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Ylide Transfer Reactions Used for the Synthesis of Di- and Trinuclear Gold Complexes. X-ray Structure of $[Au_3(\mu_2\text{-}CH_2PPh_2CH_2)_2(PPh_3)_2]TCNQ$ (TCNQ = 7,7′,8,8′-Tetracyanoquinodimethane)

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Reactions of the dinuclear derivative $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$ with $[AuL_2]ClO_4$ (L = PPh_3, PPh_2Me, tht) or $Q[AuX_2]$ (X = Cl, Q = $N(PPh_3)_2$; X = Br, Q = PPh_3Bz), in a 1:2 molar ratio, proceed with partial transfer of the bis(ylide) ligand to afford the cationic or anionic derivatives $[Au_2(\mu\text{-}CH_2PPh_2CH_2)L_2]ClO_4$ (L = PPh_3, PPh_2Me, tht) or $Q[Au_2(\mu\text{-}CH_2PPh_2CH_2)X_2]$ (X = Cl, Q = $N(PPh_3)_2$; X = Br, Q = PPh_3Bz), respectively. When $[Au(PPh_3)_2]ClO_4$ is used and the reaction is performed in a 1:1 molar ratio, the trinuclear derivative $[Au_3(\mu_2\text{-}CH_2PPh_2CH_2)_2(PPh_3)_2]ClO_4$ is obtained. Complexes $[Au_2(\mu\text{-}CH_2PPh_2CH_2)L_2]ClO_4$ (L = PPh_3, tht) can be also obtained by reaction of $Q[Au_2(\mu\text{-}CH_2PPh_2CH_2)X_2]$ (X = Cl, Br) with $[Ag(OClO_3)L]$ (L = PPh_3, tht), and the anionic derivative $[N(PPh_3)_2][Au_2(\mu\text{-}CH_2PPh_2CH_2)Cl_2]$ undergoes oxidative addition of chlorine to give the gold(II) compound $[N(PPh_3)_2][Au_2(\mu\text{-}CH_2PPh_2CH_2)Cl_4]$. The structure of $[Au_3(\mu_2\text{-}CH_2PPh_2CH_2)_2(PPh_3)_2]TCNQ$ has been determined by a single-crystal X-ray diffraction study. It crystallizes in the space group $P\bar{1}$ with a = 12.221(3) Å, b = 13.220(3) Å, c = 22.690(5) Å, α = 98.12(2)°, β = 91.39(2)°, γ = 115.76(2)°, Z = 2 (at −95 °C). Intramolecular Au⋯Au contacts of 3.391 and 3.544 Å are observed.

Introduction

Reactions that involve the transfer of groups or ligands from one metal center to another are particularly interesting because the catalytic activity of certain species requires either the mobility of groups at a metallic surface or the transfer of ligands between metal atoms.[1-3] The ylide transfer reactions previously described by us have been applied to the synthesis of ylide derivatives of gold, silver, thallium and palladium.[4-10] In this paper we report an extension of these ylide transfer reactions, starting from the dinuclear complex $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$, from which we have succeeded in preparing dinuclear gold(I) complexes $[Au_2(\mu\text{-}CH_2PPh_2CH_2)L_2]ClO_4$ (L = PPh_3, PPh_2Me, tht) and $Q[Au_2(\mu\text{-}CH_2PPh_2CH_2)X_2]$ (X = Cl or Br), which contain a single bis-ylide group ($CH_2PPh_2CH_2$) acting as a bridging ligand. This is noteworthy since dinuclear derivatives with only one bis(ylide) bridging ligand are poorly represented (by $[ClAu\{CH(PPh_3)C(O)CH(PPh_3)\}AuCl]$,[8] $[Au_2(dppm)\{(CH_2)_2S(O)N(CH_3)_2\}]BF_4$,[3] and $[Au_2(\mu\text{-}CH_2PR_2CH_2)(\mu\text{-}Ph_2PCHPPh_2)]$ (R = Me, Et, Bu)[11]), in contrast to the abundance of derivatives with two bis(ylide) bridging ligands.[12-14]

In these processes it has been possible to isolate a trinuclear derivative, which is an intermediate of these reactions. The structure of this complex with the TCNQ anion (TCNQ = tetracyanoquinodimethane), $[Au_3(\mu_2\text{-}CH_2\text{-}$

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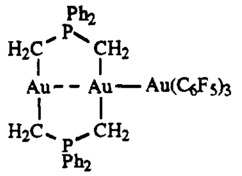
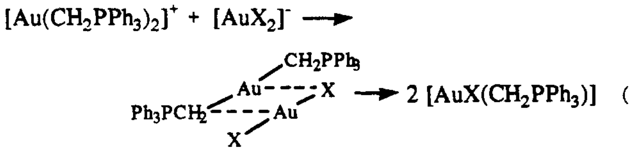


Figure 1.

$PPh_2CH_2)_2(PPh_3)_2]TCNQ$, has been determined by X-ray diffraction.

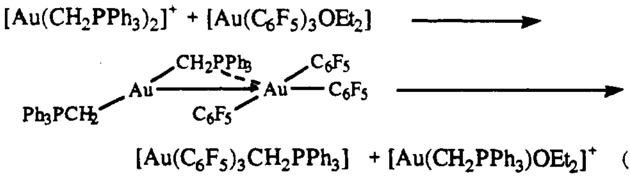
Results and Discussion

The ylide ligand transfer processes so far described seem to follow a nondissociative path, the same as that of the pentafluorophenyl group transfer. The proposed reaction intermediates are dinuclear derivatives with some groups acting as bridges[4] (eq 1).



(1)

In other processes, a dinuclear derivative with a donor-acceptor bond between the two metal centers might be proposed as intermediate[4] (eq 2).



(2)

The recent preparation of the polynuclear gold complex $[\{Au(CH_2PPh_2CH_2)_2Au\}Au(C_6F_5)_3]$[15] (Figure 1) which contains a gold(I)–gold(III) bond unbridged by any other ligand, starting from $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$, supports the last proposal. All these data led us to believe that this dinuclear complex could be a suitable precursor to transfer the bis(ylide) ligand to another selected gold center through either derivatives with gold–gold contacts or derivatives with bridging halogens.

The reactions of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$ with $[Au(PR_3)_2]ClO_4$ (PR_3 = PPh_3, PPh_2Me) in dichloromethane, 1:2 molar ratio, lead to the dinuclear derivatives $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(PR_3)_2]ClO_4$, PR_3 = PPh_3 (**1**), PPh_2Me (**2**), according to reaction i (Scheme 1).

These processes are very slow at room temperature (12 h for **1**, 24 h for **2**), but the reaction time can be halved by refluxing in chloroform. During the reactions the solutions turn red but the color fades away. Furthermore, the processes develop in a similar way in wet solvents. These data seem to indicate that, as for the other ylide transfer reactions already described, these must evolve through a nondissociative process and possibly through intermediates with gold–gold contacts.

One possible reaction process is the one presented in Scheme 2. Following the formation of an intermediate **A** containing a donor–acceptor bond, it evolves with partial transfer of the ylide ligand to give the trinuclear compound **B**, which reacts with a new molecule of $[Au(PR_3)_2]^+$ to afford the species **C**, which in turn gives rise to the formation of dinuclear derivatives **1** and **2**.

In accordance with this, the reaction of dinuclear complex $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$ with $[Au(PR_3)_2]ClO_4$, in a 1:1 molar ratio, leads to the formation of the trinuclear derivatives $[Au_3(\mu_2\text{-}CH_2PPh_2CH_2)_2(PR_3)_2]ClO_4$, PR_3 = PPh_3 (**3**), PPh_2Me (**4**), reaction ii in Scheme 1. In these reactions, we also observe a reddish color that fades away gradually.

Only in the case of PR_3 = PPh_3 is complex **3** isolated in a pure state, whereas in the case of PR_3 = PPh_2Me a mixture containing the starting product, the dinuclear derivative (**2**), and the trinuclear derivative (**4**) is obtained. These compounds cannot be separated because of their similar solubilities and the last has therefore only been characterized by spectroscopic methods.

Complex **3** reacts with $[Au(PPh_3)_2]ClO_4$ in dichloromethane, with a molar ratio of 1:1, in order to give the dinuclear derivative **1** (process iii), which seems to indicate that complex **3** is an intermediate of the reaction represented in process i (Scheme 1). The 7,7′,8,8′- tetracyanoquinodimethane (TCNQ) anion can replace the perchlorate group in complex **3** on reaction with LiTCNQ[16] (1:1 molar ratio) in ethanol (reaction iv). This complex, $[Au_3(\mu_2\text{-}CH_2PPh_2CH_2)_2(PPh_3)_2]TCNQ$ (**5**), shows ^1H and $^{31}P\{^1H\}$ NMR spectra very similar to those for complex **3** (Table 1). The structure of complex **5** was confirmed by X-ray diffraction analysis (Figure 2). The gold–gold distances of 3.391(1) and 3.544(1) Å are considerably longer than those in the dinuclear bis(ylide) complex $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$ [2.977(1) Å][13a] and in the trinuclear gold complex $[Au_3(\mu\text{-}PPh_2CH_2PPh_2)_2Cl_2]^+$ [3.067(5) and 3.164(5) Å][17] where the metal is bridged by the dppm ligand. This could be a steric effect arising from the bulky PPh_3 ligands.

The central gold atom Au(2) is bonded to two ylide carbons with Au–C distances of 2.067(12) and 2.078(12) Å, slightly shorter than Au(1)–C(1) 2.090(11) Å and Au(3)–C(4) 2.086(11) Å; the latter are more similar to those found in $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$ [2.085(7) Å]. Although the difference may not be significant, it could be associated with the higher trans influence of the PPh_3 groups. The Au–P bond lengths of 2.268(3) and 2.271(3) Å are of the same order as those in the complexes $[Au(CN)PPh_3]$ [2.278(2) Å][18] and $[Au(C_6F_5)PPh_3]$ [2.27(1) Å][19] and slightly shorter than those in $[Au\{2,6\text{-}(MeO)_2C_6H_3\}PPh_3]$ [2.284(1) Å][20] and $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$ [2.287(2) Å].[21] The geometry around the three gold atoms is linear with a maximum deviation of 5.5° for Au(3). The backbone of the cation, P1···C1···C2···C3···C4···P4 is approximately planar; all atoms except C4 (which lies 0.82 Å out of the best plane) are coplanar to within 0.03 Å. The backbone torsion angles are −2, 165, and 17° about C1···C2, C2···C3, and C3···C4, respectively.

The molecular dimensions of the counteranion $TCNQ^-$

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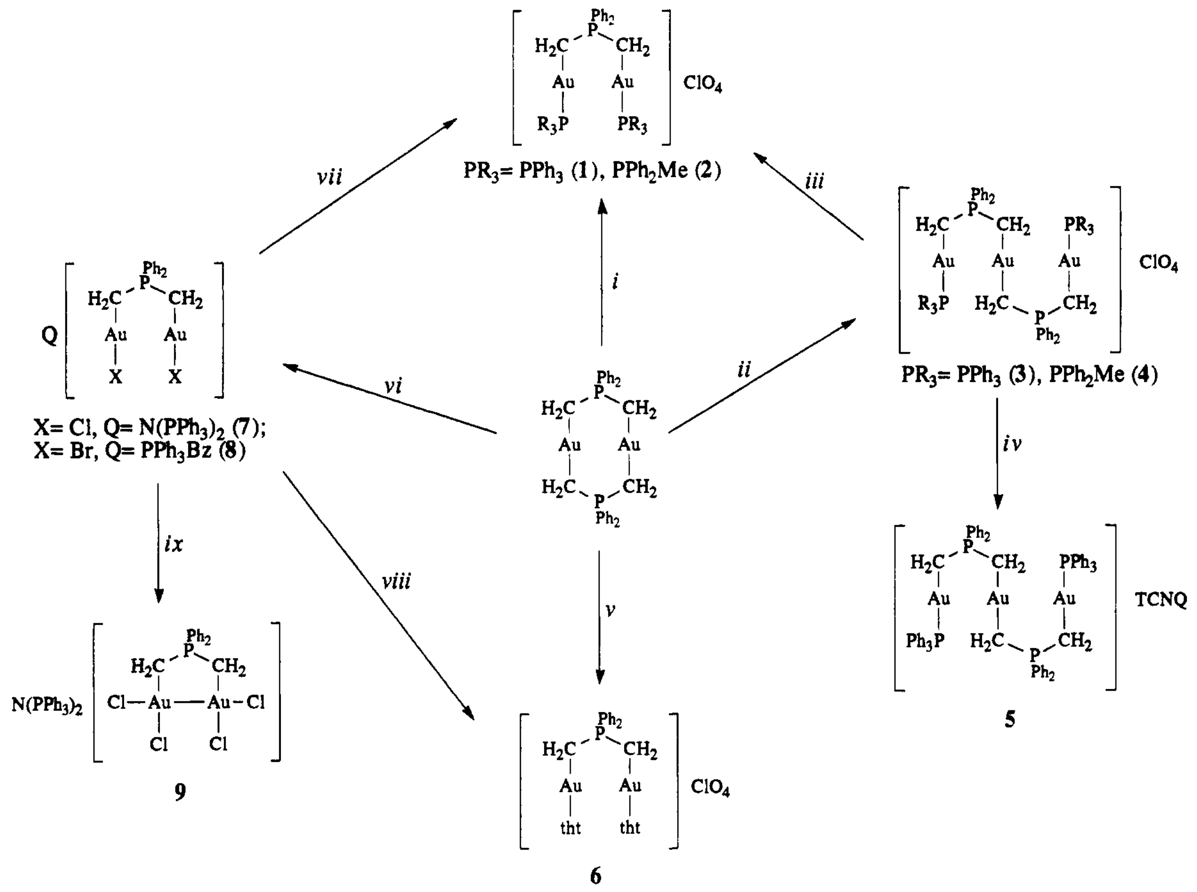
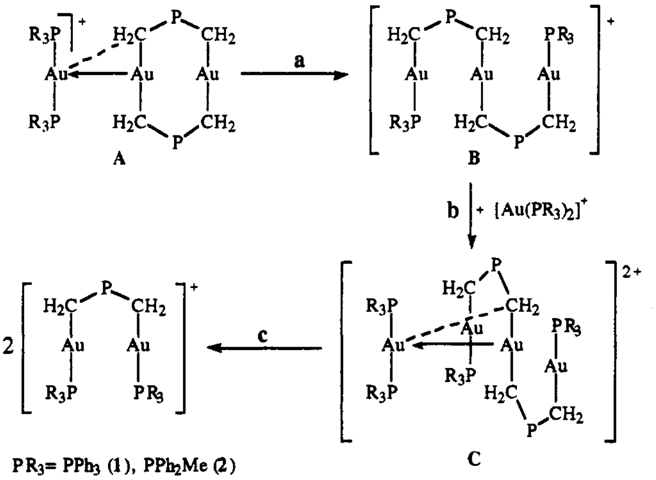
Scheme 1



[a] Key: (*i*) $2[Au(PR_3)_2]ClO_4$; (*ii* and *iii*) $[Au(PR_3)]ClO_4$; (*iv*) LiTCNQ; (*v*) $2[Au(tht)_2]ClO_4$; (*vi*) 2Q[AuX]; (*vii*) $2[Ag(OClO_3)PR_3]$; (*viii*) $2[Ag(OClO_3)tht]$; (*ix*) Cl_2.

Scheme 2



are correlated with the their charge.[22] Although in complex **5** the bond distances of the TCNQ unit are not very accurate, they are consistent with the presence of $TCNQ^-$.

The reaction of the dinuclear bis(ylide) derivative $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$ with $[Au(tht)_2]ClO_4$ (tht = tetrahydrothiophene) in dichloromethane and in a 1:2 ratio (process v) evolves in a more complicated way, since, apart from the expected dinuclear complex **6**, the previously described[23] gold(II) derivative $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(tht)_2](ClO_4)_2$ is formed. Complex **6** is more soluble in acetone, which makes separation possible. This reaction is faster than the previous ones (only 8 h at room temperature), which may arise from a greater facility of gold(I)–gold(I) contact formation, bearing in mind that tetrahydrothiophene is a poor ligand in gold chemistry.[23,24]

When this kind of reaction is carried out with anionic derivatives of the type $Q[AuX_2]$ (X = Cl, Q = $N(PPh_3)_2$; X = Br, Q = PPh_3Bz) in a 1:2 molar ratio, ylide ligand partial transfer also occurs, affording the anionic derivatives $Q[Au_2(\mu\text{-}CH_2PPh_2CH_2)X_2]$ [X = Cl, Q = $N(PPh_3)_2$ (**7**); X = Br, Q = PPh_3Bz (**8**)]; see process vi (Scheme 1). Unlike processes i, ii, and v, the reactions take place rapidly, being complete in only 15 min at room temperature. No color is observed, which implies an intermediate without gold–gold contacts but presumably with halogens as bridges.

When this reaction is performed in a 1:1 molar ratio only the final products **7** and **8** and the starting dinuclear compound are detected. This suggests that processes **b** and **c** are faster than process **a** (Scheme 3).

Complexes **7** and **8** react with $[Ag(OClO_3)L]$ (L = PPh_3, tht) in dichloromethane, 1:2 ratio, precipitating AgX to give the cationic complexes **1**, **6** (processes vii and viii). $QClO_4$ [Q = $N(PPh_3)_2$, PPh_3Bz], also formed, can be separated because of their higher solubility in methanol. With other silver complexes such as AgC_6F_5, precipitation

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Table 1. Analytical and Spectroscopic Data for Complexes 1–9

complex	analysis^a C	analysis^a H	analysis^a N	Λ_M^{b}	$^{31}P\{^1H\}$ NMR^c $\delta(PPh_2)$	$^{31}P\{^1H\}$ NMR^c $\delta(PR_3)$	$^{31}P\{^1H\}$ NMR^c $[^3J_{P-P}]^d$	^1H NMR^c $\delta(CH_2)$	^1H NMR^c $[^2J_{P-H}]^d$	$\nu(Au-C_{iluro})^g$
1, $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(PPh_3)_2]ClO_4$	48.85 (48.8)	3.65 (3.6)		119	39.2 (t)	43.2 (d)	[9.5]	1.93 (dd)	[12.7]^e	580
2, $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(PPh_2Me)_2]ClO_4$	43.0 (43.4)	3.65 (3.65)		120	39.5 (t)	28.6 (d)	[9.2]	1.84 (dd)	[13.2]^e	572
3, $[Au_3(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)_2]ClO_4$	46.75 (46.85)	3.5 (3.55)		105	37.5 (d)	41.9 (d)	[9.4]	1.62 ("t") 0.80 ("d")	[21.1]^f [12.9]^f	578
4, $[Au_3(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_2Me)_2]ClO_4$					37.8 (d)	27.3 (d)	[8.9]	1.93 ("t") 0.97 ("d")	[17.1]^f [13.0]^f	
5, $[Au_3(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)_2]TCNQ$	52.25 (52.30)	3.70 (3.35)	3.10 (3.20)	106	37.7 (d)	42.1 (d)	[9.4]	1.60 (m) 0.85 ("d")	 [11.5]^f	581
6, $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(tht)_2]ClO_4$	30.3 (29.95)	3.45 (3.4)		130	36.9 (s)			1.88 (d)	[12.5]	595
7, $[N(PPh_3)_2][Au_2(\mu\text{-}CH_2PPh_2CH_2)Cl_2]$	49.4 (49.35)	3.8 (3.65)	1.15 (1.15)	75	37.8 (s)			1.83 (d)	[12.5]	598
8, $[PPh_3Bz][Au_2(\mu\text{-}CH_2PPh_2CH_2)Br_2]$	42.1 (41.8)	3.45 (3.25)		82	36.0 (s)			1.70 (d)	[12.5]	593
9, $[N(PPh_3)_2][Au_2(\mu\text{-}CH_2PPh_2CH_2)Cl_4]$	46.75 (46.65)	3.55 (3.45)	1.05 (1.1)	104	33.1 (s)			2.10 (d)	[12.6]	600

^{a} Calculated values are given in parentheses. ^{b} In acetone (5×10^{-4} M), Ω^{-1} cm^2 mol^{-1}. ^{c} In $CDCl_3$, values in ppm. ^{d} Values of J and N in hertz. ^{e} $^3J_{P-H}$ = 8.5 Hz (**1**), 8.6 Hz (**2**). ^{f} N is the splitting between the external lines. ^{g} Values in cm^{-1}.

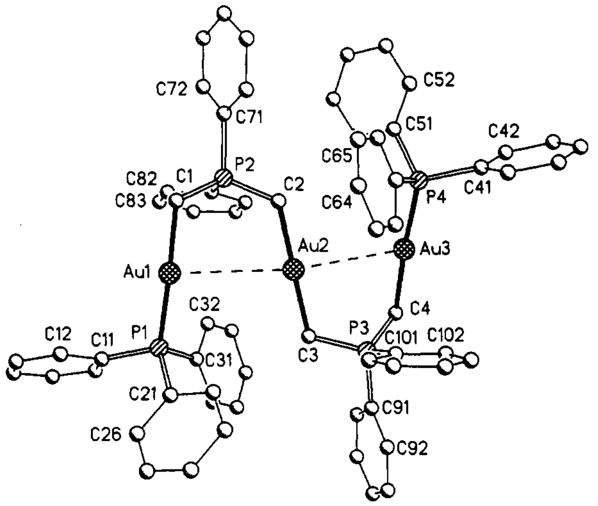
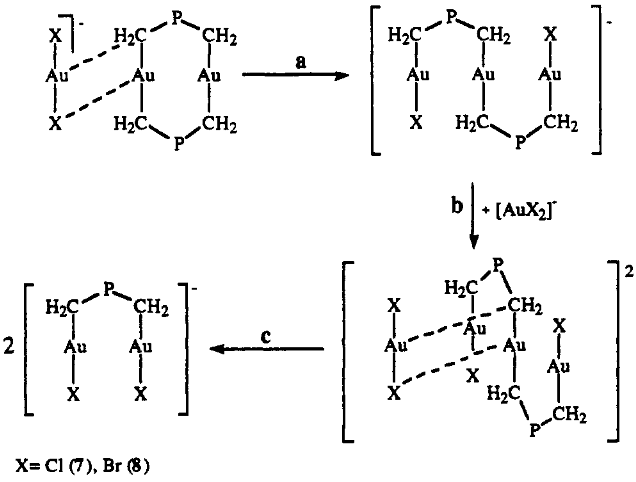


Figure 2. Cation of complex **5** in the crystal. H atoms are omitted.

Scheme 3



of AgX also takes place, but only the previously described[25] gold(II) complex $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(C_6F_5)_2]$ is obtained from the solution.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Au(1)–C(1)	2.090 (11)	Au(1)–P(1)	2.268(3)
Au(2)–C(2)	2.067(12)	Au(2)–C(3)	2.078(12)
Au(3)–C(4)	2.086(11)	Au(3)–P(4)	2.271(3)
P(1)–C(11)	1.796(11)	P(1)–C(31)	1.812(11)
P(1)–C(21)	1.833(11)	P(2)–C(1)	1.762(11)
P(2)–C(2)	1.763(12)	P(2)–C(81)	1.811(12)
P(2)–C(71)	1.821(11)	P(3)–C(3)	1.745(13)
P(3)–C(4)	1.752(12)	P(3)–C(101)	1.780(12)
P(3)–C(91)	1.799(12)	P(4)–C(51)	1.806(12)
P(4)–C(41)	1.810(13)	P(4)–C(61)	1.826(13)
C(1)–Au(1)–P(1)	175.3(4)	C(2)–Au(2)–C(3)	179.3(6)
C(4)–Au(3)–P(4)	174.4(3)	C(11)–P(1)–C(31)	103.7(5)
C(11)–P(1)–C(21)	106.0(5)	C(31)–P(1)–C(21)	106.9(5)
C(11)–P(1)–Au(1)	114.4(3)	C(31)–P(1)–Au(1)	112.1(3)
C(21)–P(1)–Au(1)	113.0(4)	C(1)–P(2)–C(2)	110.1(6)
C(1)–P(2)–C(81)	108.0(5)	C(2)–P(2)–C(81)	113.3(5)
C(1)–P(2)–C(71)	109.4(5)	C(2)–P(2)–C(71)	110.0(5)
C(81)–P(2)–C(71)	106.0(5)	C(3)–P(3)–C(4)	111.1(6)
C(3)–P(3)–C(101)	112.4(6)	C(4)–P(3)–C(101)	110.7(5)
C(3)–P(3)–C(91)	108.5(6)	C(4)–P(3)–C(91)	109.5(5)
C(101)–P(3)–C(91)	104.3(5)	C(51)–P(4)–C(41)	105.3(5)
C(51)–P(4)–C(61)	105.2(5)	C(41)–P(4)–C(61)	104.0(5)
C(51)–P(4)–Au(3)	117.5(4)	C(41)–P(4)–Au(3)	113.4(4)
C(61)–P(4)–Au(3)	110.3(4)	P(2)–C(1)–Au(1)	108.2(6)
P(2)–C(2)–Au(2)	117.2(7)	P(3)–C(3)–Au(2)	115.7(7)
P(3)–C(4)–Au(3)	109.5(6)		

The addition of Cl_2 to solutions of $[N(PPh_3)_2][Au_2(\mu\text{-}CH_2PPh_2CH_2)Cl_2]$ (**7**) in dichloromethane, 1:1 ratio, gives the dinuclear gold(II) complex $[N(PPh_3)_2][Au_2(\mu\text{-}CH_2PPh_2CH_2)Cl_4]$ (**9**) (process ix, Scheme 1). In contrast, the reaction of $[PPh_3Bz][Au_2(\mu\text{-}CH_2PPh_2CH_2)Br_2]$ (**8**) with Br_2 and the reactions of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(PPh_3)_2]ClO_4$ (**1**) with Cl_2 or Br_2 in dichloromethane give rise to a complex mixture probably because of the instability of the gold(II) complexes that presumably are formed initially. Complexes **1**–**9** are white (**1**–**8**) and yellow (**9**) solids, air- and moisture-stable at room temperature. The solutions of derivatives $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(tht)_2]ClO_4$ (**6**) and $[N(PPh_3)_2][Au_2(\mu\text{-}CH_2PPh_2CH_2)Cl_4]$ (**9**) slowly decompose to give gold(II) derivatives $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(tht)_2](ClO_4)_2$[23] and $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2Cl_2]$,[13] respectively, and metallic gold. All the complexes behave as 1:1 electrolytes in acetone solution,[26] the molar conductivity of the cationic derivatives being slightly greater than that of the anionic complexes (see Table 1).

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Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters [Å^2 × 10^3] for 5

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Au(1)	4469.3(4)	2752.0(4)	1916.1(2)	25.3(1)	C(63)	8262(13)	4420(11)	4333(7)	54(3)
Au(2)	7582.9(4)	4565.2(4)	2401.9(2)	29.0(1)	C(64)	7448(14)	4576(12)	4693(7)	56(3)
Au(3)	10427.3(4)	6646.3(4)	2883.6(2)	28.8(1)	C(65)	7351(12)	5574(12)	4770(6)	46(3)
P(1)	4790(3)	1651(2)	1144.6(13)	24.2(6)	C(66)	8132(11)	6469(11)	4495(5)	40(3)
P(2)	5308(3)	5203(2)	2640.8(13)	21.7(6)	C(71)	4899(9)	6196(9)	3112(5)	25(2)
P(3)	10057(3)	4359(3)	2084.1(14)	26.1(7)	C(72)	4392(11)	6832(9)	2878(6)	39(3)
P(4)	10023(3)	7442(3)	3753.2(13)	26.2(7)	C(73)	4069(12)	7543(10)	3254(7)	49(3)
C(1)	4114(10)	3814(9)	2576(6)	30(3)	C(74)	4244(14)	7645(12)	3856(6)	64(4)
C(2)	6669(10)	5253(10)	2954(6)	34(3)	C(75)	4749(14)	7034(13)	4106(6)	59(3)
C(3)	8520(11)	3891(12)	1849(6)	39(3)	C(76)	5070(12)	6308(11)	3733(6)	46(3)
C(4)	10871(11)	5839(10)	2136(5)	30(3)	C(81)	5433(9)	5613(8)	1908(5)	25(2)
C(11)	3547(9)	959(8)	566(5)	23(2)	C(82)	4395(10)	5240(9)	1508(5)	31(2)
C(12)	2380(10)	221(9)	707(5)	28(2)	C(83)	4470(12)	5534(10)	954(5)	36(3)
C(13)	1391(10)	−310(9)	278(6)	34(3)	C(84)	5592(11)	6195(10)	778(6)	39(3)
C(14)	1541(10)	−104(10)	−305(5)	32(2)	C(85)	6636(12)	6573(10)	1157(5)	38(3)
C(15)	2661(10)	624(10)	−457(5)	32(2)	C(86)	6554(10)	6281(9)	1720(5)	30(2)
C(16)	3658(10)	1142(9)	−27(5)	27(2)	C(91)	10687(10)	3665(9)	1552(5)	31(2)
C(21)	5090(9)	519(9)	1380(5)	27(2)	C(92)	11055(10)	2851(9)	1682(5)	34(2)
C(22)	5936(11)	821(10)	1864(5)	37(3)	C(93)	11479(11)	2309(11)	1245(6)	41(3)
C(23)	6193(11)	−11(10)	2057(6)	40(3)	C(94)	11546(11)	2563(10)	676(6)	43(3)
C(24)	5558(11)	−1138(10)	1787(5)	40(3)	C(95)	11169(12)	3341(10)	533(6)	41(3)
C(25)	4705(12)	−1429(9)	1310(6)	37(3)	C(96)	10763(11)	3903(11)	973(6)	38(3)
C(26)	4458(11)	−614(9)	1096(5)	32(2)	C(101)	10266(9)	3931(9)	2771(5)	31(2)
C(31)	6073(10)	2476(8)	755(5)	24(2)	C(102)	11404(11)	4451(10)	3106(6)	38(3)
C(32)	6324(10)	3594(9)	725(5)	31(2)	C(103)	11586(13)	4061(12)	3620(6)	51(3)
C(33)	7249(11)	4234(9)	411(5)	34(3)	C(104)	10642(11)	3165(12)	3802(6)	52(3)
C(34)	7947(12)	3763(10)	119(6)	36(3)	C(105)	9508(13)	2660(12)	3494(6)	50(3)
C(35)	7725(10)	2662(10)	159(5)	33(2)	C(106)	9316(11)	3028(10)	2976(6)	40(3)
C(36)	6805(10)	2013(9)	480(5)	30(2)	N(1)	9833(13)	2807(11)	8951(6)	61(3)
C(41)	11354(11)	8232(9)	4287(5)	28(2)	N(2)	11433(13)	560(14)	8259(7)	80(4)
C(42)	12204(11)	9317(10)	4219(5)	39(3)	N(3)	3675(12)	−1407(12)	6551(6)	63(4)
C(43)	13227(11)	9950(10)	4617(6)	43(3)	N(4)	5670(13)	−3291(12)	5767(7)	69(4)
C(44)	13429(11)	9484(9)	5094(5)	34(3)	C(111)	6662(12)	−968(10)	6939(5)	38(2)
C(45)	12618(11)	8405(10)	5169(6)	38(3)	C(112)	7730(11)	−1137(10)	6960(5)	37(3)
C(46)	11584(11)	7791(10)	4770(5)	34(3)	C(113)	8714(11)	−462(10)	7352(6)	43(3)
C(51)	9333(10)	8394(9)	3707(5)	30(2)	C(114)	8713(12)	461(11)	7760(6)	42(3)
C(52)	9334(12)	9155(10)	4197(6)	46(3)	C(115)	7679(12)	669(11)	7728(6)	40(3)
C(53)	8666(13)	9771(11)	4155(6)	53(3)	C(116)	6691(11)	−32(10)	7334(6)	38(3)
C(54)	7986(13)	9606(11)	3630(6)	49(3)	C(117)	9736(14)	1132(12)	8189(7)	49(3)
C(55)	8003(12)	8885(10)	3133(6)	39(3)	C(118)	9785(13)	2071(13)	8615(6)	45(3)
C(56)	8688(11)	8291(10)	3175(5)	33(2)	C(119)	10706(14)	869(14)	8251(6)	51(3)
C(61)	8981(11)	6334(10)	4141(5)	32(2)	C(120)	5626(13)	−1701(12)	6529(6)	45(3)
C(62)	9037(12)	5311(10)	4059(6)	48(3)	C(121)	4551(14)	−1526(13)	6546(6)	47(3)
C(122)	5625(14)	−2586(13)	6106(7)	49(3)					

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The IR spectra of complexes **1**–**4** and **6**–**9** show a weak band at *ca.* 580 cm^{-1} assignable to ν(Au–C$_{\text{ylide}}$), as has been observed in other gold–ylide complexes (for complex [Au$_2$(μ-CH$_2$PPh$_2$CH$_2$)$_2$] at 560 cm^{-1}),[27] as well as absorptions corresponding to the ClO$_4^-$ anion[28] (**1**–**4** and **6**) or the [N(PPh$_3$)$_2$]$^+$(**7**, **9**) and [PPh$_3$Bz]$^+$ (**8**) cations. Futhermore, complexes **7** and **9** show bands at 310 (**7**) and 305 and 250 cm^{-1} (**9**) assigned to ν(Au–Cl).[29] In the spectrum of complex **8** the ν(Au–Br) vibration has not been observed, probably because it lies below 200 cm^{-1}, which is the limit of the spectrophotometer.

Their ^{31}P{^{1}H} and ^{1}H NMR spectra are in accordance with the proposed formulation (see Table 1). Their ^{31}P{^{1}H} NMR spectra show a singlet (complexes **6**–**9**), a doublet (complexes **3**–**5**), and a triplet (complexes **1** and **2**) corresponding to the phosphorus atoms of the (CH$_2$PPh$_2$CH$_2$) ylide group. The last two multiplicities are consistent with coupling to one or two further phosphorus atoms, respectively. The phosphorus atoms of the PR$_3$ groups appear as doublets. For anionic complexes, a singlet assignable to the [N(PPh$_3$)$_2$]$^+$ [21.7 ppm (**7**, **9**)] and [PPh$_3$Bz]$^+$ [23.6 ppm (**8**)] cations is also observed.

The ylide methylene proton resonances in the ^{1}H NMR spectra appear as doublets for complexes **6**–**9** and as doublets of doublets for complexes **1** and **2** and are somewhat more complicated for complexes **3**–**5**, appearing as pseudotriplets for the methylene groups trans to phosphine and as pseudodoublets for the other methylene groups. For complex **9**, this signal resonates at a lower field than in the gold(I) derivative (**7**), as in other gold(II) dinuclear compounds. The spectrum of complex **2** also shows a doublet at 1.89 ppm from the methyl protons, $^2J_{\text{P-H}}$ = 9 Hz.

Experimental Section

General Data. Instrumentation and general experimental techniques were as described earlier.[24] All the reactions were carried out at room temperature except the reactions of [Au$_2$(μ-CH$_2$PPh$_2$CH$_2$)$_2$] with [Au(PPh$_3$)$_2$]ClO$_4$ (PR$_3$ = PPh$_3$, PPh$_2$Me) in a 1:2 molar ratio.

Preparation of [Au$_2$(μ-CH$_2$PPh$_2$CH$_2$)(PR$_3$)$_2$]ClO$_4$ [PR$_3$ = PPh$_3$ (1), PPh$_2$Me (2)]. (a) To a solution of [Au$_2$(μ-CH$_2$PPh$_2$-

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$CH_2)_2]$[13a] (0.041 g, 0.05 mmol) in dichloromethane (20 mL) was added $[Au(PPh_3)_2]ClO_4$[30] (0.082 g, 0.1 mmol) or $[Au(PPh_2Me)_2]ClO_4$[30] (0.070 g, 0.1 mmol). The mixture was stirred for 12 h (1) or 24 h (2) at room temperature. Concentration of the solution to *ca.* 5 mL and addition of *n*-hexane (20 mL) led to the precipitation of complexes 1 and 2.

(b) To a solution of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$ (0.041 g, 0.05 mmol) in chloroform (25 mL) was added $[Au(PPh_3)_2]ClO_4$ (0.082 g, 0.1 mmol) or $[Au(PPh_2Me)_2]ClO_4$ (0.069 g, 0.1 mmol). After stirring for 6 h (1) or 12 h (2) with refluxing, the solution was evaporated to *ca.* 5 mL. Addition of *n*-hexane (20 mL) gave complexes 1 and 2 as white solids. Yields: 90% (1), 70% (2).

Preparation of $[Au_3(\mu\text{-}CH_2PPh_2CH_2)_2(PR_3)_2]ClO_4$ [PR_3 = PPh_3 (3), PPh_2Me (4)]. To a dichloromethane solution (20 mL) of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$[13a] (0.041 g, 0.05 mmol) was added 0.05 mmol of $[Au(PPh_3)_2]ClO_4$[30] (0.041 g) or $[Au(PPh_2Me)_2]ClO_4$[30] (0.035 g). The mixtures were stirred for 6 h and then evaporated to *ca.* 5 mL. Addition of *n*-hexane (20 mL) led to the precipitation of complex 3 and a mixture of starting products, dinuclear derivative 2 and trinuclear derivative 4. Yield: 70% (3).

Preparation of $[Au_3(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)_2]TCNQ$ (5). To a solution of $[Au_3(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)_2]ClO_4$ (3) (0.184 g, 0.13 mmol) in ethanol (20 mL) was added LiTCNQ[16] (0.027 g, 0.13 mmol). After stirring for 1 h, precipitation of a green solid was observed. The mixture was stirred for 10 h and then the solid was filtered off and washed with diethyl ether (3 × 5 mL). Yield: 65%.

X-ray Structure Determination of Compound 5. Crystal Data: $C_{76}H_{62}Au_3N_4P_4$, M_r = 1746.1, triclinic, space group $P\bar{1}$, a = 12.221(3) Å, b = 13.220(3) Å, c = 22.690(5) Å, α = 98.12(2)°, β =91.39(2)°, γ = 115.76(2)°, V = 3253.3(13) Å^3, Z = 2, D_c = 1.782 Mg m^{-3}, $F(000)$ = 1686, λ(Mo $K\alpha$) = 0.710 73 Å, μ = 6.9 mm^{-1}, T = −95 °C.

Data Collection and Reduction. Single crystals of compound 5 in the form of brownish-red plates were obtained on cooling a dichloromethane/diethyl ether solution. A 0.2 × 0.2 × 0.05 mm crystal was mounted in inert oil (type RS3000, donated by Riedel-de-Haën), transferred to the cold gas stream of a Siemens R3 diffractometer, and used to collect 12 091 intensities to $2\theta_{max}$ 50° (monochromated Mo Kα radiation). An absorption correction based on Ψ-scans was applied, with transmission factors 0.53–1.00. Merging equivalents gave 11 508 unique reflections (R_{int} 0.044), of which 11 500 were used for all calculations (program system SHELXL-93).[31] Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–22°.

Structure Solution and Refinement. The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on F^2. Hydrogen atoms were included using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = F_o^2 + 2F_c^2$, with a = 0.0177 and b = 68.9716. Refinement proceeded to $wR(F^2)$ 0.121, conventional $R(F)$ 0.047 for 784 parameters and 700 restraints. S = 1.06; maximum $\Delta\rho$ 3.8 e Å^{-3}. Selected bond lengths and angles are given in Table 2; final atomic coordinates, in Table 3.

Preparation of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)(tht)_2]ClO_4$ (6). To a dichloromethane solution (20 mL) of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$[13a] (0.041 g, 0.05 mmol) was added $[Au(tht)_2]ClO_4$[30] (0.047 g, 0.1 mmol) and the mixture was stirred for 8 h. The solution was filtered off and washed with dichloromethane (3 × 5 mL). Concentration of the filtrate to *ca.* 5 mL and addition of *n*-hexane (20 mL) led to the precipitation of a mixture containing complex 6 and $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(tht)_2](ClO_4)_2$ which was washed with a mixture of acetone/*n*-hexane (30/70%). Concentration of the filtrate to *ca.* 5 mL and addition of *n*-hexane (20 mL) gave complex 6 as a white solid. Yield: 30% (6).

Preparation of $Q[Au_2(\mu\text{-}CH_2PPh_2CH_2)X_2]$ [X = Cl, Q = $N(PPh_3)_2$ (7); X = Br, Q = PPh_3Bz (8)]. To a solution of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2]$[13a] (0.041 g, 0.05 mmol) in dichloromethane (20 mL) was added $[N(PPh_3)_2][AuCl_2]$[32] (0.081 g, 0.1 mmol) or $[PPh_3Bz][AuBr_2]$[32] (0.071 g, 0.1 mmol). After stirring for 15 min, the solvent was evaporated to *ca.* 5 mL and diethyl ether (20 mL) added to precipitate complexes 7 and 8 as white solids. Yields: 75% (7, 8).

Preparation of $[N(PPh_3)_2][Au'_2(\mu\text{-}CH_2PPh_2CH_2)Cl_4]$ (9). To a dichloromethane solution (15 mL) of $[N(PPh_3)_2][Au_2(\mu\text{-}CH_2PPh_2CH_2)Cl_2]$ (7) (0.122 g, 0.1 mmol) was added 0.4 mL of a solution of chlorine in carbon tetrachloride (0.25 M). The mixture was stirred for 10 min, and then the solution was evaporated to *ca.* 5 mL. Addition of diethyl ether led to the precipitation of complex 9 as a yellow solid. Yield: 80%.

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Supplementary Material Available: A description of the crystal structure determination, including tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, and thermal parameters (9 pages). Ordering information is given on any current masthead page.

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