 28.9 (s); **4**, ^1H, δ 7.9–6.9 (m, Ph), 4.48 [d, J(PH) 13.9 Hz, CH]; ^{31}P, δ 26.45 (s); **5**, ^1H, δ 7.9–7.3 (m, Ph), 3.30 (m, CH), 1.63 [dd, J(PH) 22.1 Hz, J(HH) 8.2 Hz, Me]; **6**, ^1H, δ 7.9–7.2 (m, Ph), 2.70 (s, CH_2).

$[Au(ylide)(SbPh_3)]ClO_4$ (ylide = CH_2PPh_3 (7), CH_2PPh_2Me (8), $CHPhPPh_3$ (9) or CH_2AsPh_3 (10)

To a solution of $[Au(ylide)(tht)]ClO_4$ (0.2 mmol) in 30 ml of dichloromethane was added $SbPh_3$ (0.071 g, 0.2 mmol) and the mixture was stirred for 1 h. The solution was concentrated to 5 ml. Addition of diethyl ether (25 ml) gave complexes **7–10** as white solids. NMR: **7**, ^1H, δ 8.1–7.4 (m, Ph), 2.53 [d, J(PH) 12.9 Hz, CH_2]; **8**, ^1H, δ 7.9–6.9 (m, Ph), 2.48 [d, J(PH) 11.9 Hz, Me], 1.41 [d, J(PH) 12.7 Hz, CH_2]; **9**, ^1H, δ 7.8–6.7

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TABLE 1. Analytical data for complexes

Compound no.	Compound	Yield (%)	Analysis: found (calc.) (%)				Λ_M[a]	ν(Au–C) (cm^{-1})
			C	H	N	Au		
1	$[Au(CH_2PPh_3)(tht)]ClO_4$	90	41.6 (41.75)	3.75 (3.8)		30.3 (29.8)	148	585
2	$[Au(CH_2PPh_2Me)(tht)]ClO_4$	81	35.35 (36.1)	3.5 (3.9)		33.2 (32.8)	148	585
3	$[Au(CH_2PPhMe_2)(tht)]ClO_4$	78	28.9 (29.1)	3.85 (3.95)		36.9 (36.7)	146	562
4	$[Au(CHPhPPh_3)(tht)]ClO_4$	85	46.7 (47.25)	4.1 (3.95)		27.1 (26.7)	117	580
5	$[Au(CHMePPh_3)(tht)]ClO_4$	88	42.9 (42.7)	3.85 (4.0)		29.6 (29.2)	149	585
6	$[Au(CH_2AsPh_3)(tht)]ClO_4$	86	39.1 (39.2)	3.5 (3.6)		27.8 (27.95)	140	560
7	$[Au(CH_2PPh_3)(SbPh_3)]ClO_4$	88	48.1 (48.0)	3.65 (3.5)		21.2 (21.3)	123	585
8	$[Au(CH_2PPh_2Me)(SbPh_3)]ClO_4$	78	45.25 (44.5)	3.75 (3.5)		22.75 (23.0)	130	540
9	$[Au(CHPhPPh_3)(SbPh_3)]ClO_4$	91	51.35 (51.55)	3.6 (3.6)		17.6 (17.05)	127	580
10	$[Au(CH_2AsPh_3)(SbPh_3)]ClO_4$	76	45.8 (45.85)	3.35 (3.35)		20.1 (19.65)	133	560
11	$[Au(CH_2PPh_3)(phen)]ClO_4$	91	49.6 (49.45)	3.35 (3.35)	3.65 (3.75)	25.65 (26.15)	139	595
12	$[Au(CH_2PPh_2Me)(phen)]ClO_4$	86	44.95 (45.2)	3.3 (3.35)	4.0 (4.05)	28.05 (28.5)	154	585
13	$[Au(CH_2PPhMe_2)(phen)]ClO_4$	92	40.2 (40.1)	3.4 (3.35)	4.3 (4.45)	30.95 (31.3)	144	580
14	$[Au(CHPhPPh_3)(phen)]ClO_4$	91	53.45 (53.6)	3.5 (3.55)	3.45 (3.4)	22.9 (23.75)	146	585
15	$[Au(CH_2AsPh_3)(phen)]ClO_4$	88	46.8 (46.7)	3.2 (3.15)	3.7 (3.5)	24.5 (24.7)	144	565
16	$[\{Au(CH_2PPh_3)\}_2(dppm)](ClO_4)_2$	68	49.45 (49.45)	3.75 (3.7)		26.35 (25.75)	231	570
17	$[\{Au(CH_2PPh_2Me)\}_2(dppm)](ClO_4)_2$	63	45.35 (45.3)	3.7 (3.75)		28.4 (28.0)	228	575
18	$[\{Au(CH_2PPhMe_2)\}_2(dppm)](ClO_4)_2$	74	40.2 (40.3)	3.8 (3.75)		30.5 (30.75)	222	560
19	$[\{Au(CHPhPPh_3)\}_2(dppm)](ClO_4)_2$	74	53.8 (53.55)	3.75 (3.85)		24.05 (23.4)	225	575
20	$[\{Au(CH_2AsPh_3)\}_2(dppm)](ClO_4)_2$	65	46.85 (46.75)	3.45 (3.5)		23.75 (24.35)	234	
21	$[\{Au(CH_2PPh_3)\}_2(dpam)](ClO_4)_2$	73	46.65 (46.5)	3.5 (3.45)		24.35 (24.5)	237	
22	$[Au(CH_2PPh_3)\{Co(CO)_4\}]$	77	42.8 (42.9)	2.8 (2.65)			11	
23	$[Au(CHPhPPh_3)\{Co(CO)_4\}]$	70	48.7 (48.45)	3.0 (2.95)			16	
24	$[Au(CH_2AsPh_3)\{Co(CO)_4\}]$	62	39.9 (40.15)	2.5 (2.65)			13	

(*continued*)

TABLE 1. (*continued*)

Compound no.	Compound	Yield (%)	Analysis: found (calc.) (%)				Λ_M[a]	ν(Au–C) (cm^{-1})
			C	H	N	Au		
25	$[Au(CH_2PPh_3)(C{\equiv}CPh)]$	88	56.0 (56.5)	3.95 (3.85)		34.3 (34.2)	2	572
26	$[Au(CH_2PPh_2Me)(C{\equiv}CPh)]$	85	51.25 (51.6)	4.1 (3.95)		34.6 (34.65)	28	570
27	$[Au(CH_2PPhMe_2)(C{\equiv}CPh)]$	90	44.95 (45.35)	3.7 (4.1)		44.5 (44.2)	27	566
28	$[Au(CHPhPPh_3)(C{\equiv}CPh)]$	75	60.95 (60.8)	4.0 (3.5)		30.6 (30.3)	24	580
29	$[Au(CHMePPh_3)(C{\equiv}CPh)]$	97	56.8 (57.15)	4.5 (4.1)		33.7 (33.5)	30	570
30	$[Au(CH_2PPh_3)(C{\equiv}C^tBu)]$	83	53.85 (54.2)	4.95 (4.9)		38.65 (38.45)	13	570
31	$[Au(CH_2PPh_2Me)(C{\equiv}C^tBu)]$	80	48.45 (48.8)	5.15 (4.9)		40.25 (40.05)	13	562
32	$[Au(CH_2PPhMe_2)(C{\equiv}C^tBu)]$	75	42.5 (41.9)	4.95 (5.15)		46.1 (45.8)	8	538
33	$[Au(CHPhPPh_3)(C{\equiv}C^tBu)]$	75	59.35 (59.05)	4.65 (4.4)		33.7 (33.5)	15	575
34	$[Au(CHMePPh_3)(C{\equiv}C^tBu)]$	80	54.6 (54.95)	5.25 (4.8)		37.6 (37.45)	15	555

[a] In acetone, Ω^{-1} cm^2 mol^{-1}.

(m, Ph), 4.71 [d, J(PH) 14.2 Hz, CH]; **10**, ^{1}H, δ 7.8–6.9 (m, Ph), 1.93 (s).

$[Au(ylide)(phen)]ClO_4$ (ylide = CH_2PPh_3 (11), CH_2PPh_2Me (12), CH_2PPhMe_2 (13), $CHPhPPh_3$ (14) or CH_2AsPh_3 (15)

A mixture of $[Au(ylide)(tht)]ClO_4$ (0.2 mmol) and 1.10-phenanthroline (0.036 g, 0.2 mmol) in 30 ml of dichloromethane was stirred for 1 h. The yellow solution was concentrated to 5 ml. Addition of diethyl ether (25 ml) precipitated complexes **11–15** as yellow solids. NMR: **11**, ^{1}H, δ 8.80, 8.48, 7.95–7.4 (m, phen and Ph), 2.52 [d, J(PH) 12.0 Hz, CH_2]; **12**, ^{1}H, δ 8.95, 8.35, 7.95–7.5 (m, phen and Ph), 2.50 [d, J(PH) 13.4 Hz, Me], 2.25 [d, J(PH) 12.4 Hz, CH_2]; **13**, ^{1}H, δ 9.20, 8.4, 8.0–7.5 (m, phen and Ph), 2.24 [d, J(PH) 12.7 Hz, Me], 2.02 [d, J(PH) 12.8 Hz, CH_2]; **14**, ^{1}H, δ 8.45, 8.3, 7.8–7.2 (m, phen and Ph), 4.71 [d, J(PH) 13.4 Hz, CH]; **15**, ^{1}H, δ 8.45, 8.3, 7.9–7.1 (m, phen and Ph), 2.71 (s).

$[\{Au(ylide)\}_2(L\text{-}L)]ClO_4$ (L-L = dppm; ylide = CH_2PPh_3 (16), CH_2PPh_2Me (17), CH_2PPhMe_2 (18), $CHPhPPh_3$ (19), CH_2AsPh_3 (20) or L-L = dpam, ylide = CH_2PPh_3 (21)

To a solution of $[Au(ylide)(tht)]ClO_4$ (0.2 mmol) in 30 ml of dichloromethane was added the bidentate ligand (0.1 mmol, L-L = dppm (0.038 g) or dpam (0.047 g)) and the mixture was stirred for 1 h. The solution was concentrated to 5 ml and addition of diethyl ether (25 ml) gave complexes **16–21**. NMR: **16**, ^{1}H, δ 7.9–6.95 (m, Ph), 3.83 [t, J(PH) 11.9 Hz, P–CH_2–P], 2.43 [d, J(PH) 9.9 Hz, CH_2]; ^{31}P, δ 35.1 ('t', dppm), 31.4 ('t', PPh_3); **17**, ^{1}H, δ 8.2–6.8 (m, Ph), 3.47 [t, J(PH) 11.5 Hz, P–CH_2–P], 2.56 [d, J(PH) 9.7 Hz, Me], 2.37 [d, J(PH) 10.7 Hz, CH_2]; ^{31}P, δ 35.2 ('t', dppm), 27.7 ('t', PPh_2Me); **18**, ^{1}H, δ 7.8–7.3 (m, Ph), 3.83 [t, J(PH) 11.7 Hz, P–CH_2–P], 2.26 [d, J(PH) 13.9 Hz, CH_2], 2.06 [d, J(PH) 13.1 Hz, Me]; ^{31}P, δ 35.2 ('t', dppm), 28.9 ('t', $PPhMe_2$); **19**, ^{1}H, δ 8.2–6.7 (m, Ph), 4.7 [d, J(PH) 14.2 Hz, CH], 3.81 [t, J(PH) 10.5 Hz, P–CH_2–P]; **20**, ^{31}P, δ 35.7 (s); **21**, ^{1}H, δ 7.8–7.0 (m, Ph), 3.57 (s, As–CH_2–As), 2.53 [d, J(PH) 12.3 Hz, CH_2]; ^{31}P, δ 30.8 (s).

$[Au(ylide)\{Co(CO)_4\}]$ (ylide = CH_2PPh_3 (22), $CHPhPPh_3$ (23) or CH_2AsPh_3 (24)

The salt $[N(PPh_3)_2][Co(CO)_4]$ [7] (0.142 g, 0.2 mmol) was added to a solution of $[Au(ylide)(tht)]ClO_4$ (0.2 mmol) in 25 ml of deoxygenated dichloromethane and the mixture was stirred under nitrogen atmosphere. The reaction was completed after 5 min (IR spectra). The red solution was concentrated to 10 ml and addition of diethyl ether (20 ml) gave a white precipitate of $[N(PPh_3)_2]ClO_4$ which was filtered off. The solution was evaporated to 5 ml and addition of n-hexane (20 ml) precipitated complexes **22–24** as red solids. NMR: **22**, ^{1}H, δ 7.8–7.1 (m, Ph), 1.69 [d, J(PH) 15.1 Hz, CH_2]; ^{31}P, δ 32.1 (s); **23**, ^{1}H, δ 8.0–7.1 (m, Ph), 4.47 [d, J(PH) 13.3 Hz, CH]; **24**, ^{1}H, δ 8.05–7.2 (m, Ph), 1.83 (s).

[Au(ylide)(C≡CR)] (R = Ph, ylide = CH_2PPh_3 (25), CH_2PPh_2Me (26), CH_2PPhMe_2 (27), $CHPhPPh_3$ (28), $CHMePPh_3$ (29); R = ^{t}Bu, ylide = CH_2PPh_3 (30), CH_2PPh_2Me (31), CH_2PPhMe_2 (32), $CHPhPPh_3$ (33), $CHMePPh_3$ (34)

To a solution of KOH (0.9 mmol, 0.1 M) in methanol was added HC≡CR (0.6 mmol, R = Ph (0.0672 ml) or R = ^{t}Bu (0.077 ml)) and the mixture was stirred for 15 min. To the resulting solution was added [Au(ylide)(tht)]ClO_4 [6] (0.3 mmol) and the mixture was stirred for 3 h. A slight precipitate was formed ($KClO_4$) which was removed by filtration through a 1-cm layer of diatomaceous earth. Thereafter, the solution was dry-evaporated, washed with 2×5 ml of water, and 20 ml of acetone was added to the residue. The solution obtained was dried with anhydrous $MgSO_4$, filtered and vacuum-concentrated to 5 ml. Addition of n-hexane (20 ml) precipitated complexes **25–34** as white solids. NMR: **25**, ^{1}H, δ 7.8–7.0 (m, Ph), 1.76 [d, J(PH) 13.5 Hz, CH_2]; ^{31}P, δ 34.1 (s); **26**, ^{1}H, δ 8.0–7.0 (m, Ph), 2.43 [d, J(PH) 13.5 Hz, Me), 1.5 [d, J(PH) 14.3 Hz, CH_2]; ^{31}P, δ 31.2 (s); **27**, ^{1}H, δ 7.8–7.1 (m, Ph), 1.96 [d, J(PH) 13.9 Hz, Me), 1.29 [d, J(PH) 14.1 Hz, CH_2]; ^{31}P, δ 24.3 (s); **28**, ^{1}H, δ 7.8–6.8 (m, Ph), 3.83 [d, J(PH) 14.1, Hz, CH]; ^{31}P, δ 27.0 (s); **29**, ^{1}H, δ 7.9–7.0 (m, Ph), 2.38 [dq, J(PH) 14.3 Hz, J(HH) 10.5 Hz, CH], 1.72 [dd, J(PH) 30.9 Hz, J(HH) 10.5 Hz, Me]; ^{31}P, δ 26.4 (s); **30**, ^{1}H, δ 7.8–7.4 (m, Ph), 1.65 [d, J(PH) 12.1 Hz, CH_2], 1.33 (s, ^{t}Bu); ^{31}P, δ 34.16 (s); **31**, ^{1}H, δ 8.0–7.3 (m, Ph), 2.20 [d, J(PH) 13.1 Hz, Me], 1.40 [d, J(PH) 13.4 Hz, CH_2], 1.26 (s, ^{t}Bu); ^{31}P, δ 30.84 (s); **32**, ^{1}H, δ 8.0–7.2 (m, Ph), 2.4 [d, J(PH) 14.7 Hz, CH_2], 2.0 [d, J(PH) 10.3 Hz, Me], 1.13 (s, ^{t}Bu); ^{31}P, δ 30.61 (s); **33**, ^{1}H, δ 7.8–6.8 (m, Ph), 3.70 [d, J(PH) 14.1 Hz, CH], 1.22 (s, ^{t}Bu); **34**, ^{1}H, δ 7.9–7.3 (m, Ph), 2.20 (m), 1.52 [dd, J(PH) 20.2 Hz, J(HH) 8.2 Hz, Me], 1.21 (s, ^{t}Bu); ^{31}P, δ 29.9 (s).

Results and discussion

Reaction of [Au(ylide)Cl] and [Ag($OClO_3$)(tht)] (tht = tetrahydrothiophene) leads to [Au(ylide)(tht)]ClO_4 (see Scheme 1; ylide = CH_2PPh_3 (**1**), CH_2PPh_2Me (**2**), CH_2PPhMe_2 (**3**), $CHPhPPh_3$ (**4**), $CHMePPh_3$ (**5**) or CH_2AsPh_3 (**6**)).

Complexes **1–6** are white solids, which slowly decompose at room temperature, but remain unchanged for months when stored at −20 °C. They are soluble in dichloromethane, acetone (their solutions are conducting, 1:1 electrolytes) and chloroform, but insoluble in diethyl ether, hexane and pentane. The ^{1}H NMR spectra show a doublet (**1–4**), multiplet (**5**) or singlet (**6**) for the ylidic CH_2 or CH groups. The presence of the ClO_4 anion is confirmed by absorptions at 1100(s, br) and 625(s) cm^{-1}. The ν(Au–C) vibrations [4, 8] are collected in Table 1.

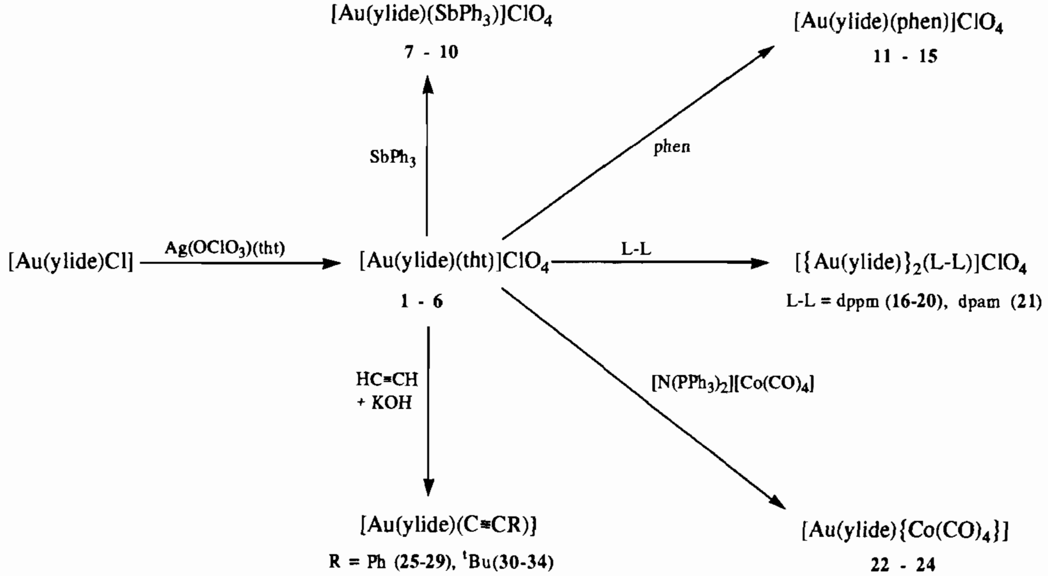
The tetrahydrothiophene in [Au(ylide)(tht)]ClO_4 is readily displaced by $SbPh_3$ to give [Au(ylide)($SbPh_3$)]ClO_4 (ylide = CH_2PPh_3 (**7**), CH_2PPh_2Me (**8**), $CHPhPPh_3$ (**9**) or CH_2AsPh_3 (**10**)) (Scheme 1), in contrast to the behaviour reported for complexes AuR(tht) (R = C_6F_5 [9], $HC_6F_4C_6F_4$ [10] or C_6Cl_5 [11]) from which the ionic derivatives [Au($SbPh_3$)$_4$][AuR_2] were obtained.

Complexes **7–10** are white solids, air- and moisture-stable at room temperature and conducting in acetone solutions (1:1 electrolytes). The IR spectra show one single band in the 585–540 cm^{-1} region, assignable to ν(Au–C) [4, 8]. The presence of the ClO_4 anion is confirmed by absorptions at 1100(s, br) and 625(s) cm^{-1}. The ^{1}H NMR spectra show a doublet (**7–9**) or singlet (**10**) for the ylidic CH_2 or CH groups.

The reaction of the tht derivatives with bidentate ligands, as 1,10-phenanthroline (phen), bis(diphenylphosphino)methane (dppm) or bis(diphenylarsino)methane (dpam), leads to the preparation of mono- ([Au(ylide)(phen)]ClO_4; ylide = -CH_2PPh_3 (**11**), CH_2PPh_2Me (**12**), CH_2PPhMe_2 (**13**), $CHPhPPh_3$ (**14**) or CH_2AsPh_3 (**15**)) or dinuclear complexes ([{Au(ylide)}$_2$(L-L)]ClO_4; L-L = dppm; ylide = CH_2PPh_3 (**16**), CH_2PPh_2Me (**17**), CH_2PPhMe_2 (**18**), $CHPhPPh_3$ (**19**), CH_2AsPh_3 (**20**) or L-L = dpam, ylide = CH_2PPh_3 (**21**)).

At room temperature complexes **11–21** are air- and moisture-stable white (**16–21**) or yellow (**11–15**) solids. Their acetone solutions show conductivities which are characteristic for 1:1 (**11–15**) or 1:2 (**16–21**) electrolytes. The ν(Au–C) vibrations are collected on Table 1. The ^{31}P NMR spectra of complexes **16–18** show two pseudotriplets of an AA′BB′ [J(BB′) = 0] system centered at 31.4 and 35.1 (**16**), 27.7 and 35.2 (**17**) and 28.9 and 35.2 ppm (**18**), corresponding to the ylidic and diphosphine phosphorous, respectively. For **20** and **21** only one peak at 35.7 and 30.8 ppm, corresponding to the two equivalent phosphorous of the diphosphine and the two equivalent ylide ligands, respectively, are observed.

Crystals of complex **13** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a layer of its dichloromethane solution. Unfortunately one of the two independent molecules is severly disordered, but the other is well-resolved and



Scheme 1.

confirms the expected nature of the compound*. The gold atom is essentially two-coordinate, with an extra weak contact to the second phenanthroline nitrogen.

If dichloromethane solutions containing equimolar amounts of $[Au(ylide)(tht)]ClO_4$ and $[N(PPh_3)_2][Co(CO)_4]$ are mixed, the rapid replacement of tht by carbonylate anions with formation of a metal–metal bond can be observed (complexes **22–24**). These reactions are always fast; after 5 min all the carbonylate of the starting product has disappeared from the solution and two new bands at 2015(s) and 1900(s) cm^{-1} can be observed in the IR spectra. Complexes **22–24** can be isolated as red solids by taking advantage of the insolubility of $[N(PPh_3)_2]ClO_4$ in diethyl ether. This is a different behaviour to that reported for the reaction of $Au(C_6F_5)(tht)$ with $[N(PPh_3)_2][Co(CO)_4]$, for which the ionic complexes $[N(PPh_3)_2][Au(C_6F_5)_2]$ and $[N(PPh_3)_2][Au\{Co(CO)_4\}_2]$ were obtained [12].

Complexes **22–24** slowly decompose at room temperature, but remain unchanged for months when stored at −20 °C. They are non-conducting in acetone solutions. These complexes should exhibit three IR-active vibrations due to $\nu(CO)$, but only two of these bands, at 2015(s) and 1900(s, br) cm^{-1}, can be observed [12]. The ^{31}P NMR spectrum of complex **22** shows a resonance at 32.1 ppm.

Reactions of $[Au(ylide)(tht)]ClO_4$ with $HC{\equiv}CR$ and KOH lead to the acetylide complexes $[Au(ylide)(C{\equiv}CR)]$, R = Ph, ylide = CH_2PPh_3 (**25**), CH_2PPh_2Me (**26**), CH_2PPhMe_2 (**27**), $CHPhPPh_3$ (**28**), $CHMePPh_3$ (**29**); R = ${}^tBu$, ylide = CH_2PPh_3 (**30**), CH_2PPh_2Me (**31**), CH_2PPhMe_2 (**32**), $CHPhPPh_3$ (**33**), $CHMePPh_3$ (**34**).

At room temperature complexes **25–34** are air- and moisture-stable white solids. Their molecular weights in chloroform are consistent with the proposed formulae. They show a measurable conductivity in acetone solutions (Table 1), but this is clearly lower than expected for 1:1 electrolytes. The $\nu(C{\equiv}C)$ appear at *c.* 2100 cm^{-1} in the IR spectra of complexes **25–29**, but it is not observable for the tert-butylacetylene complexes (**30–34**). The ^1H NMR spectra of complexes **30–34** show a singlet at *c.* 1.2 ppm for the CMe_3 group. The ^{31}P NMR for complexes **25–34** show one singlet for the phosphorous atom at 26.42–34.16 ppm.

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*$P2_1/c$, $a = 19.814(4)$, $b = 16.320(4)$, $c = 13.686(4)$ Å, $\beta = 98.26(2)°$. In view of the disorder problems we give no further details.

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