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Polynuclear Aryl Derivatives of Group 11 Metals: Synthesis, Solid State–Solution Structural Relationship, and Reactivity with Phosphines

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The synthesis of homoleptic aryl derivatives of group 11 metals has been performed by reacting the monochlorides [CuCl], [AgCl], and [AuCOCl] with MesMgBr (Mes ≡ 2,4,6-$Me_3C_6H_2$). The resulting products [Cu_5Mes_5] (1), [Ag_4Mes_4] (2), and [Au_5Mes_5]·2THF (3) have been isolated as crystalline thermally stable compounds. They have, in the solid state, cyclic structures whose molecular geometries are discussed within. MW determination by cryoscopy in benzene and ^{1}H NMR spectra in both C_6D_6 and C_6D_{12} showed that the three oligomeric structures were in equilibrium with the respective dimeric form of the molecule. In each case the dimeric form was the prevailing species in solution. The solution equilibrium was very rapidly established for the silver and gold complexes and was relatively slower for the copper complex. In the case of the copper complex the rate of equilibrium was solvent dependent, being much faster in toluene ($t_{1/2}$ for Cu_5Mes_5 being ca. 0.66 h) than in cyclohexane ($t_{1/2}$ being ca. 56 h). The addition of electron-rich arenes to cyclohexane solutions of 1 greatly enhanced the rate of conversion of the pentamer to dimer. Addition of ligands to the solution containing the dimers allowed us to isolate complexes of different molecular complexity. The addition of THT (tetrahydrothiophene) to a THF solution of 1 resulted in the formation of the complex [$Cu_4Mes_4THT_2$] (5). The results of the reactions of 1–3 with phosphines are reported and appear to be strongly dependent on the nature of the metal. PPh_3 and dppe ($Ph_2PCH_2CH_2PPh_2$) stabilize the copper(I) dimer in solution, and subsequently they promote a ligand rearrangement with the formation of the corresponding cuprate. dppm ($Ph_2PCH_2PPh_2$) reacts with 1 and 2 with the protolysis and elimination of the mesityl group to form [$Cu_3(Ph_2PCHPPh_2)_3$]·$2C_7H_8$ (8) and [$Ag_3(Ph_2PCHPPh_2)_3$]·$2C_7H_8$ (9), respectively. Complex 2 reacts with dppe in the same way as 1 or 3 depending on the nature of the solvent. Full characterization of the complexes was prevented by their thermal and photochemical instability. The reaction of phosphines PPh_3, dppm, and dppe did not affect the [AuMes] functionality; in all three cases formation of the [P–Au–Mes] dicovalent gold(I) complexes [$AuMesPPh_3$] (10), [$Au_2Mes_2(\mu\text{-dppm})$] (11), and [$Au_2Mes_2(\mu\text{-dppe})$] (12) was observed. The structures of six compounds have been determined. Crystallographic details for complexes 1, 2, 3, 5, 9, and 12 are as follows: Complex 1: space group $P2_1/n$ (monoclinic), a = 16.094 (4) Å, b = 16.022 (4) Å, c = 19.259 (5) Å, β = 97.49 (3)°, V = 4924 (2) Å^3, Z = 4, D_{calcd} = 1.232 g cm^{-3}. The final R factor was 0.10 for 1629 observed reflections. Complex 2: space group $R3$ (rhombohedral), $a = b = c$ = 18.395 (3) Å, $\alpha = \beta = \gamma$ = 116.28 (2)°, V = 3038 (4) Å^3, Z = 3, D_{calcd} = 1.489 g cm^{-3}. The final R factor was 0.062 (R_w = 0.064) for 1966 observed reflections. Complex 3: space group $Pnma$ (orthorhombic), a = 21.864 (10) Å, b = 27.188 (11) Å, c = 8.951 (5) Å, V = 5321 (4) Å^3, Z = 4, D_{calcd} = 2.153 g cm^{-3}. The final R factor was 0.052 (R_w = 0.050) for 2023 observed reflections. Complex 5: space group $P1$ (triclinic), a = 12.907 (3) Å, b = 20.624 (6) Å, c = 8.708 (2) Å, α = 102.14 (3)°, β = 107.38 (3)°, γ = 89.64 (3)°, V = 2159 (1) Å^3, Z = 2, D_{calcd} = 1.396 g cm^{-3}. The final R factor was 0.057 (R_w = 0.062) for 3117 observed reflections. Complex 9: space group $P2_1/n$ (monoclinic), a = 14.004 (2) Å, b = 23.632 (4) Å, c = 24.572 (4) Å, β = 101.66 (1)°, V = 7964 (2) Å^3, Z = 4, D_{calcd} = 1.384 g cm^{-3}. The final R factor was 0.061 for 5695 observed reflections. Complex 12: space group $P1$ (triclinic), a = 11.700 (2) Å, b = 12.475 (2) Å, c = 7.647 (1) Å, α = 101.52 (1)°, β = 95.81 (1)°, γ = 109.55 (1)°, V = 1013.4 (3) Å^3, Z = 1, D_{calcd} = 1.650 g cm^{-3}. The final R factor was 0.036 for 3659 observed reflections.

Introduction

Two general aspects of group 11 metal aryl chemistry will be described in this paper, namely, the synthesis and isolation of stable homoleptic [M–Ar]$_n$ compounds for the three metals, together with a full description of the solid state–solution structural relationship.

There are a very few examples of a homogeneous series of homoleptic aryl or alkyl derivatives for a transition metal group.[1] Such a series would allow a trend in thermodynamic properties and the reactivity of the M–C bond functionality to be established down a group. In spite of the relevant role of the group 11 metals, and particularly that of copper,[2] in organometallic and organic synthesis, information is available only on a number of unrelated examples for the three metals.[3-5] Reports describing the preparation of complexes of group 11 metals are restricted mainly to in situ synthesis. In the case of copper and silver, the isolation of the so-called copper phenyl and silver

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phenyl dates back to 1923[6] and 1919,[7] respectively, but their structural characterization has never been achieved.

Historically, it was believed that the instability of the metal–carbon bond functionality was due to the absence around the metal of the suitable ancillary ligands;[8] this was also believed to be the case for group 11 metals. Some metal–aryl compounds of Cu, Ag, and Au having phosphines as ancillary ligands have been synthesized having the empirical formula $[(PR_3)_nM\text{–}Ar]_m$,[3,4] while homoleptic compounds, which are very rare for silver and gold(I), have some precedence in copper(I) chemistry.[3,9] Some of those compounds, however, have substituents at the aryl residue acting as internal stabilizing ligands. It is worth mentioning that for a stoichiometric formula like [M–Ar], in the absence of any ancillary ligand, the aryl group is found to display a bridging bonding mode and the compounds to have either a cyclic or a polymeric structure allowing the metal to achieve at least the bicoordination.[3] Such a coordination number is the most common for the organometallic derivatives of the group 11 metals in the +1 oxidation state. The degree of molecular aggregation is, however, very variable, depending on the nature of the metal, the organic residue, and the reaction solvent. An even more intriguing aspect of such a chemistry is the solid state–solution structural relationship of the various species.[3]

Applying the usual approach consisting of using organic residues, such as mesityl groups,[8] which prevent decomposition by either α- or β-elimination and at the same time are rather hindered, we managed to obtain and fully characterize the compounds $[M_nMes_n]$ (Mes ≡ 2,4,6-$Me_3C_6H_2$; M = Cu, Ag, Au; $n = 5$ for Cu and Au; $n = 4$ for Ag) which are a rather unique series in transition-metal chemistry.

Because of their easy synthesis together with their thermal stability, such materials are excellent starting materials: (i) for reactions with active proton sources allowing the metallation of organic substrates;[10] (ii) for metal deposition purposes without contamination by any ancillary ligand.

Moreover, we established the solid-state–solution relationship of the $[M_nMes_n]$ compounds, which, regardless of the solid-state molecular complexity, form dimers in solution. Preliminary communications concerning the synthesis and solid-state structure of $[M_nMes_n]$ complexes (M = Cu,[11] Ag,[12] Au[13]) have been published, the copper(I) derivative being the only one synthesized before our reports.[14]

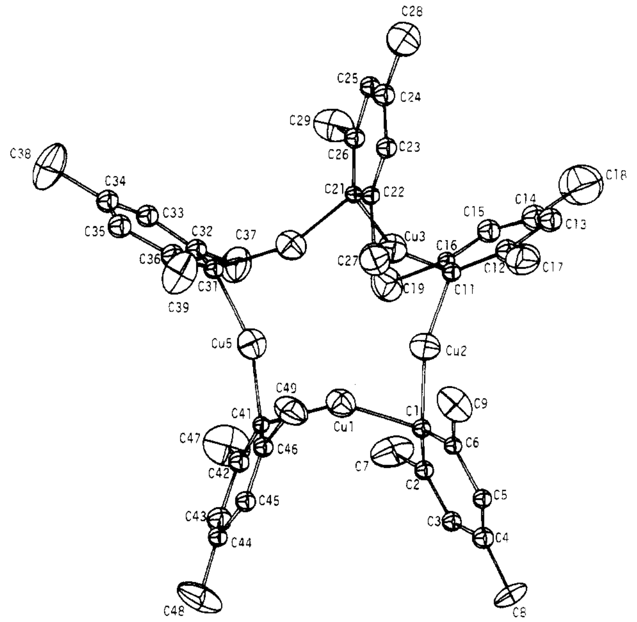

Figure 1. ORTEP drawing for complex 1 (30% probability ellipsoids).

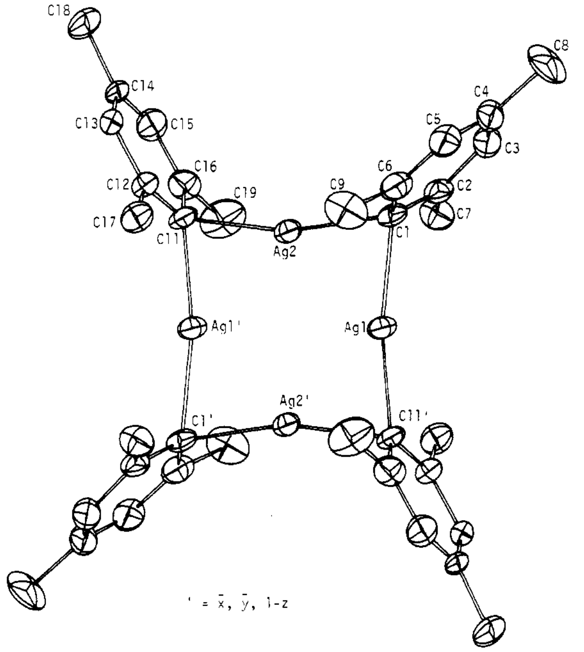

Figure 2. ORTEP drawing for complex 2 (30% probability ellipsoids). The prime indicates a transformation of $-x$, $-y$, $1 - z$.

Results and Discussion

The synthesis of homoleptic mesityl (Mes ≡ 2,4,6-$Me_3C_6H_2$) derivatives of group 11 metals has been performed by a standard procedure requiring the addition of the Grignard reagent to a THF suspension of the anhydrous metal halide at low temperature (see Experimental Section). In case of gold, the reaction was carried out by using $[AuCOCl]$[15] as $[AuCl]$ substitute.

$$[MCl] + MesMgBr \xrightarrow{-MgX_2} {}^{1}\!/_{n}[M_nMes_n] \quad (1)$$

$$M = Cu, Ag \qquad \begin{array}{l} 1\text{: } M = Cu,\ n = 5 \\ 2\text{: } M = Ag,\ n = 4 \end{array}$$

$$[AuCOCl] + MesMgBr \xrightarrow[-MgX_2]{-CO} {}^{1}\!/_{5}\underset{3}{[Au_5Mes_5]} \quad (2)$$

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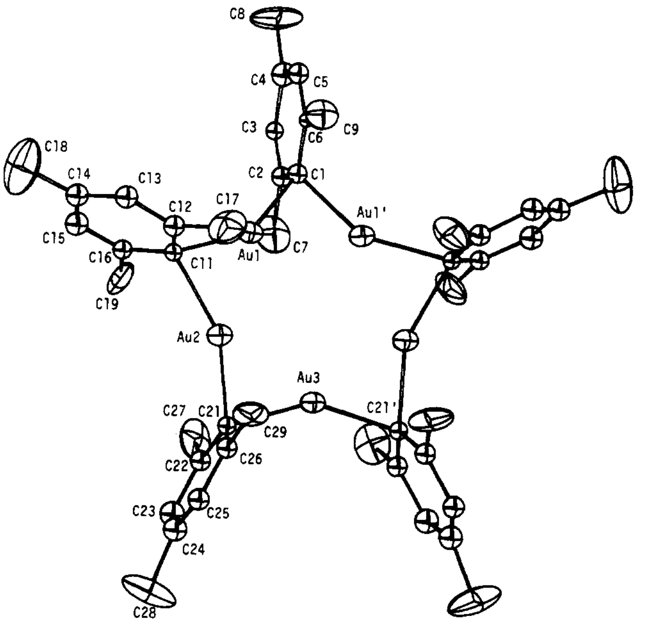


Figure 3. ORTEP drawing for complex **3** (30% probability ellipsoids). The prime indicates a transformation of x, $^1/_2 - y$, z.

Table I

A. Half-Life Time of Cu_5Mes_5 in Different Media, As Deduced from the ^1H NMR Spectra

medium	$t_{1/2}$,^{c} h
toluene-d_8	0.66
cyclohexane-d_{12}	56.00
$C_6F_6(C_6D_{12})^a$	17.56
2,4,6-*o*-$Me_3C_6H_3(C_6D_{12})^a$	7.00
$C_6Me_6(C_6D_{12})^a$	2.50
$C_8H_{12}{}^c(C_6D_{12})^b$	0.60

B. Apparent Molecular Complexity at the Equilibrium in Various Media at 25 °C

medium	$n_{calcd}{}^d$	$MW_{calcd}{}^d$	time,^{e} days
toluene-d_8	2.32	424	20
cyclohexane-d_{12}	2.15	393	18
$C_6F_6(C_6D_{12})^a$	2.19	399	5
2,4,6-*o*-$Me_3C_6H_3(C_6D_{12})^a$	2.18	398	9
$C_6Me_6(C_6D_{12})^a$	2.19	399	9
$C_8H_{12}(C_6D_{12})^b$	2.16	394	6

^{a} Substituted arenes in cyclohexane-d_{12} have been used in a 1:1 Cu/arene molar ratio. ^{b} C_8H_{12} is 1,5-cyclooctadiene used in a 1:1 to Cu molar ratio. ^{c} At $t_{1/2}$, n is 2.86 and the apparent MW = 521. ^{d} Calcd MW and molecular complexity n for the $[Cu_nMes_n]$ species. ^{e} The system was assumed at the equilibrium.

The complexes were crystallized from toluene solution and were thermally stable. Their solid-state structure was elucidated by an X-ray analysis. Details on the structures are provided in the final part of the discussion section. Complexes **1** and **3** adopt cyclic pentameric structures, while **2** is a cyclic tetramer, as depicted in Figures 1–3. The molecular complexity of the oligomers varied from the solid state to solution. MW determination by cryoscopy in benzene revealed that all three compounds have a molecular weight approaching that of a dimeric structure. MW determination of **1** in cyclohexane gave almost the same result, when the system reached equilibrium.

$$\underset{\mathbf{1-3}}{[M_nMes_n]} \rightleftarrows \tfrac{n}{2}\underset{\mathbf{4}}{[M_2Mes_2]} \tag{3}$$

$$M = Cu, Au;\ n = 5$$

$$M = Ag;\ n = 4$$

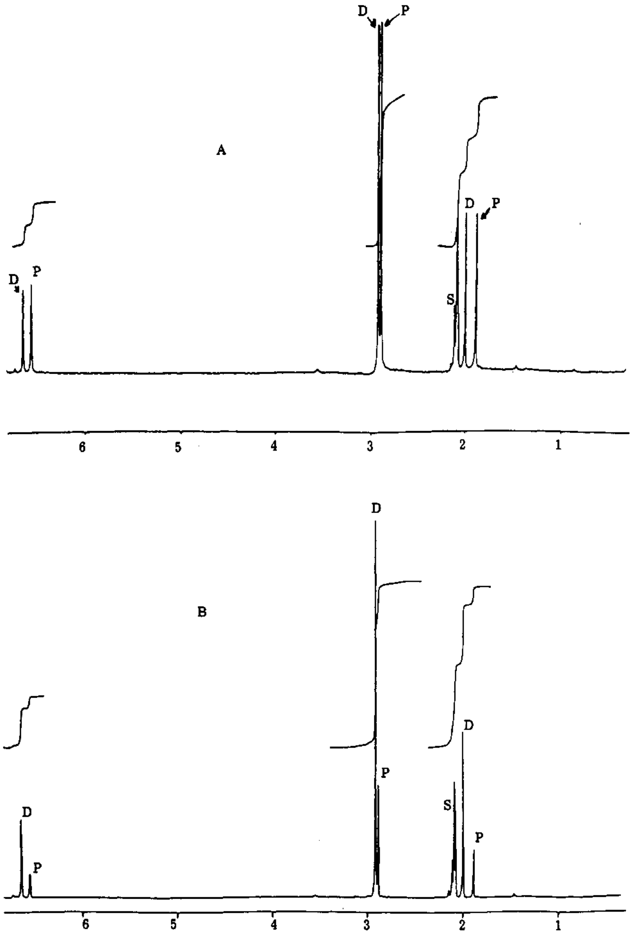


Figure 4. ^1H NMR spectrum of **1** dissolved in toluene-d_8 at 25 °C (S = solvent; D = dimer; P = pentamer): A, spectrum taken 35 min after the dissolution of **1** (n value calculated for Cu_nMes_n is 2.88); B, spectrum taken 530 h after the dissolution of **1** (n value calculated for Cu_nMes_n is 2.32).

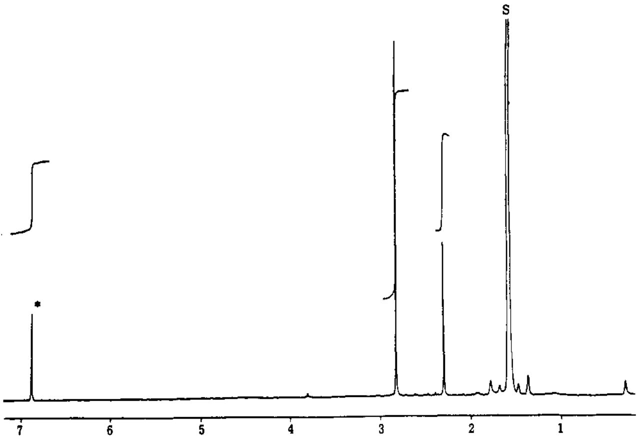


Figure 5. ^1H NMR spectrum of **3** in C_6D_{12} at 25 °C immediately after the dissolution.

In addition, the ^1H NMR spectra at room temperature of compounds **1**–**3** showed two sets of singlets for the aromatic and methyl protons, respectively, supporting the existence of two forms of mesityl derivatives corresponding to dimer and pentamer structures (see Figures 4 and 5). The equilibrium was largely shifted toward the dimer, the pentamer at equilibrium being only observed by ^1H NMR in case of silver and copper (ca. 5–6%). The equilibrium was reached in a matter of minutes for **2** and **3**, while the conversion of **1** to **4** was significantly slower and depended on the solvent or on the presence of a ligand in solution.

Table II. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes 1, 2, 3, 5, 9, and 12

	1	**5**	**2**	**3**	**9**	**12**
formula	$C_{45}H_{55}Cu_5$	$C_{44}H_{60}Cu_4S_2$	$C_{36}H_{44}Ag_4$	$C_{45}H_{55}Au_5\cdot 2C_4H_8O$	$C_{89}H_{79}Ag_3P_6$	$C_{42}H_{46}Au_2P_2$
cryst syst	monoclinic	triclinic	rhombohedral	orthorhombic	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$R\bar{3}$	$Pnma$	$P2_1/n$	$P\bar{1}$
cell parameters						
a, Å	16.094 (4)	12.907 (3)	18.395 (3)	21.864 (10)	14.001 (2)	14.004 (2)
b, Å	16.022 (4)	20.624 (6)	18.395 (3)	27.188 (11)	23.632 (4)	12.475 (2)
c, Å	19.259 (5)	8.708 (2)	18.395 (3)	8.951 (5)	24.572 (2)	7.647 (1)
α, deg	90	102.14 (3)	116.28 (2)	90	90	101.52 (1)
β, deg	97.49 (3)	107.38 (3)	116.28 (2)	90	101.66 (1)	95.81 (1)
γ, deg	90	89.64 (3)	116.28 (2)	90	90	109.55 (1)
V, Å^3	4924 (2)	2159 (1)	3038 (4)	5321 (4)	7964 (2)	1013.4 (3)
Z	4	2	3	4	4	1
D_{calcd}, gcm^{-3}	1.232	1.396	1.489	2.153	1.384	1.650
mol wt	913.7	907.3	908.2	1725.0	1659.1	1006.7
cryst dimens, mm	0.17 × 0.21 × 0.35	0.25 × 0.51 × 0.61	0.29 × 0.48 × 0.61	0.31 × 0.40 × 0.55	0.24 × 0.32 × 0.40	0.27 × 0.53 × 0.63
linear abs coeff, cm^{-1}	25.2	20.7	19.1	137.5	8.8	73.21
diffractometer	Siemens	Philips	Philips	Philips	Philips	Philips
scan type	$\theta/2\theta$	$\omega/2\theta$	$\omega/2\theta$	ω	ω	$\omega/2\theta$
scan speed, deg/min	3–12	0.075	0.075	0.075	0.100	0.100
scan width, deg	$(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$ $(\Delta\theta = (\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda \tan\theta)$	1.00	1.30	1.60	1.50	1.20
radiatn	Ni-filtered Cu Kα (λ = 1.5418 Å)	graphite-monochromated Mo Kα (λ = 0.7107 Å)				
2θ range, deg	6–110	6–48	6.52	6.47	6.46	6–58
reflcns measd	$\pm h,k,l$	$\pm h,\pm k,l$	$\pm h,k,l$	h,k,l	$\pm h,k,l$	$\pm h,\pm k,l$
measd total data	6195	6792	4610	4400	10802	5360
unique total data	1629	6792	3959	4400	5695	5360
criterion for obsn	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
measd obsd data	1629	3117	2286	2023	5695	3659
unique obsd data	1629	3117	1966	2023	5695	3659
agreement between equiv obsvd reflns			0.057			
no. of variables	301	469	181	191	285	217
overdetermination ratio	5.4	6.6	10.9	10.6	20	16.9
GOF		1.3	2.4	1.7		
R	0.10	0.057	0.062	0.052	0.061	0.036
R_w		0.062	0.064	0.050		

Table III. Fractional Atomic Coordinates (×10^4) for Complex 1

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cu1	1530 (3)	2362 (4)	3855 (3)	C6	1750 (23)	3721 (23)	2920 (18)
Cu2	2007 (4)	3703 (4)	4411 (3)	C11	2543 (26)	4242 (26)	5248 (20)
Cu3	3143 (4)	3200 (4)	5271 (3)	C12	3100 (32)	4931 (30)	5179 (26)
Cu4	3172 (4)	1675 (4)	5372 (3)	C13	3248 (31)	5687 (32)	5558 (25)
Cu5	1987 (4)	1121 (4)	4591 (3)	C14	2661 (37)	5733 (37)	6009 (29)
C7	0 (25)	3592 (34)	4068 (22)	C15	2141 (31)	5213 (32)	6181 (24)
C8	−10 (36)	4626 (30)	1605 (22)	C16	2047 (23)	4461 (24)	5782 (19)
C9	2720 (27)	3507 (28)	2937 (21)	C21	4100 (18)	2454 (24)	5536 (16)
C17	3711 (30)	4851 (30)	4607 (25)	C22	4673 (19)	2434 (26)	5107 (17)
C18	2685 (43)	6604 (40)	6509 (31)	C23	5559 (21)	2509 (29)	5278 (20)
C19	1416 (30)	3735 (30)	5879 (22)	C24	5834 (25)	2621 (29)	5964 (22)
C27	4372 (27)	2301 (27)	4258 (20)	C25	5290 (23)	2710 (25)	6488 (19)
C28	6807 (23)	2766 (30)	6206 (24)	C26	4451 (23)	2602 (28)	6228 (20)
C29	3840 (26)	2641 (32)	6870 (22)	C31	2541 (27)	681 (26)	5468 (20)
C37	1554 (34)	1503 (28)	6201 (24)	C32	2118 (27)	717 (28)	6089 (23)
C38	2761 (39)	−1346 (34)	7127 (26)	C33	2255 (27)	97 (29)	6588 (22)
C39	3429 (36)	−263 (31)	4815 (26)	C34	2707 (28)	−638 (30)	6548 (24)
C47	−35 (35)	1147 (40)	4304 (26)	C35	3042 (30)	−743 (30)	5895 (25)
C48	−167 (30)	−2 (36)	1887 (27)	C36	2974 (31)	−74 (32)	5417 (26)
C49	2617 (27)	1064 (28)	3018 (23)	C11	1321 (23)	1144 (22)	3698 (17)
C1	1303 (26)	3549 (24)	3537 (19)	C42	493 (28)	996 (27)	3665 (23)
C2	493 (25)	3741 (24)	3398 (20)	C43	0 (32)	624 (30)	3054 (27)
C3	76 (25)	4083 (25)	2812 (21)	C44	348 (26)	347 (25)	2527 (21)
C4	451 (28)	4297 (27)	2258 (24)	C15	1259 (26)	531 (25)	2475 (20)
C5	1361 (24)	4065 (24)	2284 (20)	C46	1690 (26)	886 (26)	3072 (21)

In toluene, the half-life time of 1 converting to 4 is about 40 min, while it is 3.36 × 10^3 min in cyclohexane (see Table I). Such a difference suggests that toluene or benzene are crucial in promoting the conversion of 1 to 4. In order to gain insight on this problem, we carried out ^{1}H NMR measurements in pure cyclohexane-d_{12} and in cyclohexane-d_{12} containing substituted arenes in a 1:1 molar ratio. We found that arenes greatly enhanced the rate of the conversion of 1 to 4 (see Table I), while the equilibrium position is almost the same as in the pure solvent with only 6% of the pentamer being present. In addition, the rate of pentamer to dimer conversion is increased by the presence of an arene having electron-donating substituents. On the basis of the results discussed above, we conclude

Table IV. Fractional Atomic Coordinates (×10^4) for Complex **2**

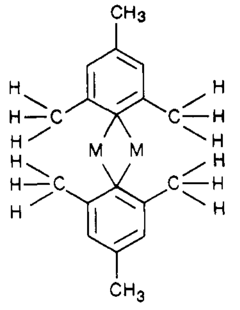
atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Ag1	–334 (1)	66 (1)	5903 (1)	C9	–482 (17)	–2024 (14)	5521 (17)
Ag2	1339 (1)	340 (1)	6071 (1)	C11	1900 (13)	325 (14)	5226 (14)
C1	1187 (13)	464 (13)	7240 (14)	C12	1621 (14)	–728 (15)	4617 (14)
C2	2236 (14)	1728 (15)	8566 (15)	C13	2631 (16)	–503 (17)	5003 (15)
C3	2748 (15)	1932 (15)	9569 (15)	C14	3895 (16)	736 (21)	5995 (16)
C4	2212 (21)	874 (21)	9262 (19)	C15	4169 (14)	1755 (17)	6564 (16)
C5	1132 (19)	–415 (19)	7930 (20)	C16	3231 (14)	1581 (15)	6222 (14)
C6	665 (15)	–616 (16)	6959 (17)	C17	176 (16)	–2180 (16)	3464 (16)
C7	2909 (16)	2933 (15)	8988 (16)	C18	4975 (22)	980 (27)	6448 (21)
C8	2771 (25)	1164 (23)	10404 (20)	C19	3634 (17)	2805 (17)	6921 (19)

Table V. Fractional Atomic Coordinates (×10^4) for Complex **3**[a]

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Au1	427 (1)	2005 (1)	1712 (1)	C12	201 (12)	1143 (10)	3746 (32)
Au2	1415 (1)	1676 (1)	3214 (1)	C13	–102 (13)	700 (10)	3779 (33)
Au3	2070 (1)	2500	3788 (2)	C14	–7 (13)	363 (10)	2678 (34)
C7	723 (20)	2500	–1548 (49)	C15	404 (13)	484 (10)	1537 (32)
C8	–1493 (19)	2500	–2971 (56)	C16	675 (12)	915 (9)	1432 (28)
C9	–936 (17)	2500	2287 (41)	C21	2329 (11)	1738 (8)	4001 (29)
C17	90 (14)	1504 (11)	4986 (37)	C22	2811 (12)	1626 (9)	2945 (30)
C18	–302 (20)	–143 (12)	2693 (40)	C23	3353 (14)	1370 (11)	3447 (36)
C19	1100 (13)	1033 (10)	165 (35)	C24	3395 (14)	1277 (11)	4910 (37)
C27	2725 (15)	1713 (10)	1259 (34)	C25	2973 (13)	1367 (9)	5949 (31)
C28	4041 (14)	1055 (15)	5314 (40)	C26	2440 (13)	1620 (10)	5492 (32)
C29	1964 (13)	1698 (11)	6669 (33)	C1S	2367 (36)	52 (31)	–1069 (89)
C1	–114 (17)	2500	381 (42)	C2S	2860 (36)	–269 (25)	–1618 (74)
C2	56 (18)	2500	–1162 (45)	C3S	3338 (35)	–185 (27)	–414 (89)
C3	–357 (16)	2500	–2201 (37)	C4SA	3302 (34)	386 (27)	–6 (85)
C4	–995 (20)	2500	–1811 (55)	C4SB	3465 (77)	244 (63)	–1165 (196)
C5	–1137 (18)	2500	–348 (46)	C5SA	2819 (40)	470 (27)	–1102 (91)
C6	–740 (15)	2500	788 (35)	C5SB	2633 (39)	395 (30)	–94 (102)
C11	589 (11)	1264 (8)	2569 (28)				

[a] The site occupation factors for the toluene solvent atoms are as follows: 1.0 for C1S,C2S and C3S; $^2/_3$ for C4SA and C5SA; $^1/_3$ for C4SB and C5SB.

that arenes can serve as a catalyst for reaction 3, but they do not provide any stabilization to the resulting dimer, which may have the structure shown below:



A

Structure A proposed for dimers **4** involve a bridging bonding mode of the aryl group which was observed for the three metals in the solid state of **1**–**3**. A similar dimeric unit has been observed in gold chemistry only for complexes $[Au_2(PR_3)_2(\mu_2\text{-}R)]^+$[16] [R = aryl, ferrocenyl, etc.]. Weak coordination of arenes to the copper may induce a labilization of the Cu–Mes bond facilitating the rearrangement from the pentamer to the dimer. Assuming that in the dimer coordination of the metals and bonding mode of the aryl groups are very close to those in the pentamer, we can understand the rearrangement based on some significant entropic effects. In addition, the ortho-methyl groups provide a significant steric protection generating a cavity for the metal centers. A few π-arene complexes have been isolated and even structurally identified for copper[17] and silver,[18] while no gold(I) complex has been so far invoked as containing an arene ligand. The breakdown of the cyclic oligomeric structures of copper(I) aryls by the action of N- and P-donor ligands[19] has been observed and may be similar to the observed effects of arenes on the oligomeric structures discussed.

For homoleptic organometallic derivatives of group 11 metals, which do not contain a donor atom on the organic residue, a difference between the structure in the solid state and in solution is a frequent observation.[20] This is well established in the case of copper, while the paucity of homoleptic derivatives for silver and gold and the diversity in the nature of the organic residue make the correlation between the group 11 metals difficult. In almost no case do compounds of this group contain the same organic group.[3] $[CuCH_2SiMe_3]_n$,[21] which is a tetramer in the solid state and in benzene and hexamer in cyclohexane, exemplifies how the molecular complexity can vary from solid state to solution and as a function of the solvent. In

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Table VI. Fractional Atomic Coordinates ($\times 10^4$) for Complex 5[a]

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu1	2821 (1)	−1881 (1)	4177 (2)	C22	3577 (8)	−3856 (5)	1364 (13)
Cu2	4160 (1)	−2724 (1)	4241 (2)	C23	3685 (8)	−4505 (5)	612 (14)
Cu3	2252 (1)	−3144 (1)	3297 (2)	C24	3753 (9)	−5016 (5)	1453 (14)
Cu4	919 (1)	−2294 (1)	3165 (2)	C25	3710 (8)	−4852 (5)	3053 (15)
S2A	−874 (3)	−2002 (2)	3229 (5)	C26	3601 (8)	−4202 (5)	3820 (13)
S2B	−801 (12)	−2111 (8)	1179 (21)	C27	3514 (10)	−3334 (6)	344 (14)
C5	−1340 (12)	−1351 (7)	1961 (21)	C28	3786 (11)	−5727 (6)	611 (17)
C6A	−2080 (18)	−1683 (10)	410 (27)	C29	3586 (11)	−4068 (6)	5586 (15)
C6B	−2216 (71)	−1395 (36)	2300 (119)	C31	665 (8)	−3280 (5)	3132 (13)
C7	−2740 (12)	−2260 (8)	764 (23)	C32	467 (8)	−3387 (5)	4597 (13)
C8	−1904 (10)	−2645 (7)	1722 (20)	C33	−216 (9)	−3921 (6)	4571 (15)
S1	5934 (3)	−2873 (2)	4014 (4)	C34	−711 (9)	−4359 (6)	3082 (17)
C1	6443 (11)	−3668 (6)	4387 (19)	C35	−543 (8)	−4273 (5)	1631 (14)
C2	7250 (12)	−3507 (8)	6080 (24)	C36	135 (8)	−3744 (5)	1634 (13)
C3	7814 (12)	−2856 (9)	6279 (20)	C37	984 (9)	−2912 (6)	6262 (13)
C4	6969 (10)	−2383 (6)	5759 (18)	C38	−1457 (11)	−4935 (6)	3043 (19)
C11	4410 (8)	−1759 (5)	5574 (12)	C39	266 (10)	−3667 (6)	29 (13)
C12	4571 (8)	−1698 (5)	7302 (13)	C41	1530 (7)	−1355 (5)	3310 (12)
C13	5213 (8)	−1165 (5)	8438 (13)	C42	1439 (8)	−1221 (6)	1706 (13)
C14	5707 (9)	−665 (5)	7947 (15)	C43	1292 (9)	−570 (6)	1506 (15)
C15	5572 (9)	−721 (5)	6331 (18)	C44	1280 (9)	−48 (5)	2775 (16)
C16	4937 (8)	−1249 (5)	5082 (13)	C45	1369 (10)	−166 (6)	4311 (15)
C17	4084 (10)	−2199 (6)	7949 (14)	C46	1497 (8)	−823 (6)	4576 (13)
C18	6358 (11)	−88 (6)	9292 (18)	C17	1488 (12)	−1754 (6)	279 (15)
C19	4829 (10)	−1289 (6)	3335 (14)	C48	1146 (11)	664 (6)	2492 (20)
C21	3547 (7)	−3677 (5)	2993 (12)	C49	1594 (11)	−930 (6)	6303 (15)

[a] The site occupation factors for the atoms S2A, C6A and S2B, C6B are 0.7774 and 0.2226, respectively.

the above studies MW determination and ^1H NMR studies never reached the stage to give a clear picture of the equilibrium involved in solution and the structure of the corresponding species. It has to be mentioned that dimeric structures have never been claimed or identified so far, though a dependence of the size of the aggregate upon the nature of the organic group was observed. For example, whereas (3-methylphenyl)copper[22] is a tetranuclear species, (3-(trifluoromethyl)phenyl)copper[23] is octanuclear. Such a lability of the solid-state structure of $(MR)_n$ compounds on solubilization is associated to the potential coordinative unsaturation of the metal centers. As a matter of fact, those compounds containing donor atoms assuring the coordinative substitution of the metal on the organic residue, like $[Cu_4(C_6H_3CH_2NMe_2\text{-}2\text{-}Me\text{-}5)_4]$[24] and $[Cu_6Br_2(C_6H_4NMe_2\text{-}4)_4]$,[25] maintain their solid-state molecular complexity in solution.

In order to trap some of the $[MMes]_n$ fragments forming from the dynamic behavior of complexes **1**–**3**, we examined their reactions with THT (tetrahydrothiophene) and phosphine ligands. THF solutions containing THT of either complexes **2** and **3** led to no reaction and **2** and **3** were recovered unchanged. The tetrameric complex **5** formed from **1** under the same mild conditions.

$$\underset{\mathbf{1}}{{}^4\!/_5[Cu_5Mes_5]} \xrightarrow{THT} \underset{\mathbf{5}}{[Cu_4Mes_4(THT)_2]} \qquad (4)$$

We assume that complex **5** is formed by aggregation of the dimers present in solution. The structure of **5** was determined by an X-ray analysis and is shown in Figure 6.

The reaction of **1**–**3** with phosphines is rather complex and largely dependent on the nature of the metal and the density of the phosphine ligand. The reactivity with three different phosphines, PPh_3, $Ph_2PCH_2PPh_2$ (dppm), and $Ph_2PCH_2CH_2PPh_2$ (dppe), was studied.

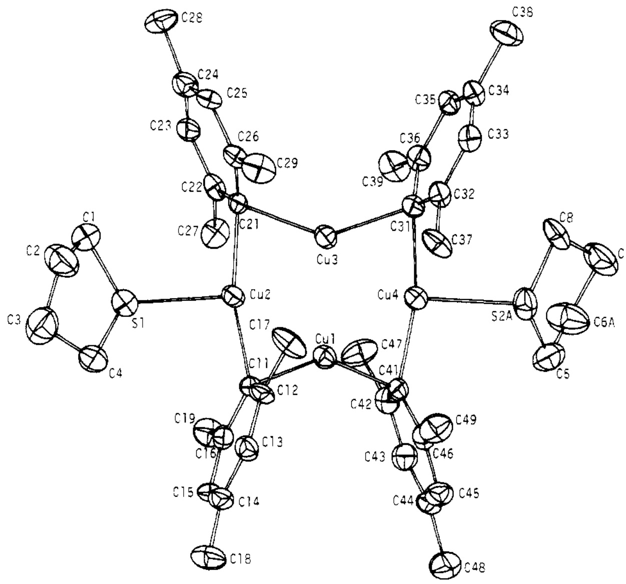

Figure 6. ORTEP drawing for complex **5** (30% probability ellipsoids).

Reaction of **1** with PPh_3 led to the isolation of $[CuMes(PPh_3)_2]\cdot C_7H_8$ (**6**), whose formula is supported by analytical data and ^1H NMR spectra (see Experimental Section). The X-ray analysis of **6** was prevented by its low thermal stability. We suggest for **6** either a dimeric structure closely related to that proposed in solution for the dimers **4** or a monomeric complex containing a σ bonded mesityl.

$$\underset{\mathbf{1}}{{}^1\!/_5(Cu_5Mes_5)} + 2PPh_3 \rightarrow \underset{\mathbf{6}}{{}^1\!/_n[CuMes(PPh_3)_2]_n} \qquad (5)$$

A monomeric structure was proposed for several copper(I)–alkyl derivatives containing phosphines and was structurally identified in the case of [Cu(TRIPHOS)Ph][26] [TRIPHOS ≡ 1,1,1-tris((diphenylphosphino)methyl)-

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Table VII. Fractional Atomic Coordinates ($\times 10^4$) for Complex 9

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Ag1	6258 (1)	2152 (0)	3310 (0)	C62	3818 (7)	1065 (3)	3616 (4)
Ag2	4300 (1)	2590 (0)	3314 (0)	C63	3657 (7)	576 (3)	3903 (4)
Ag3	4908 (1)	2459 (0)	2025 (0)	C64	3301 (7)	89 (3)	3610 (4)
P1	6578 (3)	2051 (1)	4330 (1)	C65	3105 (7)	91 (3)	3030 (4)
P2	4615 (3)	2578 (2)	4346 (1)	C66	3266 (7)	580 (3)	2743 (4)
P3	5837 (3)	1408 (1)	2571 (1)	C71	2621 (5)	1813 (4)	2236 (3)
P4	3837 (3)	1721 (1)	2683 (1)	C72	1815 (5)	1800 (4)	2490 (3)
P6	4315 (2)	3413 (1)	2675 (1)	C73	874 (5)	1852 (4)	2170 (3)
P5	6397 (3)	3108 (1)	2847 (1)	C74	739 (5)	1916 (4)	1594 (3)
C17	5732 (10)	2321 (6)	4692 (5)	C75	1546 (5)	1928 (4)	1340 (3)
C57	4625 (9)	1572 (5)	2196 (5)	C76	2486 (5)	1876 (4)	1660 (3)
C97	5339 (9)	3317 (5)	2329 (5)	C81	6834 (7)	3721 (3)	3286 (4)
C1	6828 (7)	1306 (3)	4560 (4)	C82	7016 (7)	4240 (3)	3057 (4)
C2	7688 (7)	1031 (3)	4508 (4)	C83	7284 (7)	4707 (3)	3401 (4)
C3	7835 (7)	467 (3)	4671 (4)	C84	7371 (7)	4655 (3)	3975 (4)
C4	7122 (7)	178 (3)	4884 (4)	C85	7190 (7)	4136 (3)	4205 (4)
C5	6262 (7)	453 (3)	4936 (4)	C86	6921 (7)	3669 (3)	3860 (4)
C6	6115 (7)	1018 (3)	4774 (4)	C91	7370 (6)	3038 (4)	2443 (4)
C11	7795 (7)	2348 (4)	4627 (4)	C92	8337 (6)	3048 (4)	2734 (4)
C12	8058 (7)	2499 (4)	5186 (4)	C93	9097 (6)	2971 (4)	2450 (4)
C13	9003 (7)	2689 (4)	5404 (4)	C94	8890 (6)	2883 (4)	1876 (4)
C14	9684 (7)	2729 (4)	5062 (4)	C95	7924 (6)	2873 (4)	1586 (4)
C15	9421 (7)	2578 (4)	4502 (4)	C96	7163 (6)	2951 (4)	1870 (4)
C16	8477 (7)	2388 (4)	4284 (4)	C101	4352 (7)	4144 (3)	2937 (4)
C21	3624 (8)	2160 (5)	4555 (5)	C102	4362 (7)	4604 (3)	2581 (4)
C22	3780 (8)	1849 (5)	5048 (5)	C103	4395 (7)	5154 (3)	2789 (4)
C23	3018 (8)	1537 (5)	5188 (5)	C104	4419 (7)	5245 (3)	3353 (4)
C24	2101 (8)	1535 (5)	4836 (5)	C105	4410 (7)	4786 (3)	3709 (4)
C25	1945 (8)	1845 (5)	4342 (5)	C106	4376 (7)	4235 (3)	3501 (4)
C26	2706 (8)	2158 (5)	4202 (5)	C111	3216 (6)	3450 (4)	2118 (3)
C31	4407 (7)	3263 (3)	4673 (4)	C112	3264 (6)	3513 (4)	1559 (3)
C32	3475 (7)	3480 (3)	4661 (4)	C113	2407 (6)	3560 (4)	1157 (3)
C33	3364 (7)	4007 (3)	4897 (4)	C114	1502 (6)	3544 (4)	1313 (3)
C34	4186 (7)	4317 (3)	5145 (4)	C115	1454 (6)	3482 (4)	1872 (3)
C35	5118 (7)	4101 (3)	5157 (4)	C116	2312 (6)	3434 (4)	2274 (3)
C36	5229 (7)	3574 (3)	4921 (4)	C1A	4156 (20)	−485 (8)	1084 (10)
C41	6610 (6)	1405 (4)	2047 (3)	C2A	3352 (20)	−236 (8)	1244 (10)
C42	7612 (6)	1343 (4)	2246 (3)	C3A	3092 (20)	320 (8)	1088 (10)
C43	8243 (6)	1307 (4)	1873 (3)	C4A	3636 (20)	626 (8)	772 (10)
C44	7871 (6)	1333 (4)	1302 (3)	C5A	4440 (20)	376 (8)	611 (10)
C45	6869 (6)	1395 (4)	1103 (3)	C6A	4700 (20)	−179 (8)	767 (10)
C46	6239 (6)	1431 (4)	1475 (3)	C7A	4178 (42)	−1075 (26)	1209 (25)
C51	5873 (7)	653 (3)	2749 (4)	C1B	5150 (20)	5231 (8)	1308 (11)
C52	5937 (7)	492 (3)	3302 (4)	C2B	4568 (20)	4850 (8)	953 (11)
C53	5926 (7)	−80 (3)	3441 (4)	C3B	4944 (20)	4325 (8)	844 (11)
C54	5851 (7)	−491 (3)	3027 (4)	C4B	5901 (20)	4180 (8)	1090 (11)
C55	5787 (7)	−330 (3)	2474 (4)	C5B	6483 (20)	4561 (8)	1445 (11)
C56	5798 (7)	242 (3)	2335 (4)	C6B	6107 (20)	5086 (8)	1554 (11)
C61	3622 (7)	1067 (3)	3036 (4)	C7B	5087 (40)	5713 (26)	1454 (24)

Table VIII. Fractional Atomic Coordinates ($\times 10^4$) for Complex 12

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Au	2682 (1)	391 (1)	2895 (1)	C12	−1442 (7)	−2180 (7)	1686 (11)
P	970 (2)	−1068 (1)	1075 (2)	C13	−2256 (8)	−2765 (8)	2700 (14)
C1	4176 (6)	1742 (6)	4588 (11)	C14	−1831 (10)	−2989 (8)	4238 (14)
C2	4678 (7)	1634 (7)	6264 (10)	C15	−606 (10)	−2660 (8)	4823 (12)
C3	5642 (8)	2577 (7)	7423 (11)	C16	241 (7)	−2068 (7)	3879 (10)
C4	6144 (7)	3636 (7)	6965 (11)	C21	1272 (6)	−2224 (5)	−452 (9)
C5	5636 (6)	3749 (6)	5344 (11)	C22	2256 (7)	−1876 (7)	−1347 (12)
C6	4690 (6)	2818 (6)	4100 (10)	C23	2496 (8)	−2688 (8)	−2649 (13)
C7	4134 (10)	529 (9)	6860 (15)	C24	1732 (9)	−3871 (8)	−3028 (12)
C8	7195 (10)	4626 (9)	8249 (16)	C25	774 (9)	−4216 (7)	−2116 (12)
C9	4254 (9)	2987 (8)	2323 (12)	C26	514 (7)	−3404 (6)	−862 (10)
C11	−179 (6)	−1818 (5)	2294 (9)	C27	162 (7)	−508 (6)	−502 (9)

ethane]. The structures proposed for **6** parallel the monomeric and dimeric structures found for copper(I)–phenoxo complexes, i.e. $[Cu(p\text{-}MeC_6H_4NC)_2(2,6\text{-}Bu^t{}_2\text{-}C_6H_3O)]$[27] and $[Cu_2(\mu\text{-}OPh)_2(PPh_3)_4]$.[27] The formulation of **6** in the cuprato form $[Cu(PPh_3)_4][CuMes_2]$ (vide infra) was ruled out on the basis of IR and ^{1}H NMR spectra obtained which were significantly different from those of $[Cu(dppe)_2][CuMes_2]$.[28] We found a close similarity in the structural and chemical behavior of the Cu–Ar and Cu–OAr functionalities.[27] Bidentate ligands promote the disproportionation to the cuprato form of the [Cu–OPh] functionality, leading to the formation of $[Cu(OPh)_2]^-$ $[Cu(BEN)_2]^+$ [BEN ≡ *N,N'*-ethylenebis(benzaldimine)],[27] likewise dppe was reported to react with **1** leading to $[Cu(dppe)_2]^+[CuMes_2]^-$ (**7**).[28] The later transformation

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[27] Fiaschi, P.; Floriani, C.; Pasquali, M.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 462.

Table IX. Bond Distances (Å) and Angles (deg) for Complex 1

Cu1-Cu2	2.48 (1)	Cu3-C11	1.93 (4)
Cu1-Cu5	2.50 (1)	Cu3-C21	1.96 (3)
Cu1-C1	2.02 (4)	Cu4-Cu5	2.44 (1)
Cu1-C41	2.00 (4)	Cu4-C21	1.94 (3)
Cu2-Cu3	2.44 (1)	Cu4-C31	1.91 (4)
Cu2-C1	1.92 (4)	Cu5-C31	1.94 (4)
Cu2-C11	1.93 (4)	Cu5-C41	1.91 (3)
Cu3-Cu4	2.45 (1)		
C1-Cu1-C41	149 (2)	Cu1-C1-Cu2	78 (1)
Cu5-Cu1-C41	49 (1)	Cu2-C1-C6	113 (3)
Cu5-Cu1-C1	162 (1)	Cu2-C1-C2	127 (3)
Cu2-Cu1-C41	162 (1)	Cu1-C1-C6	109 (3)
Cu2-Cu1-C1	49 (1)	Cu1-C1-C2	114 (3)
Cu2-Cu1-Cu5	113.2 (3)	C2-C1-C6	111 (3)
Cu1-Cu2-C11	146 (1)	Cu2-C11-Cu3	78 (2)
Cu1-Cu2-C1	53 (1)	Cu3-C11-C16	122 (3)
Cu1-Cu2-Cu3	99.8 (3)	Cu3-C11-C12	111 (3)
C1-Cu2-C11	160 (2)	Cu2-C11-C16	119 (3)
Cu3-Cu2-C11	51 (1)	Cu2-C11-C12	119 (3)
Cu3-Cu2-C1	149 (1)	C12-C11-C16	107 (4)
Cu2-Cu3-C21	151 (1)	Cu3-C21-Cu4	78 (1)
Cu2-Cu3-C11	51 (1)	Cu4-C21-C26	118 (3)
Cu2-Cu3-Cu4	112.8 (3)	Cu4-C21-C22	118 (3)
C11-Cu3-C21	155 (2)	Cu3-C21-C26	111 (3)
Cu4-Cu3-C21	51 (1)	Cu3-C21-C22	116 (3)
Cu4-Cu3-C11	151 (1)	C22-C21-C26	112 (3)
Cu3-Cu4-C31	147 (1)	Cu4-C31-Cu5	79 (2)
Cu3-Cu4-C21	52 (1)	Cu5-C31-C36	115 (3)
Cu3-Cu4-Cu5	108.0 (3)	Cu5-C31-C32	119 (3)
C21-Cu4-C31	158 (2)	Cu4-C31-C36	116 (3)
Cu5-Cu4-C31	51 (1)	Cu4-C31-C32	111 (3)
Cu5-Cu4-C21	149 (1)	C32-C31-C36	112 (4)
Cu1-Cu5-Cu4	102.1 (3)	Cu1-C41-Cu5	80 (1)
Cu4-Cu5-C41	149 (1)	Cu5-C41-C46	120 (3)
Cu4-Cu5-C31	50 (1)	Cu5-C41-C42	118 (3)
Cu1-Cu5-C41	52 (1)	Cu1-C41-C46	109 (3)
Cu1-Cu5-C31	149 (1)	Cu1-C41-C42	109 (3)
C31-Cu5-C41	159 (2)	C42-C41-C46	115 (4)

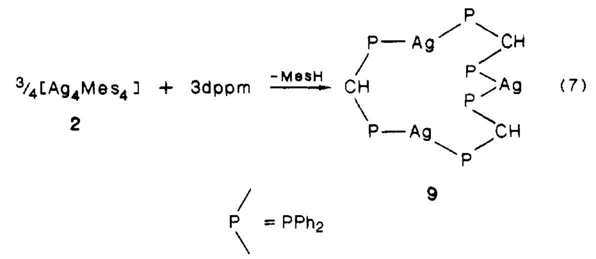
may involve an intermediate similar to **6**, as we reported for the rearrangement of copper(I)-phenoxo derivatives.[27]

Complex **1** behaves like copper phenyl in the reaction with dppm. The phosphine ligand acts as a proton donor[29] displacing the Mes residue in the form of mesitylene to form the known trinuclear copper(I) complex **8**.

$$\underset{\mathbf{1}}{\tfrac{3}{5}[Cu_5Mes_5]} + 3dppm \xrightarrow{-MesH} \underset{\mathbf{8}}{[Cu_3(Ph_2PCHPPh_2)_3]} \qquad (6)$$

Reaction 6 exemplifies one of the reactions with active proton donor molecules.[10,14]

The silver-mesityl derivative **2** has a significantly different behavior toward phosphine ligands, though the reaction of **2** with dppm to produce complex **9** is similar to reaction 6.



9

The structure of **9**, which is isostructural with **8**, was determined by X-ray analysis (see Figure 7) and its rather

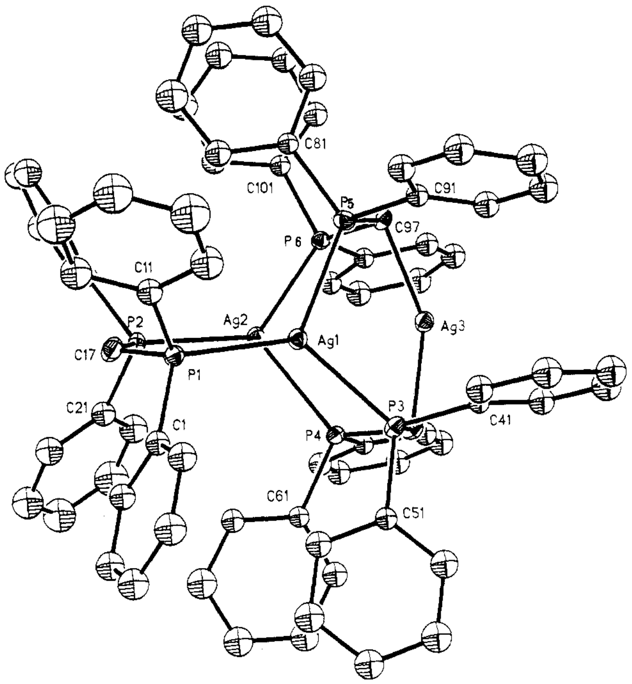


Figure 7. ORTEP drawing for complex **9** (30% probability ellipsoids).

complex ^1H NMR spectrum is in agreement with this structure. Complex **2** could be recrystallized unreacted from THF or toluene containing THT, 2,2′-bipyridine, or PPh_3. In addition, PPh_3 does not affect the ^1H NMR spectrum of **2** in solution, where the dimer **4** is present.

Reaction of **2** with dppe was carried out in THF and toluene. In both cases the full characterization of the reaction products was prevented due to their very high thermal and photochemical sensitivity. The IR spectrum of the complex formed in toluene was very similar to that of $[Au_2Mes_2(\mu\text{-dppe})]$ (**12**) and differed significantly from the IR spectrum of the compound obtained when the reaction was carried out in THF. The IR spectrum of this latter product resembles very much the spectrum of $[Cu(dppe)_2][CuMes_2]$ (**7**).[28] This result is in agreement with our observations made in case of the reaction of **1** with dppe, which leads to a preliminary coordination of the phosphorus ligand to the metal, followed by the disproportionation reaction, which is promoted by a polar solvent.[30] The [Au-Mes] functionality does not undergo any of the transformations observed for copper and silver promoted by phosphorus ligands. Coordination of phosphorus to the metal and the formation of linear dicovalent complexes [L-Au-Mes],[4] containing the Au-C σ bond, were observed.

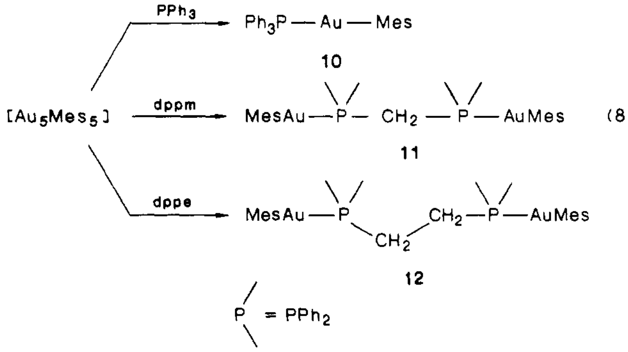


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Table X. Bond Distances (Å) and Angles (deg) for Complex 2[a]

Ag1–Ag2	2.733 (3)	Ag1–C11′	2.16 (3)
Ag1–C1	2.22 (3)	Ag2–C1	2.22 (3)
Ag1–Ag2′	2.755 (3)	Ag2–C11	2.21 (3)
Ag2′–Ag1–C11′	51.7 (5)	Ag1–C1–Ag2	76.1 (7)
C1–Ag1–C11′	169.0 (9)	Ag2–C1–C6	115 (1)
C1–Ag1–Ag2′	139.2 (6)	Ag2–C1–C2	116 (2)
Ag2–Ag1–C11′	139.0 (5)	Ag1–C1–C6	115 (1)
Ag2–Ag1–Ag2′	87.3 (1)	Ag1–C1–C2	112 (2)
Ag2–Ag1–C1	51.9 (7)	C2–C1–C6	116 (2)
Ag1–Ag2–Ag1′	92.7 (1)	Ag2–C11–Ag1′	78.1 (7)
Ag1–Ag2–C11	142.9 (5)	Ag2–C11–C16	110 (1)
Ag1–Ag2–C1	51.9 (7)	Ag2–C11–C12	108 (2)
C11–Ag2–Ag1′	50.2 (5)	C16–C11–Ag1′	120 (2)
C1–Ag2–Ag1′	144.7 (6)	C12–C11–Ag1′	119 (1)
C1–Ag2–C11	165.2 (8)	C12–C11–C16	114 (2)

[a] The prime (′) indicates a transformation of $-x, -y, 1 - z$.

Complexes **10**–**12** have been fully characterized, and the proposed structure of **10**[31] and **12** was verified by an X-ray analysis. Details are reported for complex **12** only (see Figure 7). The [P–Au–C] fragment is very common in gold(I) organometallic chemistry[4] and accessible by various synthetic routes, the most usual being the alkylation of the [PR_3AuCl] complex.

A detailed description of the structure of some of the key compounds is reported below.

Complex 1. The structure of complex **1** (Figure 1) consists of polynuclear molecules having a ten-membered ring where five copper atoms are bridged by phenyl groups.[3] The ring is puckered, with a total puckering amplitude[32] of 1.47 (4) Å, and it has a pseudo C_m symmetry with a mirror plane through the Cu1⋯C21 line. The dihedral angles of the planar mesitylene about the best plane through the five copper atoms range from 91.4 (6) to 104.8 (4)°. The Cu–C [1.90 (3)–2.02 (3) Å] and Cu⋯Cu [2.437 (8)–2.496 (9) Å] distances and C–Cu–C angles [149 (1)–160 (2)°] (Table IX) are close to those found in complex **5**. The Cu–C–Cu angles [78 (1)–79 (1)°] agree well with those observed in complexes **2**, **3**, and **5**.

Complex 2. Crystals of complex **2** consist of centrosymmetric tetrameric units of Ag_4Mes_4 in which the silver atom has a nearly linear coordination, the angles around Ag1 and Ag2 being 169.0 (9) and 165.2 (8)°, respectively (Figure 2). The Ag–C–Ag angles are 76.1 (7) and 78.1 (7)° about C1 and C11, respectively. The mesityl group displays a bonding mode very similar to that observed in the present copper and gold complex. The Ag_4C_4 framework is planar within experimental error, the total puckering amplitude[32] being 0.01 (1) Å. The four independent Ag–C bond distances [mean value 2.20 (3) Å] (Table X) are not significantly different, and the planar mesityl groups are nearly perpendicular to the eight-membered ring, the dihedral angles being 88.8 (5) and 89.3 (3)°. The most relevant structural comparison of **3** is with the structure of [$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3CH_2NMe_2\text{-}2\text{-}Ag]_4$,[33] in which the silver atom has nearly linear coordination geometry in a tetranuclear structure and the Ag–C bond distances [2.14 (2) and 2.20 (2) Å] are very close to those found in complex **3**. The distances between adjacent silver atoms [2.733 (3) and 2.755 (3) Å] compare very well with the corresponding ones in the ferrocenyl silver compound.[33] The Ag1⋯Ag1′ and Ag2⋯Ag2′ separation [3.971 (3) and 3.788 (3) Å, respectively] rules out any interaction between opposite silver atoms.

Table XI. Bond Distances (Å) and Angles (deg) for Complex 3

Au1–Au2	2.697 (1)	Au2–C11	2.20 (2)
Au1–C1	2.15 (3)	Au2–C21	2.13 (2)
Au1–C11	2.18 (2)	Au3–C21	2.16 (2)
Au2–Au3	2.708 (2)		
C1–Au1–C11	149.4 (6)	C2–C1–C6	120 (3)
Au2–Au1–C11	52.4 (6)	Au1–C11–Au2	75.9 (7)
Au2–Au1–C1	157.5 (6)	Au2–C11–C16	115 (2)
Au1–Au2–C21	153.1 (6)	Au2–C11–C12	115 (2)
Au1–Au2–C11	51.8 (6)	Au1–C11–C16	113 (2)
Au1–Au2–Au3	104.11 (5)	Au1–C11–C12	113 (2)
C11–Au2–C21	153.9 (8)	C12–C11–C16	118 (2)
Au3–Au2–C21	51.3 (6)	Au2–C21–Au3	78.5 (8)
Au3–Au2–C11	154.7 (6)	Au3–C21–C26	111 (2)
Au2–Au3–C21	50.3 (6)	Au3–C21–C22	110 (2)
C21–Au3–C21′	147.8 (9)	Au2–C21–C26	118 (2)
Au1–C1–C6	112.9 (1)	Au2–C21–C22	117 (2)
Au1–C1–C2	113.1 (1)	C22–C21–C26	117 (2)
Au1–C1–Au1′	77.3 (1)		

Complex 3. The structure of **3** consists of ten-membered rings of alternate gold and carbon atoms (Figure 3) which form a five pointed star shaped skeleton, similar to that found for **1**. Disordered molecules of crystallization of toluene are present in the 1:2 ratio of complex to toluene. The complex molecular has a C_m crystallographic symmetry with the mirror plane containing Au3 and the mesityl ligand C1⋯C9. Therefore the four atoms Au1, Au2, Au1′, and Au2′ define a plane, perpendicular to the *b* axis, from which Au3, C1, C11, and C21 are displaced by 0.321 (2), 0.39 (4), −0.46 (2), and 0.46 (3) Å, respectively (Table SXII). The total puckering amplitude[32] of the polynuclear ring is 0.92 (3) Å. As observed in the preceding complexes, the planar mesitylene groups are nearly perpendicular to the mean plane through the gold atoms, the dihedral angles they form varying from 86.2 (6) to 89.8 (6)°. All the Au–C bond distances (Table XI) are very close ranging from 2.13 (2) to 2.20 (2) Å, while C–Au–C and Au–C–Au bond angles range from 147.8 (9) to 153.9 (8)° and from 75.9 (7) to 78.5 (8)°, respectively. The Au–C bond distances are very close to those found in complex [$(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_4\text{-}(AuPPh_3)_2\}]^+$ [34] where two gold(I) ions are bridged by an aromatic carbon at 2.15 and 2.28 Å. The Au–C bond distances are substantially independent of the bonding mode displayed by the C-donor ligands: they are 2.062 (8) and 2.041 (9) Å in [$Au(C_6F_5)_2]^-$,[35] 2.050 (4) Å in [$Au\{2,6\text{-}(MeO)_2C_6H_3\}(PPh_3)$],[36] and 2.09 (3) and 2.10 (3) Å in [$Au_2\{\mu\text{-}(CH_2)_2PEt_2\}_2$].[37] The C–Au–C angle values in complex **3** suggest a significant deviation from the linear geometry preferred by Au(I) and normally encountered, i.e. in all the related complexes mentioned above.

Complex 5. Complex **5** contains molecules having an eight-membered puckered ring where four mesityl ligands are bridging four coppers in an usual fashion[3] as observed in complexes **1**, **2**, and **3**. Two metal atoms (Cu2 and Cu4) achieve a pseudotrigonal coordination through the sulfur atoms from THT molecules (Figure 6). The geometry of the M_4C_4 framework is different from that found in complex **2** as far as the puckering of ring, the metal–metal separations, and the C–M–C bond angles are concerned.

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Table XII. Bond Distances (Å) and Angles (deg) for Complex 5

Cu1–Cu2	2.441 (3)	Cu2–C21	2.068 (9)
Cu1–Cu3	2.600 (3)	Cu3–Cu4	2.444 (3)
Cu1–Cu4	2.439 (2)	Cu3–C21	2.047 (10)
Cu1–C11	2.034 (9)	Cu3–C31	2.027 (11)
Cu1–C41	2.023 (10)	Cu4–S2A	2.401 (4)
Cu2–Cu3	2.451 (2)	Cu4–S2B	2.459 (15)
Cu2–S1	2.369 (4)	Cu4–C31	2.055 (11)
Cu2–C11	2.056 (10)	Cu4–C41	2.060 (11)

C11–Cu1–C41	141.5 (4)	Cu1–Cu4–C41	52.6 (3)
Cu4–Cu1–C41	54.0 (3)	Cu1–Cu4–C31	114.9 (3)
Cu4–Cu1–C11	159.3 (3)	Cu1–Cu4–S2B	139.7 (4)
Cu3–Cu1–C41	109.9 (3)	Cu1–Cu4–S2A	143.0 (2)
Cu3–Cu1–C11	108.6 (3)	C31–Cu4–C41	167.3 (4)
Cu3–Cu1–Cu4	57.9 (1)	S2B–Cu4–C41	90.9 (5)
Cu2–Cu1–C41	160.3 (3)	S2B–Cu4–C31	100.1 (5)
Cu2–Cu1–C11	53.8 (3)	S2A–Cu4–C41	97.5 (3)
Cu2–Cu1–Cu4	116.0 (1)	S2A–Cu4–C31	95.0 (3)
Cu2–Cu1–Cu3	58.1 (1)	S2A–Cu4–S2B	43.0 (4)
Cu1–Cu2–C21	115.5 (3)	Cu1–C11–Cu2	73.3 (4)
Cu1–Cu2–C11	53.0 (3)	Cu2–C11–C16	121.2 (7)
Cu1–Cu2–S1	140.3 (2)	Cu2–C11–C12	113.8 (7)
Cu1–Cu2–Cu3	64.2 (1)	Cu1–C11–C16	108.1 (7)
C11–Cu2–C21	166.2 (4)	Cu1–C11–C12	113.9 (8)
S1–Cu2–C21	95.6 (3)	C12–C11–C16	117.6 (9)
S1–Cu2–C11	98.2 (3)	Cu2–C21–Cu3	73.1 (4)
Cu3–Cu2–C21	53.1 (3)	Cu3–C21–C26	107.2 (7)
Cu3–Cu2–C11	113.6 (3)	Cu3–C21–C22	114.8 (7)
Cu3–Cu2–S1	147.4 (1)	Cu2–C21–C26	121.8 (7)
Cu1–Cu3–Cu2	57.7 (1)	Cu2–C21–C22	115.4 (8)
Cu2–Cu3–C31	1262.4 (3)	C22–C21–C26	116.0 (9)
Cu2–Cu3–C21	53.8 (3)	Cu3–C31–Cu4	73.6 (4)
Cu2–Cu3–Cu4	115.4 (1)	Cu4–C31–C36	121.3 (8)
Cu1–Cu3–C31	109.5 (3)	Cu4–C31–C32	113.3 (7)
Cu1–Cu3–C21	110.0 (3)	Cu3–C31–C36	108.9 (8)
Cu1–Cu3–Cu4	57.7 (1)	Cu3–C31–C32	115.3 (8)
C21–Cu3–C31	140.6 (4)	C32–C31–C36	116.7 (9)
Cu4–Cu3–C31	53.7 (3)	Cu1–C41–Cu4	73.3 (3)
Cu4–Cu3–C21	161.7 (3)	Cu4–C41–C46	121.5 (8)
Cu1–Cu4–Cu3	64.3 (1)	Cu4–C41–C42	112.9 (7)
Cu3–Cu4–C41	114.7 (3)	Cu1–C41–C46	108.2 (7)
Cu3–Cu4–C31	52.7 (3)	Cu1–C41–C42	113.9 (7)
Cu3–Cu4–S2B	136.2 (4)	C42–C41–C46	118.2 (10)
Cu3–Cu4–S2A	147.3 (2)		

In complex **5** the ring is puckered, the total puckering amplitude[32] being 1.052 (9) Å. The four copper atoms lie in a plane bisecting the tetrahedron formed by the carbon atoms. The four Cu⋯Cu distances between adjacent coppers range from 2.439 (2) to 2.451 (2) Å (Table XII) and are in agreement with those observed for complex **1**. The separation between opposite coppers is 2.600 (3) Å for Cu1⋯Cu3 and 4.138 (3) Å for Cu2⋯Cu4. The value of the Cu1⋯Cu3 distance along with the remarkable bending of the C11–Cu1–C41 [140.6 (3)°] and C21–Cu3–C31 [141.5 (4)°] angles with respect to C11–Cu2–C21 [166.2 (4)°] and C31–Cu4–C41 [167.3 (4)°] suggest a considerable metal–metal bond interaction.

As observed in the preceding compounds the planar mesitylene groups are nearly perpendicular to the plane of copper atoms, the dihedral angles ranging from 85.8 (2) to 88.2 (2)°. Copper–carbon distances involving the three-coordinated (Cu2 and Cu4) copper atoms [mean value 2.059 (10) Å] are not significantly longer than those involving Cu1 and Cu3 [mean value 2.033 (12) Å]. The Cu–C–Cu angles [73.1 (3) and 73.6 (4)°] are close to those observed in **1**, **2**, and **3**. The Cu–S bond distances [Cu2–S1 = 2.369 (4), Cu4–S2A = 2.401 (4), Cu4–S2B = 2.46 (1) Å] are significantly different probably as a consequence of the disorder involving the THT molecule S2–C5⋯C8 (see Experimental Section). The two disordered coordination planes (Cu4, S2A, C31, C41 and Cu4, S2B, C31, C41) form a dihedral angle of 41.3 (3)°. The ordered THT molecule and the two positions of the disordered one have an envelope conformation (Table SXII). The trend of the C–C bond distances within the aromatic rings indicate a slight lengthening of the C sp^3–C sp^2 distances with respect to the C sp^2–C sp^2 ones [1.43 (2) vs 1.39 (1) Å].

Table XIII. Bond Distances (Å) and Angles (deg) for Complex 9

Ag1–P1	2.467 (3)	P2–C31	1.856 (9)
Ag1–P3	2.511 (2)	P3–C57	1.80 (1)
Ag1–P5	2.555 (3)	P3–C41	1.842 (9)
Ag2–P2	2.485 (3)	P3–C51	1.835 (8)
Ag2–P4	2.576 (2)	P4–C57	1.82 (1)
Ag2–P6	2.502 (3)	P4–C61	1.827 (9)
Ag3–C57	2.19 (1)	P4–C71	1.843 (7)
Ag3–C97	2.20 (1)	P5–C97	1.82 (1)
P1–C17	1.74 (2)	P5–C81	1.836 (8)
P1–C1	1.861 (8)	P5–C91	1.85 (1)
P1–C11	1.85 (1)	P6–C97	1.82 (1)
P2–C17	1.73 (1)	P6–C101	1.841 (8)
P2–C21	1.86 (1)	P6–C111	1.843 (8)

P3–Ag1–P5	109.0 (1)	P2–Ag2–P6	128.8 (1)
P1–Ag1–P5	121.6 (1)	P2–Ag2–P4	125.2 (1)
P1–Ag1–P3	129.4 (1)	C57–Ag3–C97	149.8 (4)
P4–Ag2–P6	106.0 (1)		
P1–C17–P2	121.2 (7)	Ag3–C57–P4	95.6 (5)
P3–C57–P4	109.8 (7)	Ag3–C57–P3	96.6 (5)
		P5–C97–P6	108.3 (6)

Complex 9. Crystals of complex **9** are isostructural with those of the corresponding copper derivative.[29] They are built up from trimeric silver units and toluene molecules of crystallization in a $^1/_2$ molar ratio. The trinuclear unit consists of silver atoms arranged at the vertices of a nearly regular isosceles triangle (Figure 7), with the base Ag1–Ag2 of length 2.933 (2) Å and sides of length 3.414 (1) (Ag1–Ag3) and 3.456 (1) Å (Ag2–Ag3). Coordination around the basal silver atoms, which are bridged by the three ligands through their phosphorus atoms, is trigonal (Tables XIII and SXII). The two coordiantion planes are parallel, the dihedral angle they form being 0.2 (1)°. The methyne carbon atoms of two ligands (C57 and C97) are bridged by the Ag3 silver atom with a C–Ag–C angle of 149.8 (4)° and Ag–C bond distances of 2.19 (1) and 2.20 (1) Å. The Ag1–P1 [2.485 (3) Å] and Ag2–P2 [2.467 (3) Å] bond lengths are very close and are significantly shorter than the Ag–P distances involving the tridentate phosphines ranging from 2.502 (3) to 2.576 (3) Å (Table XIII). They fall in the range of values usually observed for (triphenylphosphine)silver(I) compounds.[38] The two tridentate phosphine molecules are geometrically equivalent. The values of the P–C–P and Ag–C–P angles [mean values 109.0 (7) and 95.9 (6)°, respectively], involving the coordinating C57 and C97 carbon atoms, indicate a sp^3 hybridization state in agreement with the single bond distances observed for the P–C bonds [mean value 1.82 (1) Å]. The uncoordinating C17 carbon atom shows an sp^2 hybridization state as indicated by the P1–C17–P2 angle [121.2 (7)°] and the P1–C17 [1.74 (2) Å] and P2–C17 [1.73 (1) Å] distances which show a considerable amount of double-bond character.

The molecule has a pseudo C_{2v} symmetry with the phenyl groups bonded to the same phosphorus atom being nearly orthogonal to each other [the dihedral angles range from 74.6 (3) to 90.0 (3)°] and pairs of phenyl rings being nearly parallel as can be seen from Figure 5 and the following dihedral angles between the ring planes: C41–

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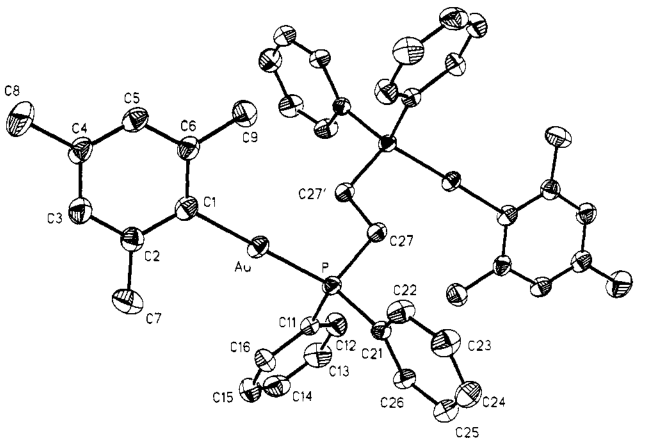

Figure 8. ORTEP drawing for complex **12** (30% probability ellipsoids). The prime indicates a transformation of $-x$, $-y$, $-z$.

Table XIV. Bond Distances (Å) and Angles (deg) for Complex 12

Au–P	2.290 (2)	P–C21	1.822 (7)
Au–C1	2.067 (6)	P–C27	1.840 (9)
P–C11	1.820 (7)	C27–C27′	1.53 (1)
P–Au–C1	177.5 (2)	C11–P–C21	105.7 (3)
Au–P–C27	111.9 (2)	Au–C1–C6	120.2 (6)
Au–P–C21	115.2 (3)	Au–C1–C2	121.2 (6)
Au–P–C11	114.5 (2)	C2–C1–C6	118.6 (7)
C21–P–C27	102.5 (3)	P–C27–C27′	111.6 (5)
C11–P–C27	105.9 (4)		

C46,C91–C96, 10.2 (3)°; C51–C56,C101–C106, 3.1 (3)°; C61–C66,C81–C86, 5.6 (3)°; C71–C76,C111–C116, 1.6 (3)°.

Complex 12. The structure of complex **12** consists of centrosymmetric dimeric [Au_2Mes_2(dppe)] units, with the center of symmetry lying in the middle point of the ethane C–C bond (Figure 8). The gold atom exhibits a linear coordination, the C1–Au–P angle being 177.5 (2)°. The Au–C1 bond length [2.067 (6) Å] is significantly shorter than those found in complex **3** and fall in the lower range of the values cited above. The gold atom is significantly displaced from the plane of the aromatic ring by a value of 0.116 (1) Å. The Au–P distance [2.290 (2) Å] agrees well with those observed in dicovalent gold(I) derivatives.[4,34,36,37] The geometry of the phosphine ligand is not unusual (Table XIV). The P–C bond distances are not significantly diffferent. The Au–P–C bond angles are larger, while the C–P–C angles are narrower than expected tetrahedral values. The C27–C27′ bond distance [1.53 (1) Å] is as expected. The phenyl rings are nearly perpendicular, the dihedral angle between them being 84.7 (3)°.

Experimental Section

All the operations were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Infrared spectra were recorded with a Perkin-Elmer 283 or 983 spectrophotometer. ^{1}H NMR spectra were taken with a E-360 (60 MHz) Varian and a WM 300 Bruker apparatus. Copper(I) chloride was prepared as reported.[39] Gold(I) carbonyl chloride was prepared according to ref 15 and as described below. Abbreviations: dppm ≡ bis(diphenylphosphino)methane; dppe ≡ bis(diphenylphosphino)ethane; Mes ≡ 2,4,6-trimethylphenyl ≡ mesityl; THT ≡ tetrahydrothiophene; bby ≡ 2,2′-bipyridine.

Preparation of Au(CO)Cl.[15] A thionyl chloride suspension (155 mL) of anhydrous $AuCl_3$ (15.58 g, 51.3 mmol) was placed under a dry CO atmosphere and stirred magnetically. After 1 h the gold(III) chloride was dissolved and the red solution was filtered. CO uptake continued for 18 h while a very slow agitation was maintained and Au(CO)Cl crystallized. Hexane (200 mL) was then added dropwise (under CO atmosphere); Au(CO)Cl was collected and washed with four portions of CO-saturated hexane and dried under a stream of CO. Yield: 11.03 g, 42.35 mmol, 82.5%. Au(CO)Cl is best stored under CO atmosphere and should not be dried under vacuum as CO loss is facile and promotes decomposition of the material.

Synthesis of [Cu_5Mes_5] (1). A THF solution (178 mL) of MesMgBr (0.895 M, 0.159 mole) was added dropwise to a cooled (−25 °C) suspension of anhydrous [CuCl] (15.8 g, 0.159 mol) in 280 mL of THF. The gray-brown reaction mixture was stirred for 20 h and warmed to room temperature. *p*-Dioxane (95 mL, 1.08 mol) was added dropwise, and stirring was continued for 12 h. The magnesium halides were filtered off, and the green filtrate was brought to dryness, the residue being dried under high vacuum for 2 h. It was redissolved in warm (50 °C) toluene (200 mL), the remaining magnesium halides were filtered out, and the solution was carefully concentrated to 80 mL and allowed to stand in the refrigerator. Yellow crystals of **1** (15.32 g) could be isolated. From the mother liquor another crop of 3.74 g of **1** separated after concentration. The crystals were washed with a small volume of cooled toluene and dried under vacuum for a short time. Total yield: 19.06 g, 0.104 mol (65%). MW: in benzene (cryoscopy), 485; in cyclohexane (cryoscopy), 498. Anal. Calcd for $C_{45}H_{55}Cu_5$: C, 59.16; H, 6.07; Cu, 34.77. Found: C, 58.50; H, 5.9; Cu, 33.9. ^{1}H NMR (toluene-d_8): for [Cu_5Mes_5], δ 6.54 (s, 2 H, C_6H_2), 2.88 (s, 6 H, *o*-Me), 1.88 (s, 3 H, *p*-Me); for [Cu_2Mes_2], δ 6.62 (s, 2 H, C_6H_2), 2.91 (s, 6 H, *o*-Me), 1.99 (s, 3 H, *p*-Me). ^{1}H NMR (cyclohexane-d_{12}): for [Cu_5Mes_5], δ 6.77 (s, 2 H, C_6H_2), 2.86 (s, 6 H, *o*-Me), 2.24 (s, 3 H, *p*-Me); for [Cu_2Mes_2], δ 6.84 (s, 2 H, C_6H_2), 2.99 (s, 6 H, *o*-Me), 2.27 (s, 3 H, *p*-Me).

Synthesis of [Ag_4Mes_4] (2). A THF solution (98 mL) of MesMgBr (1.32 M, 0.129 mol) was added dropwise to a cooled (−25 °C) suspension (280 mL) of anhydrous AgCl (18.5 g, 0.129 mol). The reaction mixture was stirred for another 18 h. The magnesium halide complexes were filtered out, and the filtrate was brought to dryness, the residue being dried under high vacuum for 2 h. The solid was redissolved in warm (40 °C) toluene (200 mL), the remaining halides were filtered out, and the colorless solution was carefully concentrated to 80 mL on a hot water bath. When the solution was left standing at room temperature, white crystals of **2** separated out and cooling completed the crystallization (15.56 g, 68.4 mmol). From the mother liquor another crop of 1.85 g of **2** was obtained. Total yield: 17.4 g, 77.4 mmol (60%). Compound **2** is stable at room temperature in the absence of light. Because of its photosensitivity, all the operations were carried out in the absence of light. Anal. Calcd for $C_{36}H_{44}Ag_4$: C, 47.61; H, 4.88. Found: C, 47.30; H, 4.93. ^{1}H NMR (C_6D_6): δ 6.79 (m, 2 H, C_6H_2), 2.75 (s, 6 H, *o*-CH_3), 2.15 (s, 3 H, *p*-Me). ^{1}H NMR (C_6D_{12}): δ, 6.90 (s, 2 H, C_6H_2), 2.81 (s, 6 H, *o*-CH_3), 2.30 (s, 3 H, *p*-Me). The ^{1}H NMR spectra correspond to the dimer present in solution, the pentamer being almost undetectable.

Synthesis of [Au_5Mes_5]·2THF (3). A THF solution (17.1 mL) of MesMgBr (1.15 M, 19.7 mmol) was added dropwise under exclusion of light to a cold (−40 °C) THF suspension (110 mL) of Au(CO)Cl, which was prepared at −50 °C to avoid decomposition of Au(CO)Cl. As the reaction proceeded, CO evolved gently from the yellow grayish suspension which was allowed to slowly reach room temperature after all the MesMgBr had been added. *p*-Dioxane (15 mL, 170 mmol)) was added, and stirring was continued for 2 h. Decantation (3 h) and filtration gave a yellow-orange solution. It was carefully concentrated to 75 mL on the water bath (40–45 °C). When the solution was cooled in the refrigerator, yellow crystals of **3** began to separate. The product (2.01 g) was isolated, and the mother liquors yielded another 0.51 g of product. Total yield: 2.52 g (40.5%). All the operations must be carried out under exclusion of light. Complex **3** can be recrystallized from toluene, THF, and benzene. Recrystallization from THF yielded crystals suitable for X-ray analysis. Anal. Calcd for [Au_5Mes_5]·2THF, $C_{53}H_{71}Au_5O_2$: C, 36.93; H, 4.15. Found: C, 37.12; H, 4.31. ^{1}H NMR (toluene-d_8): δ 6.57 (m, 2 H, C_6H_2), 2.83 (s, 6 H, *o*-Me), 1.85 (s, 3 H, *p*-Me). ^{1}H NMR (C_6D_{12}): δ 6.86 (s, 2 H, C_6H_2), 2.80 (s, 6 H, *o*-Me), 2.27 (s, 3 H, *p*-Me). MW determination in benzene was carried out by using the [Au_5Mes_5] recrystallized from benzene. Several determinations

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[39] Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic: New York, 1965; Vol. 2; pp 1005–1007.

led to an average value of 685 ± 45 corresponding to a *n* value of 2.15 ± 0.15 for the [Au_nMes_n] formula.

Synthesis of [$Cu_4Mes_4THT_2$]$_2$ (5). THT (3 mL, 26.8 mmol) was added at room temperature to a THF solution (50 mL) of 1 (1.89 g, 10.4 mmol). When the solution was left standing at −20 °C, crystals of 2 formed slowly (1.582 g). Anal. Calcd for $C_{44}H_{60}Cu_4S_2$: C, 58.2; H, 6.60; S, 7.10. Found: C, 57.40; H, 6.30; S, 6.90. ^{1}H NMR (toluene-d_8): δ 3.26 (s, 6 H, *o*-Me), 2.25 (s, 3 H, *p*-Me), 7.47 (m, 2 H, C_6H_2), 2.68 (m, 2 H, CH_2), 1.70 (m, 2 H, CH_2-CH_2).

Reaction of [Cu_5Mes_5] with Triphenylphosphine: Synthesis of [CuMes(PPh_3)$_2$] (6). A toluene solution (30 mL) of triphenylphoshine (2.07 g, 7.89 mmol) was added to a toluene solution (50 mL) of Cu_5Mes_5 (1) (1.41 g, 7.73 mmol) at room temperature. The yellow solution was concentrated carefully to 30 mL. When the solution was left standing in the refrigerator, light yellow crystals of 6 separated (1.80 g). The low thermal stability of 6 prevented X-ray crystal structure analysis and the high reactivity toward moisture did not allow for a reliable elemental analysis. Nevertheless, the agreement is reasonable. Anal. Calcd for [CuMes(PPh_3)$_2$]·C_7H_8, $C_{52}H_{49}CuP_2$: C, 79.48; H, 6.44; P. 6.95; Cu, 7.13. Found: C, 78.92; H, 5.54; P, 6.11; Cu, 7.88. ^{1}H NMR (toluene-d_8): δ 7.3 (m, 12 H, *o*-PPh_3), 7.0 (m, 28 H, *m*-PPh_3, *o*-PPh_3, C_7H_8), 6.62 (d, 2 H, *m*-Mes), 2.90 (s, 6 H, *o*-Mes), 2.10 (s, 6 H, C_7H_8), 1.98 (s, 3 H, *p*-Mes). The IR spectrum of 6 (Nujol) showed characteristic bands of copper aryls at 883 cm^{-1} and of triphenylphosphine at 740 and 690 cm^{-1}.

Reaction of [Cu_5Mes_5] with dppe: Synthesis of [$CuMes_2$]$^-$[Cu(dppe)$_2$]$^+$ (7).[25] Two toluene solutions of Cu_5Mes_5 (0.93 g, 5.09 mmol in 100 mL) and dppe (2.09 g, 5.24 mmol in 25 mL) were mixed together at room temperature. A yellowish crystalline product formed, which was crystallized from hot toluene, yielding colorless-beige needles (1.58 g). Anal. Calcd for $C_{70}H_{70}Cu_2P_4$: C, 72.26; H, 6.07; P, 10.65; Cu, 10.93. Found: C, 72.62; H, 5.89; P, 9.97; Cu, 9.55.

Reaction of [Cu_5Mes_5] with dppm: Synthesis of [Cu_3($Ph_2PCHPPh_2$)$_3$]·2C_7H_8 (8).[26] A toluene solution (25 mL) of dppm (2.27 g, 5.92 mmol) was added to a toluene solution (25 mL) of Cu_5Mes_5 (1.02 g, 1.12 mmol) at room temperature. The orange-yellow solution was then concentrated to 25 mL where upon standing yellow diamagnetic crystals of 9 separated (1.73 g). Complex 9 was identified by analysis and its IR spectrum and compared with an authentic sample.

Reaction of [Ag_4Mes_4] with THT. THT (1 mL, 8.93 mmol) was added at room temperature to a THF solution (50 mL) of Ag_4Mes_4. The solution was concentrated, and diethyl ether (50 mL) was added. When the solution was left standing at 20 °C, crystals of unreacted Ag_4Mes_4 separated.

Reaction of [Ag_4Mes_4] with bpy. bpy (1.0 g, 6.33 mmol) was added to a toluene solution (50 mL) of Ag_4Mes_4 (1.088 g, 4.80 mmol). When the solution was left standing in the freezer, unreacted Ag_4Mes_4 separated as crystalline material.

Reaction of [Ag_4Mes_4] with Triphenylphoshine. A toluene solution (25 mL) of triphenylphosphine (1.36 g, 5.21 mmol) was added to a toluene solution (25 mL) of silver mesityl (1.117 g, 4.92 mmol) at room temperature. The solution was concentrated carefully to 20 mL and allowed to stand in the freezer for 5 days; 0.626 g of colorless transparent crystals of Ag_4Mes_4 could be isolated.

Reaction of [Ag_4Mes_4] with dppm: Synthesis of [Ag_3($Ph_2PCHPPh_2$)$_3$]·2C_7H_8 (9). A toluene solution (25 mL) of dppm (2.27 g, 5.92 mmol) was added at room temperature to a toluene solution (25 mL) of silver mesityl (1.305 g, 5.74 mmol), giving a yellow solution which was concentrated to 25 mL and allowed to stand to room temperature for several days as crystallization was slow. Yellow diamagnetic crystals of 9 were collected after 6 days (2.35 g, yield 67%). Recrystallization from toluene yielded crystals suitable for X-ray diffraction analysis. Anal. Calcd for [Ag_3($Ph_2PCHPPh_2$)$_3$]·2C_7H_8, $C_{89}H_{79}Ag_3P_6$: C, 64.47; H, 4.80; P, 11.21. Found: C, 64.05; H, 4.71, P, 11.41. ^{1}H NMR (C_6D_6): δ, 8.14 (b t, 6 H), 7.43 (b m, 6 H), 7.19 (t, 6 H), 7.05–6.85 (m, 31 H), 6.70 (b m, 6 H), 6.54 (t, 2 H), 6.33 (t, 6 H).

Reaction of [Ag_4Mes_4] with dppe. Method A. Toluene solutions (2 × 25 mL) of dppe (1.08 g, 2.71 mmol) and 2 (0.598 g, 2.63 mmol) were mixed at room temperature in the dark and cooled immediately in the freezer. A white solid mixed with some oily decomposition product deposited overnight. It was recrystallized from toluene at room temperature. When the solution was left standing at −25 °C, a crystalline, colorless material formed. Such a solid is very light sensitive and decomposed slowly even at 0 °C, preventing reliable elemental analysis. Its IR spectrum (Nujol) showed a similar pattern to complex 7, unlike complex 8 and the product of the same reaction carried out in THF. IR (Nujol, cm^{-1}): 510 (s), 690 (vst), 720 (vst), 832 (sh st), 1000 (w), 1027 (m), 1100 (m br). Abbreviations: st, strong; vst, very strong; sh st, sharp strong; w, weak; m, medium, m br, medium broad.

Method B. Two THF solutions (2 × 30 mL) of dppe (2.30 g, 5.80 mmol) and 2 (1.315 g, 5.79 mmol) were mixed together at room temperature. A slight amount of decomposition products were filtered off, and the clear orange solution was cooled immediately in the freezer. After several days, 2.00 g of microcrystalline gray material was isolated. Recrystallization from THF yielded colorless crystals at low temperature which turned gray and opaque upon isolation. The IR spectrum of the solid (Nujol) was quite different from that of 7 and the product formed in toluene. It has a pattern very similar to that of 8. The very high instability prevented any reliable elemental analysis.

Reaction of [Au_5Mes_5] with Triphenylphosphine: Synthesis of [$AuMesPPh_3$] (10). A toluene solution (30 mL) of 3 (0.4 g, 0.25 mmol) was reacted with the stoichiometric amount of PPh_3. The solution became colorless and then was concentrated to a small volume and collected with Et_2O (30 mL). When the solution was left standing at −30 °C, nice white crystals of [AuMes(PPh_3)] precipitated, whose structure was elucidated by X-ray analysis.[30] Yield: 0.3 g (41%). Anal. Calcd for [AuMes(PPh_3)], $C_{27}H_{26}AuP$: C, 56.1; H, 4.5. Found: C, 55.90; H, 4.4.

Reaction of [Au_5Mes_5] with dppm: Synthesis of [Au_2Mes_2(μ-dppm)] (11). A toluene solution (25 mL) of dppm (1.06 g, 2.77 mmol) was added at room temperature to a toluene solution (50 mL) of 3 (0.835 g, 2.64 mmol). Instant decoloration took place and the solution was concentrated to 25 mL. When the solution was left standing at −25 °C, only a small quantity of a microcrystalline white material separated. Concentration to 15–20 mL and addition of 10 mL of hexane produced about 50 mg of small crystals of poor quality, 11. The IR spectrum (solid, Nujol mull) showed only a single sharp band at 845 cm^{-1}, unlike 8 and 9, indicating that the structure of 11 is different, probably showing complexation of two AuMes units by dppm, similar to the spectrum of 12 since both spectra are quite similar. ^{1}H NMR (C_7D_8): δ, 7.62 (m, 8 H, *o*-dppm), 6.95 (m, 16 H, *m*-dppm, *p*-dppm, *m*-Mes), 3.19 (t, 2 H, P–CH_2–P, *J* = 8.75 Hz), 2.57 (s, 12 H, *o*-Mes), 2.33 (s, 6 H, *p*-Mes).

Reaction of [Au_5Mes_5] with dppe: Synthesis of [Au_2Mes_2(μ-dppe)] (12). A toluene solution (25 mL) of dppe (0.670 g, 1.69 mmol) was added at room temperature to a toluene solution (50 mL) of 3 (0.514 g, 1.62 mmol), while decoloration took place. Addition of hexane (50 mL) and cooling to 0 °C yielded white crystals of 12 (0.475 g). Crystals suitable for X-ray structural analysis were obtained from the mother liquor after cooling to −25 °C. Total yield: 0.62 g. Anal. Calcd for $C_{44}H_{46}Au_2P_2$: C, 51.27; H, 4.50. Found: C, 52.65; H, 4.67. ^{1}H NMR (toluene-d_8): δ 7.64 (m, 8 H, *o*-dppe), 7.11 (s, 4 H, *m*-Mes), 6.9 (m, 12 H, *m*-dppe, *p*-dppe), 2.87 (s, 16 H, *o*-CH_3 Mes, CH_2 dppe), 2.36 (s, 6 H, *p*-CH_3 Mes). The IR spectrum (Nujol) shows a characteristic sharp band at 845 cm^{-1}.

X-ray Crystallography. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circle diffractometer. Crystal data and details of the parameters associated with the data collection are given in Table II. The reduced cells quoted were obtained with use of TRACER.[40] For intensities and background individual reflection profiles were analyzed as described by Lehmann and Larsen[41] for complex 1; the "three-point" technique was used for complexes 2, 3, 5, 9, and 12. The structure amplitudes were obtained after the usual

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(40) Lawton, S. L.; Jacobson, R. A. TRACER, a cell reduction program; Ames Laboratory, Iowa State University of Science and Technology: Ames, IO, 1965.

(41) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580–584.

Lorentz and polarization reduction[42] and the absolute scale was established by the Wilson method.[43] The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected for complexes **2**, **3**, and **12** so the data for these compounds were corrected for absorption by a semiempirical method[44] with maximum and minimal absorption corrections of 1.235–1.000, 1.543–1.009, and 1.095–1.000, respectively. The function minimized during the full-matrix least-squares refinement was $\sum w|\Delta F|^2$. Unit weights were applied for complexes **1**, **9**, and **12** since these gave acceptable agreement analysis. The weighting scheme used was $w = k/[\sigma^2(F_o) + |g|F_o^2]$; k is redetermined after each structure factor calculation and refined by fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) + |g|F_o^2]/k$. The value for g was that giving the smallest variation of the mean values of $w(|F_o| - |F_c|)^2$ as a function of the magnitude of F_o. Anomalous scattering corrections were included in all structure factor calculations. Scattering factors for neutral atoms were taken from ref 45 for non-hydrogen atoms and from ref 46 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map for complexes **3** and **12**. For complexes **1**, **5**, **2**, and **9** the coordinates of the metal atoms were obtained by MULTAN.[47] Solutions and refinements were based on the observed reflections.

Structure Refinement for Complex 1. Because of the low quality and small dimensions of the available crystals only 1629 reflections of 6195 collected ones could be considered as observed $[I > 3\,\sigma(I)]$, so the crystal analysis is rather poor. Refinement was by full-matrix least squares first isotropically down to $R = 0.142$ and then anisotropically only for the copper and methyl carbon atoms. Refinement stopped at $R = 0.101$. The hydrogen atoms were neither located nor put in calculated positions. In the final difference map there were some peaks of about 0.7 e Å^{-3} (general background 0.4 e Å^{-3}) having no chemical meaning. Attempts to apply a weighting scheme failed.

Structure Refinement for Complex 2. The structure was refined by full-matrix least squares first isotropically ($R = 0.110$) and then anisotropically for non-hydrogen atoms. The hydrogen atoms, either located from a ΔF synthesis or put in calculated positions, were introduced in the least-squares refinement as fixed contributors ($U = 0.10$ Å^2). At the end of the refinement the values for k and g were 1.6908 and 0.000 851, respectively. In the final difference map there were no peaks above the general background which was about 0.4 e Å^{-3}.

Structure Refinement for Complex 3. The structure was refined by full-matrix least squares with anisotropic thermal parameters for the gold and methyl carbon atoms. The X-ray analysis revealed the presence of disordered THF molecules of crystallization in a complex to THF molar ratio of 1:2. The one independent THF molecule was found to be disordered. Disorder was solved in terms of "partial" atoms considering the molecule distributed over three positions with the site occupation factors given in Table V. Because of disorder it was not possible to distinguish the oxygen atom, so all the atoms were considered as carbons. All the hydrogen atoms of the complex were located from a difference map and introduced in the last stages of refinement as fixed contributors ($U = 0.05$ Å^2). In the final cycle no parameter shifted by more than 0.1 of its standard deviation for the complex and 0.9 for THF. The final values for k and g were 1.1711 and 0.000 461, respectively (see the weighting scheme above). The final difference map showed no unusual feature with only three peaks (1.5 e Å^{-3}) in the neighborhood of the gold atoms greater than the general background which was about 1.0 e Å^{-3}.

Structure Refinement for Complex 5. The isotropic refinement stopped at $R = 0.098$. The subsequent anisotropic refinement of all atoms gave $R = 0.069$. At this point the extremely large U_{ij} values reached by the S2 sulfur atom indicated some disorder affecting the THT molecule. It was solved considering sulfur and C6 carbon distributed over two positions (A and B). The anisotropic refinement of these "partial" atoms and their site occupation factors (Table VI) stopped at $R = 0.059$, $R_w = 0.063$. In the final stage of refinement the values for k and g (see the weighting scheme above) were 1.0787 and 0.002 113, respectively. All the hydrogen atoms but those associated to the THT disordered molecule (which were ignored) were located from a difference map and introduced as fixed contributors in the final stages of refinement ($U = 0.12$ Å^2). The final difference map showed no unusual features with no peak greater than 0.4 e Å^{-3} and no holes less than -0.3 e Å^{-3}.

Structure Refinement for Complex 9. The isotropic refinement gave $R = 0.087$. Owing to the limitations of the local version of SHELX [$(N_{iso} + 2N_{anis})_{max} = 160$, where N_{iso} and N_{anis} are the isotropic and anisotropic atoms, respectively] only the silver, phosphorus, and nonaromatic carbon (C17, C57, C97) atoms were allowed to vary anisotropically. During refinement the phenyl rings were constrained to be regular hexagons (C–C = 1.39 Å). Most of the hydrogen atoms were located from a different map but could not be introduced in calculations because of the cited limitations. The two toluene molecules of crystallization appeared to be affected by high thermal motion as often it happens in situations like this. Attempts to interpret this in terms of disorder failed. In the final difference map no significant peak was above the general background of about 0.5 e Å^{-3}.

Structure Refinement for Complex 12. The structure was refined by full-matrix least squares first isotropically ($R = 0.099$) and then anisotropically for non-hydrogen atoms. All the hydrogen atoms were located from a difference map and introduced in calculations as fixed contributors (U = 0.05 Å^2) prior to the final refinement. The final difference map showed no peak above the general background (0.2 e Å^3).

Residual R and weighted residual R_W indices were defined as $R = \sum|\Delta F|/\sum|F_o|$ and $R_w = \sum\sqrt{w}|\Delta F|/\sum\sqrt{w}|F_o|$. The "goodness of fit" parameter (GOF) was determined by the equation $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ where NO is the number of observed reflections and NV the number of variables refined.

Final atomic coordinates are listed in Tables III–VIII and SI–SIV, and thermal parameters are given in Tables SV–SX.[48]

Registry No. **1**, 88760-64-9; **2**, 89265-09-8; **3**, 89340-03-4; **5**, 88760-65-0; **6**, 119413-73-9; **7**, 86940-33-2; **8**, 111071-23-9; **9**, 119413-75-1; **10**, 104717-87-5; **11**, 119390-67-9; **12**, 119390-68-0; **14**, 50960-82-2.

Supplementary Material Available: Tables of not refined hydrogen coordinates (Tables SI–SIV), thermal parameters (Tables SV–SX), nonessential bond distances and angles (Table SXI), and least-squares planes (Table SXII) (21 pages); listings of observed and calculated structure factors for **5**, **9**, and **12** (51 pages). Ordering information is given on any current masthead page.

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(42) Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using: Sheldrick, G. *SHELX-76. System of Crystallographic Computer Programs*; University of Cambridge: Cambridge, England, 1976.

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(48) See paragraph at the end of paper regarding supplementary material.