Complexes containing the Diradical 1,2,3,4-Tetraphenylbuta-1,3-diene-1,4-diyl; Crystal Structure of [AuCl(C_4Ph_4)(phen)] †

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The reaction between [{AuCl(C_4Ph_4)}$_2$] (C_4Ph_4 = 1,2,3,4-tetraphenylbuta-1,3-diene-1,4-diyl) or [AuCl(C_4Ph_4)(tht)] and neutral unidentate ligands L gives rise to bridge cleavage or to displacement of the tetrahydrothiophen ligand (tht) yielding neutral complexes of the type [AuCl(C_4Ph_4)L] [L = pyridine, PPh_3, $P(C_6H_{11})_3$, or CNBu^t]. The reaction of the dimeric complex with NEt_4Cl leads to the anionic complex [NEt_4][$AuCl_2$(C_4Ph_4)]. The use of bidentate ligands allows the preparation of two different types of complexes: [Au(C_4Ph_4)(L–L)][$AuCl_2$(C_4Ph_4)] [L–L = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), or $Ph_2P(CH_2)_2PPh_2$ (dppe)] and [AuCl(C_4Ph_4)(L–L)] [L–L = phen or 2,2′-biquinolyl (bquin)]. Preparations of the probably non-heterocyclic [Pd_2Cl_2(C_4Ph_4)(bipy)$_2$] and two gold(I) complexes [Au_2(C_4Ph_4)(PPh_3)$_2$] and [Au_2(C_4Ph_4)(dppe)] are also described. The crystal structure of [AuCl(C_4Ph_4)(phen)] has been determined: space group $P\bar{1}$, a = 11.040(2), b = 12.283(2), c = 13.670(3) Å, α = 99.76(2), β = 113.58(2), γ = 101.94(2)°, R = 0.030. Distorted five-co-ordination is observed [Au–N 2.184(4) and 2.755(4) Å].

Recently we have reported [1] the preparation of the heterocyclic gold(III) derivatives [{AuCl(C_4Ph_4)}$_2$] and [AuCl(C_4Ph_4)(tht)] (C_4Ph_4 = 1,2,3,4-tetraphenylbuta-1,3-diene-1,4-diyl, tht = tetrahydrothiophen), obtained by the reaction of $SnMe_2(C_4Ph_4)$ with [$AuCl_3$(tht)]. The resulting complexes have been used in the synthesis of [Au(acac)(C_4Ph_4)] (acac = acetylacetonate) which is the precursor for neutral and cationic complexes containing the heterocycle 'Ph_4C_4Au'.

Herein we report the behaviour of the dimer [{AuCl(C_4Ph_4)}$_2$] towards uni- and bi-dentate ligands. As has previously been shown, this type of reaction can also be carried out with the monomeric complex [AuCl(C_4Ph_4)(tht)], because of the lability of the tetrahydrothiophen ligand. Some of the results have been the subject of a preliminary communication.[2]

Results and Discussion

Reactions with Unidentate Ligands.—Addition of neutral unidentate ligands, such as pyridine (py), triphenylphosphine, tricyclohexylphosphine, or t-butyl isocyanide, to [{AuCl(C_4Ph_4)}$_2$] leads instantaneously to the formation of yellow solutions from which complexes of the type [AuCl(C_4Ph_4)L] [L = py (1), PPh_3 (2), $P(C_6H_{11})_3$ (3), or CNBu^t (4)] can be isolated. They result from cleavage of the chloro-bridges (see Scheme 1). In the corresponding reaction with triphenylarsine the dimeric complex again goes into solution, although all attempts to isolate the product proved unsuccessful and the starting material was recovered. As has already been shown for L = tht,[1] the cleavage of the chloro-bridges should be an equilibrium, which because of the insolubility of the precursor is readily displaced towards the left. This type of bridge-cleavage reaction and equilibrium of dimeric–monomeric complexes is well known in the chemistry of Au^{III}.[3]

Complexes (1)—(4) are non-conducting in acetone and monomeric in benzene. Their i.r. spectra exhibit a strong band towards 300 cm^{-1}, assignable to ν(Au–Cl), along with absorptions characteristic of the 'Ph_4C_4Au' group[1] and those arising from the respective neutral ligands. For complex (4) the location of the band due to ν(CN) at 2 240 cm^{-1} coincides with that observed for other gold(III) complexes, such as [Au(C_6F_5)X_2(CNBu^t)].[4]

The cleavage of the chloro-bridge in the dimeric complex can also be accomplished by the addition of an ionic chloride, such as $NEt_4Cl{\cdot}5H_2O$, leading to the formation of the anionic complex [NEt_4][$AuCl_2$(C_4Ph_4)] (5). This process should also be an equilibrium, which in this case can be reversed by adding methanol to an acetone solution of complex (5), giving rise to precipitation of the starting complex. Complex (5) is a 1 : 1 electrolyte. Its spectrum shows two strong bands assignable to ν(Au–Cl) at 298 and 275 cm^{-1}, in good agreement with those observed for other *cis*-dichlorogold(III) complexes.[5]

Reactions with Bidentate Ligands.—Addition of bidentate ligands [L–L = 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), or 1,2-bis(diphenylphosphino)ethane (dppe)] in 1 : 2 L–L : Au ratio to dichloromethane suspensions of the dimeric complex [{AuCl(C_4Ph_4)}$_2$] leads to solutions from which complexes of the type [Au(C_4Ph_4)(L–L)][$AuCl_2$(C_4Ph_4)] [L–L = phen (6), bipy (7), or dppe (8)] can be isolated (see Scheme 1). The i.r. spectra of these three complexes show two strong bands coincident with those observed for complex (5). This, along with the analytical data, supports the proposed structure; moreover, the same behaviour is observed for other gold(III) complexes of the type [AuR_2X] if these are treated in the same L–L : Au ratio with the same bidentate ligands.[6,7] Nonetheless, in solution these complexes should be in equilibrium with neutral species since their molar conductivities in acetone are lower than those expected for 1 : 1 electrolytes. The same anomaly is also observed for the complexes [Au($C_{12}H_8$)(L–L)][$AuCl_2$($C_{12}H_8$)] ($C_{12}H_8$ = 2,2′-biphenyl; L–L = phen or bipy).[7]

Two different types of reaction take place if these or other bidentate ligands such as 2,2′-biquinolyl (bquin) or *o*-phenylenebis(dimethylarsine) (pdma) are used in 1 : 1 or higher L–L : Au ratio.

(*i*) With 2,2′-bipyridine only complex (7) can be isolated.

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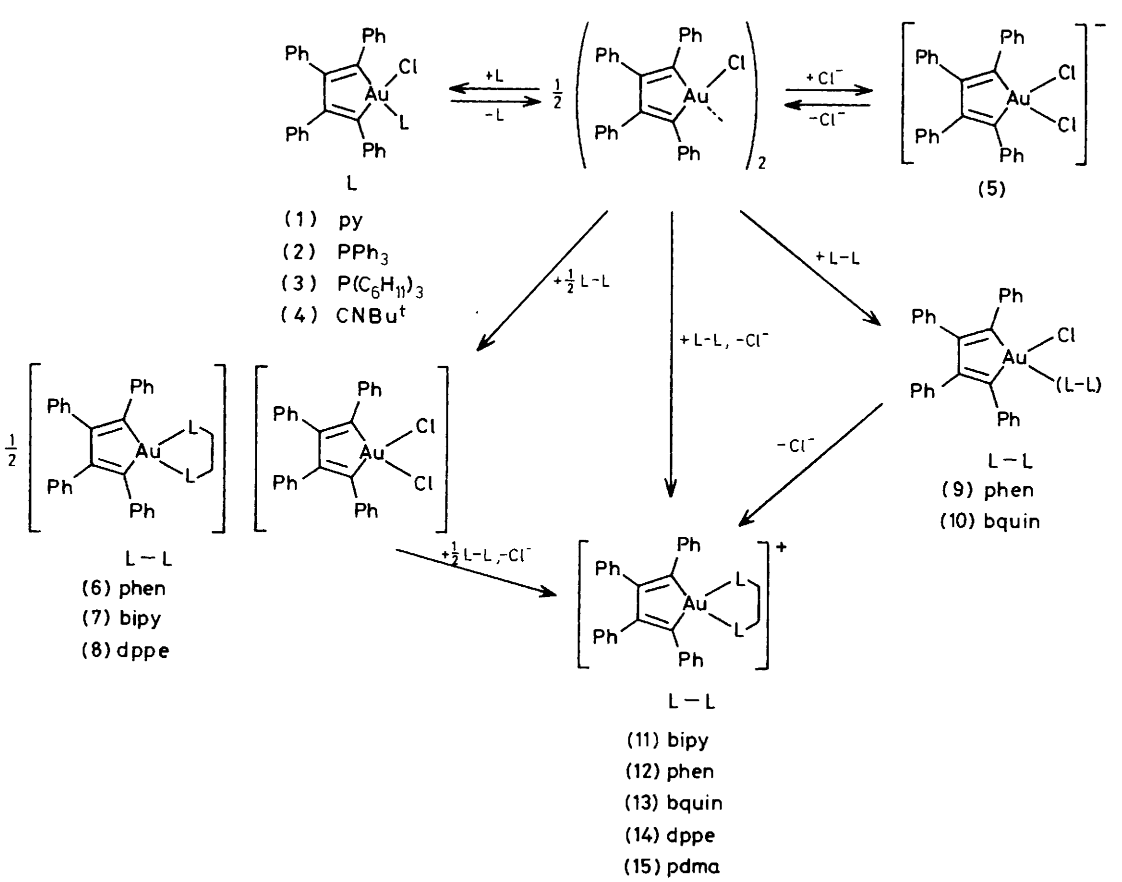
† Chloro(1,10-phenanthroline)(1,2,3,4-tetraphenylbuta-1,3-diene-1,4-diyl)gold.

Supplementary data available (No. SUP 23567, 38 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Scheme 1. Reactions of [{AuCl$_2$(C$_4$Ph$_4$)}$_2$] with uni- and bi-dentate ligands

It seems noteworthy that the same behaviour is observed in the reaction of 2,2′-bipyridine with [(AuEt$_2$Br)$_2$], since only [AuEt$_2$(bipy)][AuEt$_2$Br$_2$] can be isolated, even if an excess of the ligand is used. This is quite different from the reaction with 1,10-phenanthroline which leads to the complex [AuEt$_2$(phen)]Br.[6b]

(*ii*) 1,10-Phenanthroline and 2,2′-biquinolyl lead to complexes whose analytical data, low conductivities in acetone, molecular weights (osmometrically in chloroform solution), and i.r. spectra (a strong band towards 280 cm^{-1}) support their formulation as [AuCl(C$_4$Ph$_4$)(L–L)] [L–L = phen (9) or bquin (10)]. Since this type of bidentate ligand is usually chelating, these complexes seemed likely to be the first known five-co-ordinate organogold(III) derivatives. Single crystals of complex (9) were obtained from dichloromethane–light petroleum (b.p. 40—60 °C) (diffusion method); an *X*-ray structure determination (see below) confirms the distorted five-co-ordination in the solid state, as observed in related complexes of Au^{III} and Pd^{II}.[8]

Although the gold atom may be formally described as five-co-ordinate, the Au–N(2) interaction is very much weaker (almost 0.6 Å longer) than Au–N(1) (see Figure). The ligand atoms C(1), C(4), Cl, and N(1) lie in a plane [root mean square (r.m.s.) deviation 0.02 Å] with Au displaced out of this plane by 0.09 Å towards N(2). The phenanthroline ligand is planar (r.m.s. deviation 0.04 Å) with the gold atom lying 0.39 Å from this plane; the AuC$_4$ ring is also planar (r.m.s. deviation 0.01 Å), as was observed in the only other Ph$_4$C$_4$Au ring studied by *X*-ray methods.[9]

Cationic complexes of the type [Au(C$_4$Ph$_4$)(L–L)]ClO$_4$ can be obtained by any of the following methods: (*a*) starting from [{AuCl(C$_4$Ph$_4$)}$_2$] or [AuCl(C$_4$Ph$_4$)(tht)] and adding stoicheiometric amounts of the respective ligand together with NaClO$_4$·H$_2$O in acetone; (*b*) starting from complexes of the type [Au(C$_4$Ph$_4$)(L–L)][AuCl$_2$(C$_4$Ph$_4$)] and adding stoicheiometric amounts of the respective ligand along with NaClO$_4$·H$_2$O in acetone; and (*c*) starting from complexes of the type [AuCl(C$_4$Ph$_4$)(L–L)] and adding stoicheiometric amounts of NaClO$_4$·H$_2$O in acetone (for L–L = phen) or AgClO$_4$ in toluene (for L–L = bquin).

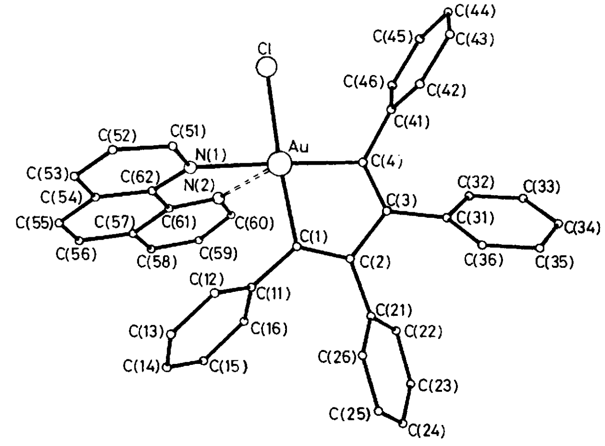


Figure. The molecule of complex (9), showing the atom-numbering scheme. The weak Au–N(2) interaction is shown as a broken line

The complexes [Au(C$_4$Ph$_4$)(L–L)]ClO$_4$ [L–L = bipy (11), phen (12), bquin (13), dppe (14), or pdma (15)] are 1 : 1 electrolytes in acetone or in acetonitrile [complex (13)]. The reactions are summarized in Scheme 1, and analytical

Physical and analytical data for complexes

Complex	M.p. (°C)	Λ_M [a]/ Ω^{-1} cm^2 mol^{-1}	Analytical data [b] (%) C	H	N	Au	Yield (%)	*M* [b]	ν̄(Au
$AuCl(C_4Ph_4)(py)]$	176	0	59.55	3.40	2.35	29.9	90	705 [c]	3
			(59.35)	(3.75)	(2.10)	(29.5)		(668)	
$AuCl(C_4Ph_4)(PPh_3)]$	187	0	62.85	3.85		23.05	76	887 [c]	3
			(63.65)	(4.30)		(24.0)		(831)	
$AuCl(C_4Ph_4)\{P(C_6H_{11})_3\}]$	180	1.6	64.45	6.35		21.95	52	892 [d]	3
			(63.55)	(6.15)		(22.65)		(869)	
$AuCl(C_4Ph_4)(CNBu^t)]$	168 (decomp.)	1.3	58.6	4.45	2.30	29.0	86	699 [d]	2
			(59.0)	(4.35)	(2.10)	(29.3)		(672)	
$NEt_4][AuCl_2(C_4Ph_4)]$	189 (decomp.)	107.4	56.45	5.00	2.00	25.85	80		298s
			(57.3)	(5.30)	(1.85)	(26.1)			
$Au(C_4Ph_4)(phen)][AuCl_2(C_4Ph_4)]$	170 (decomp.)	49.7	58.25	3.50	2.15	29.8	79		298r
			(60.15)	(3.55)	(2.05)	(29.0)			
$Au(C_4Ph_4)(bipy)][AuCl_2(C_4Ph_4)]$	185 (decomp.)	61.0	60.0	3.95	2.20	29.05	100		290r
			(59.4)	(3.65)	(2.10)	(29.55)			
$Au(C_4Ph_4)(dppe)][AuCl_2(C_4Ph_4)]$	236	75.1	62.9	4.35		25.2	76		290r
			(62.5)	(4.10)		(25.0)			
$AuCl(C_4Ph_4)(phen)]$	227 (decomp.)	13.1	62.15	3.90	3.55	24.5	72	781 [d]	2
			(62.45)	(3.65)	(3.65)	(25.2)		(769)	
$AuCl(C_4Ph_4)(bquin)]$	217 (decomp.)	31.0	64.05	3.90	2.95	25.1	88	853 [d]	2
			(65.35)	(3.80)	(3.30)	(23.3)		(845)	
$Au(C_4Ph_4)(bipy)]ClO_4$	166 (decomp.)	144.6	56.0	3.60	3.50	24.5	80		
			(56.4)	(3.50)	(3.45)	(24.35)			
$Au(C_4Ph_4)(phen)]ClO_4$	227 (decomp.)	117.5	56.65	3.00	3.45	22.45	65		
			(57.4)	(3.85)	(3.35)	(23.55)			
$Au(C_4Ph_4)(bquin)]ClO_4$	153 (decomp.)	117.1 [e]	59.45	3.65	2.95	22.5	66		
			(60.75)	(3.55)	(3.10)	(21.65)			
$Au(C_4Ph_4)(dppe)]ClO_4$	219	132.2	62.35	4.25		19.45	71		
			(61.7)	(4.20)		(18.75)			
$Au(C_4Ph_4)(pdma)]ClO_4$	156 (decomp.)	141.5	47.25	3.90		21.65	40		
			(48.6)	(3.85)		(21.0)			
$Pd_2Cl_2(C_4Ph_4)(bipy)_2]$	206 (decomp.)	4.9	59.85	3.80	5.80		17	911 [d]	
			(60.5)	(3.80)	(5.90)			(952)	
$Au_2(C_4Ph_4)(PPh_3)_2]$	230 (decomp.)	0.5	60.85	4.15		29.75	74	1 111 [c]	
			(60.3)	(3.95)		(30.9)		(1 275)	
$Au_2(C_4Ph_4)(dppe)]$	187 (decomp.)	*f*	55.45	4.15		33.65	31	*f*	
			(56.45)	(3.85)		(34.3)			

ne unless otherwise stated (*ca.* 10^{-4} mol dm^{-3}). [b] Calculated values are given in parentheses. [c] In benzene. [d] In chloroform. [e] In acetonitrile. [f] Not soluble enough for de

Table 2. Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Au	2 342(1)	4 050(1)	2 945(1)	C(33)	2 388(7)	1 616(5)	−1 578(4)
Cl	2 228(2)	5 930(1)	2 819(1)	C(34)	3 578(7)	1 329(5)	−1 379(5)
N(1)	2 338(4)	4 584(3)	4 551(3)	C(35)	4 482(6)	1 378(4)	−310(5)
N(2)	−148(4)	3 040(3)	2 918(4)	C(36)	4 174(5)	1 743(4)	565(4)
C(1)	2 575(5)	2 453(4)	3 022(4)	C(41)	2 639(5)	4 397(4)	883(4)
C(2)	2 714(5)	1 881(4)	2 163(4)	C(42)	3 907(6)	5 058(4)	1 050(5)
C(3)	2 709(5)	2 517(4)	1 328(4)	C(43)	4 028(6)	5 815(5)	422(5)
C(4)	2 561(5)	3 568(4)	1 537(4)	C(44)	2 872(7)	5 945(5)	−368(4)
C(11)	2 437(5)	1 962(4)	3 896(4)	C(45)	1 582(7)	5 288(5)	−562(4)
C(12)	3 349(6)	2 455(4)	5 013(4)	C(46)	1 462(6)	4 522(5)	70(4)
C(13)	3 219(6)	1 964(5)	5 820(4)	C(51)	3 473(5)	5 401(4)	5 333(4)
C(14)	2 169(7)	963(6)	5 517(5)	C(52)	3 708(6)	5 767(5)	6 437(4)
C(15)	1 263(6)	442(5)	4 428(5)	C(53)	2 739(7)	5 279(5)	6 721(4)
C(16)	1 363(5)	944(4)	3 602(4)	C(54)	1 514(6)	4 423(5)	5 920(4)
C(21)	2 844(6)	680(4)	2 039(4)	C(55)	462(8)	3 881(6)	6 196(6)
C(22)	1 923(8)	−209(5)	1 070(6)	C(56)	−683(8)	3 050(6)	5 429(7)
C(23)	2 029(11)	−1 335(5)	1 022(8)	C(57)	−935(6)	2 718(5)	4 296(5)
C(24)	2 991(14)	−1 575(8)	1 873(10)	C(58)	−2 138(7)	1 868(5)	3 457(7)
C(25)	3 914(11)	−688(8)	2 810(9)	C(59)	−2 318(7)	1 619(5)	2 394(7)
C(26)	3 864(7)	444(6)	2 898(6)	C(60)	−1 303(6)	2 234(5)	2 149(5)
C(31)	2 974(5)	2 052(4)	373(4)	C(61)	50(5)	3 264(4)	3 982(4)
C(32)	2 063(6)	1 964(4)	−719(4)	C(62)	1 324(5)	4 105(4)	4 816(4)

data and physical properties of the complexes are listed in Table 1.

Other Reactions.—We have tried to extend the use of $SnMe_2(C_4Ph_4)$ to the preparation of palladium(II) and gold(I) complexes. Refluxing of the stannole with $[PdCl_2(bipy)]$ in toluene for 4 h leads to the formation of palladium metal and to a solution from which a yellow compound can be isolated. It is non-conducting in acetone and its analytical data and molecular weight (osmometrically in chloroform) are consistent with its formulation as $[Pd_2Cl_2(C_4Ph_4)(bipy)_2]$ (16). We postulate a structure in which the two PdCl(bipy) moieties are bridged by the diradical C_4Ph_4 (Scheme 2). The assignment of the band due to ν(PdCl) is prevented by several other absorptions in the 350—250 cm^{-1} region.

There was no reaction between $SnMe_2(C_4Ph_4)$ and $[AuCl(PPh_3)]$ in refluxing chloroform. The complex $[Au_2(C_4Ph_4)(PPh_3)_2]$ (17) can, however, be synthesized by the reaction of $[AuCl(PPh_3)]$ with $Li_2(C_4Ph_4)$ (2 : 1). In the structure of (17) the two $Au(PPh_3)$ moieties can again be assumed to be bridged by the Ph_4C_4 group (see Scheme 2). The existence of a Ph_4C_4 bridging group has been demonstrated by *X*-ray analysis of the complex $[Hg_3(CN)_2(C_4Ph_4)_2]$.[10] The reaction between complex (17) and 1,2-bis(diphenylphosphino)ethane yields a complex of formula $[Au_2(C_4Ph_4)(dppe)]$ (18), which because of its insolubility in organic solvents and because of the tendency of gold(I) complexes to exhibit linear co-ordination is probably polymeric.

Experimental

Infrared spectra were recorded (over the range 4 000—200 cm^{-1}) on a Perkin-Elmer 577 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in 5×10^{-4} mol dm^{-3} solutions with a Philips PW 9501/01 conductimeter. Molecular weights were determined with a Hitachi Perkin-Elmer 115 osmometer. Carbon, H, and N analyses were carried out with a Perkin-Elmer 240 microanalyser. Gold was determined by ashing the sample together with an aqueous solution of hydrazine.

Table 3. Bond lengths (Å) and angles (°) at gold

Au–Cl	2.368(2)	Au–N(1)	2.184(4)
Au–N(2)	2.755(4)	Au–C(1)	2.046(5)
Au–C(4)	2.039(4)		
N(1)–Au–Cl	85.3(2)	N(2)–Au–Cl	102.8(2)
N(2)–Au–N(1)	66.8(2)	C(1)–Au–Cl	175.2(2)
C(1)–Au–N(1)	97.7(2)	C(1)–Au–N(2)	81.8(2)
C(4)–Au–Cl	96.5(2)	C(4)–Au–N(1)	173.9(2)
C(4)–Au–N(2)	118.2(2)	C(4)–Au–C(1)	80.2(2)

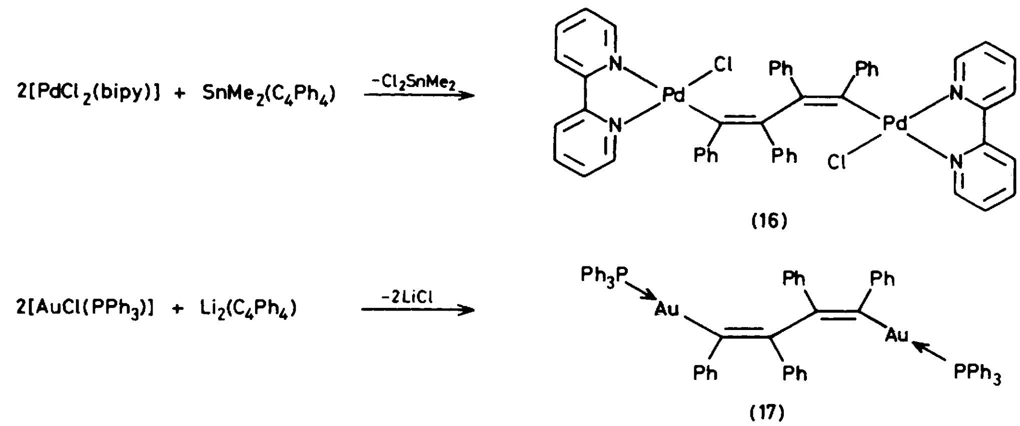
Unless otherwise stated, all the reactions were carried out at room temperature. All the complexes are yellow. The starting materials $[\{AuCl(C_4Ph_4)\}_2]$, $[AuCl(C_4Ph_4)(tht)]$,[1] $SnMe_2(C_4Ph_4)$ [11] and $Li_2(C_4Ph_4)$ [12] were prepared as described in the literature.

Although some of the complexes can be obtained by several routes, only the most convenient method is described in the following.

Complexes of the Type $[AuCl(C_4Ph_4)L]$ (1)—(4).—The ligand L (0.05 mmol) was added to a suspension of $[\{AuCl(C_4Ph_4)\}_2]$ (0.1 mmol) in dichloromethane (15 cm^3). The resulting solution was stirred for 30 min, concentrated to *ca.* 5 cm^3, and n-hexane (20 cm^3) slowly added to precipitate the required complex, which was then filtered off, washed with n-hexane (2 × 5 cm^3), and dried under vacuum.

$[NEt_4][AuCl_2(C_4Ph_4)]$ (5).—The salt $NEt_4Cl{\cdot}5H_2O$ (66 mg, 0.26 mmol) was added to a suspension of $[\{AuCl(C_4Ph_4)\}_2]$ (151 mg, 0.13 mmol) in acetone (15 cm^3). The resulting solution was stirred for 30 min, concentrated to 5 cm^3, and diethyl ether (20 cm^3) was slowly added to precipitate complex (5), which was filtered off, washed with diethyl ether (2 × 5 cm^3), and dried under vacuum.

Complexes of the Type $[Au(C_4Ph_4)(L\text{–}L)][AuCl_2(C_4Ph_4)]$ (6)—(8).—The ligand L–L (0.1 mmol) was added to a suspension of $[\{AuCl(C_4Ph_4)\}_2]$ (0.1 mmol) in dichloromethane (15 cm^3). The resulting solution was stirred for 4 h, concentrated to 5 cm^3, and diethyl ether (20 cm^3) slowly added to precipitate the required complex, which was filtered off, washed with diethyl ether (2 × 5 cm^3), and dried under vacuum.



(16)

(17)

Scheme 2. Palladium(II) and gold(I) complexes

$[AuCl(C_4Ph_4)(phen)]$ (9).—1,10-Phenanthroline hydrate (103 mg, 0.52 mmol) was added to a suspension of $[\{AuCl(C_4Ph_4)\}_2]$ (204 mg, 0.17 mmol) in dichloromethane (15 cm^3). The resulting solution was stirred for 3 h and concentrated to dryness. The residue was recrystallized from dichloromethane–diethyl ether (2 : 1).

$[AuCl(C_4Ph_4)(bquin)]$ (10).—2,2′-Biquinolyl (90 mg, 0.35 mmol) was added to a solution of $[AuCl(C_4Ph_4)(tht)]$ (120 mg, 0.18 mmol) in dichloromethane (20 cm^3), stirred for 30 min, and concentrated to 10 cm^3. Slow addition of n-hexane (20 cm^3) caused precipitation of the complex, which was filtered off and washed with diethyl ether (3 × 20 cm^3).

$[Au(C_4Ph_4)(bipy)]ClO_4$ (11).—2,2′-bipyridine (27 mg, 0.17 mmol) and $NaClO_4 \cdot H_2O$ (23 mg, 0.16 mmol) were added to a suspension of complex (7) (110 mg, 0.08 mmol) in acetone (30 cm^3) and stirred for 6 h. After evaporating the solvent the mixture was extracted with dichloromethane (30 cm^3) and filtered. The filtrate was concentrated to 5 cm^3 and diethyl ether (20 cm^3) was slowly added to precipitate the required complex, which was recrystallized from dichloromethane–diethyl ether (2 : 1).

$[Au(C_4Ph_4)(phen)]ClO_4$ (12).—The salt $NaClO_4 \cdot H_2O$ (23 mg, 0.16 mmol) was added to a solution of complex (9) (123 mg, 0.16 mmol) in acetone (30 cm^3). After stirring for 6 h the solvent was evaporated, the mixture was extracted with dichloromethane (25 cm^3), and filtered. The filtrate was concentrated to 10 cm^3 and diethyl ether (20 cm^3) slowly added to precipitate the complex, which was filtered off, washed with diethyl ether, and dried under vacuum.

$[Au(C_4Ph_4)(bquin)]ClO_4$ (13).—Silver perchlorate (13.7 mg, 0.066 mmol) was added to a suspension of complex (10) (56 mg, 0.066 mmol) in toluene (30 cm^3) and stirred for 5 h in the absence of light. The solvent was evaporated and the resulting mixture was extracted with dichloromethane (30 cm^3) and filtered. The filtrate was concentrated to 5 cm^3 and diethyl ether (20 cm^3) slowly added to precipitate the complex, which was washed with diethyl ether (2 × 5 cm^3), dried first under vacuum and then in an oven (70 °C, 30 min).

$[Au(C_4Ph_4)(dppe)]ClO_4$ (14).—1,2-Bis(diphenylphosphino)ethane (16 mg, 0.04 mmol) was added to a suspension of $[\{AuCl(C_4Ph_4)\}_2]$ (24 mg, 0.02 mmol) in dichloromethane (30 cm^3). After stirring for 2 h the solvent was evaporated and the residue was washed with diethyl ether. The compound obtained, which is not analytically pure, corresponds to the formula $[AuCl(C_4Ph_4)(dppe)]$ (see Results and Discussion section). It was dissolved in acetone (20 cm^3) and $NaClO_4 \cdot H_2O$ (6 mg, 0.04 mmol) was added. After stirring for 6 h the solvent was evaporated and the resulting mixture was extracted with dichloromethane (15 cm^3) and filtered. The filtrate was concentrated to 5 cm^3 and diethyl ether (20 cm^3) slowly added to precipitate the complex, which was washed with diethyl ether (4 × 5 cm^3) and dried under vacuum.

$[Au(C_4Ph_4)(pdma)]ClO_4$ (15).—*o*-Phenylenebis(dimethylarsine) (1.4 cm^3, 0.05 mol dm^{-3} solution in toluene) was added to a solution of $[AuCl(C_4Ph_4)(tht)]$ (32 mg, 0.047 mmol) in dichloromethane (20 cm^3). After stirring for 45 min, the solvent was evaporated and the resulting residue was washed with diethyl ether (2 × 5 cm^3) and dried under vacuum. The product, which is not analytically pure, corresponds to the formula $[AuCl(C_4Ph_4)(pdma)]$ (see Results and Discussion section). It was dissolved in acetone (20 cm^3) and $NaClO_4 \cdot H_2O$ (6.6 mg, 0.07 mmol) added. The solution was stirred for 6 h, whereafter the solvent was evaporated, the resulting mixture was extracted with dichloromethane (20 cm^3), and filtered. The filtrate was concentrated to 8 cm^3 and diethyl ether (20 cm^3) slowly added to precipitate the complex, which was washed with diethyl ether (2 × 5 cm^3) and dried under vacuum.

$[Pd_2Cl_2(C_4Ph_4)(bipy)_2]$ (16).—The complex $SnMe_2(C_4Ph_4)$ (310 mg, 0.61 mmol) was added to a suspension of $[PdCl_2(bipy)]$ (150 mg, 0.45 mmol) in toluene (30 cm^3) and refluxed for 4 h. The palladium metal formed was filtered off and the solution concentrated to precipitate the complex, which was filtered off, washed with diethyl ether, and dried under vacuum.

$[Au_2(C_4Ph_4)(PPh_3)_2]$ (17).—A solution of $Li_2(C_4Ph_4)$ (3.37 mmol) in diethyl ether (50 cm^3) was added dropwise to a suspension of $[AuCl(PPh_3)]$ (3.33 mg, 6.73 mmol) in diethyl ether. After stirring for 2.5 h the solvent was evaporated and the resulting residue was extracted with dichloromethane, filtered through Celite, and concentrated to 15 cm^3. Slow addition of hexane (20 cm^3) led to the precipitation of the complex, which contained traces of $[AuCl(PPh_3)]$. The pure product was obtained by Soxhlet extraction with diethyl ether and recrystallization from dichloromethane–n-hexane (1 : 1).

$[Au_2(C_4Ph_4)(dppe)]$ (18).—1,2-Bis(diphenylphosphino)ethane (92 mg, 0.23 mmol) was added to a solution of complex (17) (200 mg, 0.16 mmol) in dichloromethane (20 cm^3).

After stirring for 1.5 h, addition of n-hexane led to the precipitation of the complex.

Crystal Data for Complex (9).—$C_{40}H_{28}AuClN_2$, M = 769.10, Triclinic, space group $P\bar{1}$, a = 11.040(2), b = 12.283(2), c = 13.670(3) Å, α = 99.76(2), β = 113.58(2), γ = 101.94(2)°, U = 1 595.0 Å^3, Z = 2, D_c = 1.60 g cm^{-3}, $F(000)$ = 756, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 4.7 mm^{-1}.

A crystal of dimensions 0.3 × 0.3 × 0.25 mm was used to measure 6 070 profile-fitted intensities[13] in the range $7 < 2\theta < 50°$ on a Stoe four-circle diffractometer. After Lorentz polarization and absorption corrections, merging equivalents gave 5 609 unique reflections, 5 194 of which with $F > 4\sigma(F)$ were used for all calculations (programs SHELX and SHELXTL, written by G. M. S.). Cell constants were refined from 2θ values of 44 strong reflections in the range $20 < 2\theta < 24°$.

The structure was solved by the heavy-atom method and refined with all non-hydrogen atoms anisotropic to R 0.030, R' 0.029 [weighting scheme: $w^{-1} = \sigma^2(F) + 0.0001F^2$]. Hydrogen atoms were included in the refinement on the external bisector of the appropriate angle with C–H 1.08 Å and U(H) 0.08 Å^2. A final difference map showed no peaks >1 e Å^{-3}. Final atom co-ordinates and derived parameters are given in Tables 2 and 3 respectively.

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