Mesitylgold(I) Complexes. Crystal Structures of $NEt_4[Au(mes)Cl]$ and $[N(PPh_3)_2][(mes)Au(CN)Au(mes)]$ *

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Arylation of [AuCl(tht)] (tht = tetrahydrothiophene) with $[\{Ag(mes)\}_4]$ (mes = mesityl) gives $[\{Au(mes)\}_5]$. Both the silver and gold complex can be used for the syntheses of mono- or binuclear cationic, neutral, or anionic mesitylgold complexes of the form Au(mes)L [L = PPh_3, PPh_2Me, $P(OPh)_3$, or $\frac{1}{2}(Ph_2PCH_2PPh_2)$, $[\{Au(PPh_3)\}_2(\mu\text{-mes})]ClO_4$, Q[Au(mes)X] (Q = NEt_4 or NBu_4; X = C_6F_5 or Cl), or $[N(PPh_3)_2][(mes)Au(CN)Au(mes)]$. The structures of $NEt_4[Au(mes)Cl]$ and $[N(PPh_3)_2][(mes)Au(CN)Au(mes)]$ have been determined by single-crystal *X*-ray methods. The complex $NEt_4[Au(mes)Cl]$ crystallizes in space group $P2_1/n$ with a = 8.526(1), b = 13.917(2), c = 16.457(2) Å, β = 101.14(1)°, and Z = 4; R 0.038 for 2 656 unique observed reflections. The Au–Cl bond is long and the Au–C bond short [2.328(2) and 2.018(7) Å respectively]. The complex $[N(PPh_3)_2][(mes)Au(CN)Au(mes)]$ crystallizes in space group $C2/c$ with a = 27.702(8), b = 12.318(4), c = 20.501(6) Å, β = 135.61(1)°, and Z = 4; R 0.037 for 3 576 unique observed reflections. The anion and the cation both have imposed crystallographic two-fold symmetry, and the bridging CN group must therefore be disordered. The Au–C(mesityl) bond length is 2.035(11) Å.

Following the preparation of a mesitylcopper oligomer by Tsuda *et al.*,[1] Gambarotta *et al.* have prepared mesitylsilver and mesitylgold and established the structures of $[\{Cu(mes)\}_5]$,[2] $[\{Ag(mes)\}_4]$,[3] and $[\{Au(mes)\}_5]$. All three complexes are thermally stable to at least 100 °C, but the silver complex, being light- and moisture-sensitive, decomposes rapidly in laboratory air. The complexes are soluble in common organic solvents.

Here we describe the use of both $[\{Ag(mes)\}_4]$ and $[\{Au(mes)\}_5]$ for the synthesis of various mesitylgold complexes. Until now, only $[Au(mes)(PPh_3)]$ has been mentioned, briefly, in the literature.[5] Although the recent developments of arylgold chemistry has been successful, most complexes have contained polyhalogenophenyl ligands (C_6F_5, C_6Cl_5, C_6Br_5, or $C_6F_3H_2$);[6] we therefore decided to investigate the possibility of forming other stable arylgold complexes.

Results and Discussion

The complex $[\{Ag(mes)\}_4]$ was prepared by literature methods[3] in 60% yield. Since it readily reacts with [AuCl(tht)] (tht = SC_4H_8, tetrahydrothiophene) to give $[\{Au(mes)\}_5]$ in high yield (92%) (see below), we chose this preparation of the gold complex rather than the literature method.[4]

The Scheme summarizes our studies on the reactivity of both these cyclic homoleptic compounds. The complex $[\{Ag(mes)\}_4]$ reacts with halide-containing gold complexes to give a variety of mesitylgold(I) derivatives. With $[AuX(PPh_3)]$ the complex $[Au(mes)(PPh_3)]$[5] is obtained (65% yield for X = Cl, 85% for X = Br); we did not observe the reported formation[5] of pale brown oils that require prolonged pumping to yield a solid. With [ClAu(dppm)AuCl] (dppm = $Ph_2PCH_2PPh_2$) the binuclear [(mes)Au(dppm)Au(mes)] (**1**) is obtained; it is an air- and moisture-stable white solid, soluble in acetone (non-conducting), dichloromethane, chloroform (monomeric, isopiestic method, M = 1 031, calc. 1 017), and diethyl ether and insoluble in aliphatic hydrocarbons. The ^1H n.m.r. spectrum in $CDCl_3$ shows signals at 6.74 (s, 4 H), 2.26 (s, 12 H, *o*-Me), and 2.22 (s, 6 H, *p*-Me).

The complex $[\{Ag(mes)\}_4]$ reacts with [AuCl(tht)] in tetrahydrofuran (thf), displacing both ligands to give the known pentanuclear $[\{Au(mes)\}_5]$.[4] The addition of neutral ligands L to dichloromethane solutions of $[\{Au(mes)\}_5]$ affords monomeric gold(I) derivatives [Au(mes)L] [L = PPh_3, 70%; PPh_2Me (**2**), 86%; $P(OPh)_3$ (**3**), 66%] as white solids. Nitrogen, As, or S donors such as pyridine, $AsPh_3$, or SC_4H_8 do not react under similar conditions. Complexes (**2**) and (**3**) are non-conducting in acetone and monomeric in chloroform [M 566, calc. 516 for (**2**), 681, calc. 626 for (**3**)].

Arylation of the chloride-bridged $[\{Au(PPh_3)\}_2(\mu\text{-Cl})]ClO_4$[7] with $[\{Ag(mes)\}_4]$ leads (Scheme) to the cationic mesityl-bridged $[\{Au(PPh_3)\}_2(\mu\text{-mes})]ClO_4$ (**4**), which can be isolated (84% yield) as an air- and moisture-stable white solid. An alternative synthesis (64% yield) consists in treating [Au-

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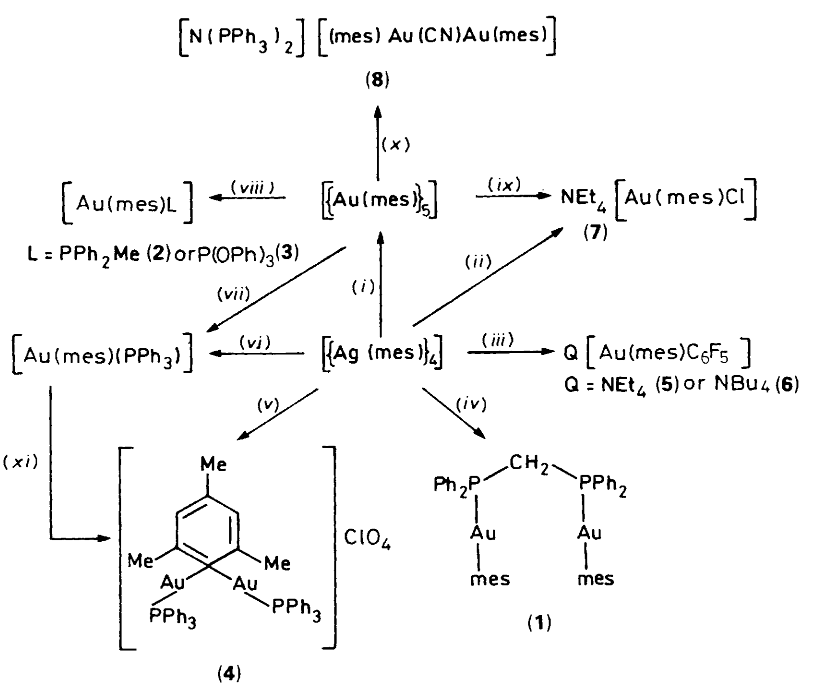
* Tetraethylammonium chloro(mesityl)aurate(I) and bis(triphenylphosphine)iminium μ-cyano-bis[mesitylaurate(I)].

Supplementary data available: complete bond lengths and angles, H-atom co-ordinates, thermal parameters, and structure factors have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, West Germany. Any request for this material should quote a full literature citation and the reference number CSD 53726.



Scheme (*i*) [AuCl(tht)]; (*ii*) $NEt_4[AuCl_2]$; (*iii*) $Q[Au(C_6F_5)Cl]$; (*iv*) [ClAu(dppm)AuCl]; (*v*) $[\{Au(PPh_3)\}_2(\mu\text{-}Cl)]$; (*vi*) $[AuX(PPh_3)]$; (*vii*) PPh_3; (*viii*) L; (*ix*) $[NEt_4]Cl$; (*x*) $[N(PPh_3)_2]CN$; (*xi*) $[Au(OClO_3)(PPh_3)]$

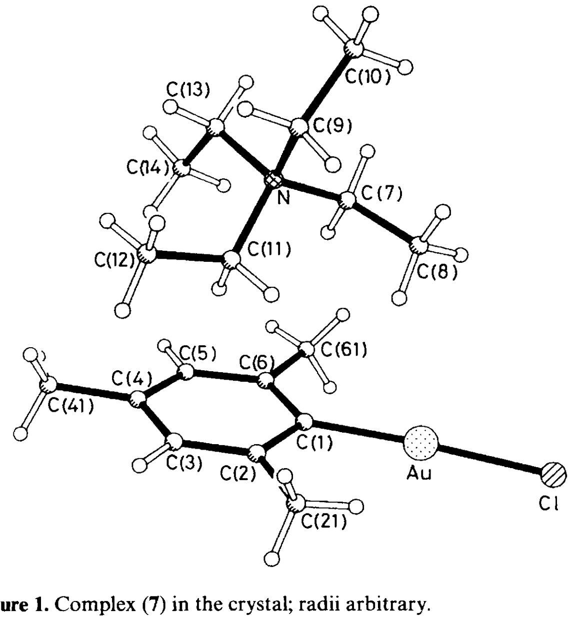


Figure 1. Complex (**7**) in the crystal; radii arbitrary.

$(mes)(PPh_3)]$ with $[Au(OClO_3)(PPh_3)]$, analogous to the synthesis of the Cl-bridged derivative.[7] Complex (**4**) is soluble in acetone (1:1 electrolyte), chloroform, dichloromethane, and tetrahydrofuran and insoluble in diethyl ether and n-hexane. Its i.r. spectrum (Nujol mull) shows bands at 1 596m and 865w cm^{-1} from the mesityl group; the ClO_4^- anion gives rise to bands at 1 094vs, br and 625m cm^{-1}.[8] Unfortunately we have not been able to obtain crystals of (**4**) suitable for *X*-ray analysis, but we tentatively propose a structure with the aryl group bridging the two gold centres, as in $[\{Au(PPh_3)\}_2(\mu\text{-}C_6F_3H_2)]ClO_4$.[9]

Halide-containing aurate(I) complexes react to afford anionic mesitylgold(I) complexes. Thus $Q[Au(C_6F_5)Cl]$ reacts with $[\{Ag(mes)\}_4]$ to give $Q[Au(mes)(C_6F_5)]$ [Q = NEt_4 (**5**) or NBu_4 (**6**)], and $NEt_4[AuCl_2]$ to form $NEt_4[Au(mes)Cl]$ (**7**). The double arylation at room temperature to give $Q[Au(mes)_2]$ is not observed starting from $Q[AuCl_2]$ or $Q[Au(mes)Cl]$ and an excess of $[\{Ag(mes)\}_4]$, and metallic gold is deposited on refluxing. Complex (**7**) can also be obtained from $[\{Au(mes)\}_5]$ and NEt_4Cl (Scheme). Complexes (**5**)—(**7**) are air- and moisture-stable white solids that behave as 1:1 electrolytes in acetone solution. The i.r. spectrum of (**7**) exhibits a band at 300m cm^{-1} [ν(Au–Cl)].[10]

The structure of complex (**7**) was established by *X*-ray diffraction methods. Single crystals were obtained by slow diffusion of hexane into a concentrated dichloromethane solution of (**7**) at −10 °C.

Figure 1 shows the structure of complex (**7**). The anion shows the expected linear co-ordination at gold, with Cl–Au–C(1) 176.9(2)°. This is only the second structure of an $[AuR(Cl)]^-$ anion, after $[Au(C_6F_5)Cl]^-$.[11] The current structure shows a long Au–Cl bond [2.328(2) Å, *cf.* 2.311 and 2.322(5) Å in the C_6F_5 analogue] and a short Au–C bond [2.018(7) Å, *cf.* 2.054(17) and 2.042(15) Å]. In fact the use of idealized rigid groups in the refinement of the C_6F_5 analogue[11] probably led to systematically shortened Au–C bond lengths, because the *ipso* C–C–C angle of the aromatic group is usually appreciably below 120° for C_6F_5[12] [*cf.* 117.2(6)° here]. The pattern of bond lengths at Au may reflect the essentially σ nature of the bonding at Au^I, with the better σ C donor leading to the short bond.

An anionic binuclear complex can be obtained by the reaction of $[\{Au(mes)\}_5]$ with $[N(PPh_3)_2]CN$ in molar ratio 1:2.5. The complex $[N(PPh_3)_2][(mes)Au(CN)Au(mes)]$ (**8**) is an air- and moisture-stable white solid, soluble in acetone (1:1 electrolyte), dichloromethane, and chloroform and insoluble in diethyl ether and hexane. Its i.r. spectrum shows ν(C≡N) at 2 063s cm^{-1}.[13]

Single crystals of (**8**) were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex, and its structure was determined by *X*-ray diffraction methods.

Figure 2 shows the structure of the anion of complex (**8**). The anion possesses crystallographic two-fold symmetry, and the C and N atoms of the bridging CN must thus be disordered. The

Table 1. Analytical data for products

	Complex	Analysis (%)* C	H	N	Au	m.p. (°C)	Λ_M/ ohm^{-1} m^2 mol^{-1}
(**1**)	[(mes)Au(dppm)Au(mes)]	50.3 (50.8)	4.4 (4.4)		38.45 (38.75)	135	9
(**2**)	[Au(mes)(PPh$_2$Me)]	50.75 (51.2)	4.9 (4.7)		37.9 (38.15)	100	1
(**3**)	[Au(mes){P(OPh)$_3$}]	51.9 (51.75)	3.9 (4.2)		31.7 (31.45)	75	1
(**4**)	[{Au(PPh$_3$)}$_2$(μ-mes)]ClO$_4$	47.75 (47.5)	3.75 (3.6)		34.0 (34.65)	120 (decomp.)	127
(**5**)	NEt$_4$[Au(mes)(C$_6$F$_5$)]	44.75 (45.0)	4.8 (5.1)	2.1 (2.2)	32.3 (32.1)	125 (decomp.)	92
(**6**)	NBu$_4$[Au(mes)(C$_6$F$_5$)]	50.8 (51.3)	6.7 (6.55)	1.9 (1.9)	27.1 (27.1)	86	122
(**7**)	NEt$_4$[Au(mes)Cl]	42.3 (42.4)	7.0 (6.5)	3.0 (2.9)	41.1 (40.9)	132	146
(**8**)	[N(PPh$_3$)$_2$][(mes)Au(CN)Au(mes)]	55.5 (55.2)	4.75 (4.4)	2.35 (2.35)	32.2 (32.9)	190 (decomp.)	102

* Calculated values in parentheses.

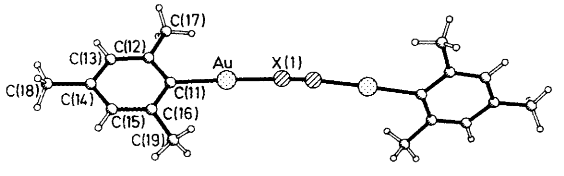


Figure 2. The anion of complex (**8**) in the crystal. Atom X(1) is a mixed C/N site (see text). Radii arbitrary.

geometry at gold is linear, with C(11)–Au–X 177.0(3)° (where X represents the disordered C/N site). The Au–X bond length should clearly be interpreted with caution, but the observed value of 2.021(11) Å lies in the expected range for Au–C or Au–N. The Au–C(11) bond length, 2.035(11) Å, is slightly longer than the corresponding bond in complex (**7**). There is no distortion of the *ipso* C–C–C angle.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 883 instrument using Nujol mulls between polyethylene sheets. Conductivities were measured in 5×10^{-4} mol dm^{-3} acetone solutions with a Crison 522 conductimeter. Molecular weights were determined in *ca.* 10^{-3} mol dm^{-3} chloroform solution using the isopiestic method on a Knauer 0600 apparatus. Proton n.m.r. spectra were recorded on a Varian XL-200 spectrometer (chemical shifts are quoted relative to SiMe$_4$). Carbon H, and N analyses were carried out with a Perkin-Elmer 240 B microanalyser; Au was determined by ashing the samples in a crucible together with an aqueous solution of hydrazine.

The C, H, and Au analyses, conductivities, and melting points of the novel complexes are listed in Table 1.

Preparation of the Complexes.—[Au(mes)(PPh$_3$)] *or* [(mes)-Au(dppm)Au(mes)] (**1**). To a tetrahydrofuran solution (50 cm^3) of [AuX(PPh$_3$)] [X = Cl,[14] 0.495 g, 1 mmol; or Br;[15] 0.539 g, 1 mmol] or [ClAu(dppm)AuCl][16] (0.426 g, 0.5 mmol) was added [{Ag(mes)}$_4$] (0.250 g, 0.27 mmol). The mixture was stirred for 2 h at room temperature. The precipitated AgCl was filtered off and the solution was evaporated to dryness. The white solid was recrystallized from diethyl ether–hexane to give [Au(mes)-(PPh$_3$)] (65%, X = Cl; or 85% yield, X = Br) [^{1}H n.m.r. 6.93 (s, 2 H), 2.60 (s, 6 H, *o*-Me), and 2.27 (s, 3 H, *p*-Me)] or (**1**) (62% yield) [^{1}H n.m.r. 7.5 (m, 20 H, Ph), 6.74 (m, 4 H), 2.26 (s, 12 H, *o*-Me), and 2.22 (s, 6 H, *p*-Me)].

[{Au(mes)}$_5$]. To a tetrahydrofuran solution (50 cm^3) of [AuCl(tht)][14] (0.321 g, 1 mmol) at −20 °C was added [{Ag-(mes)}$_4$] (0.250 g, 0.27 mmol). After 10 min of stirring the mixture was allowed to warm to room temperature (1 h) and stirred for 2 h. The insoluble AgCl was filtered off, and the filtrate was evaporated to dryness. The yellow [{Au(mes)}$_5$] was recrystallized from dichloromethane–hexane (92% yield) [^{1}H n.m.r. 6.75 (s, 2 H), 2.60 (s, 6 H, *o*-Me), and 2.10 (s, 3 H, *p*-Me)].

[Au(mes)L] [L = PPh$_3$, PPh$_2$Me (**2**) *or* P(OPh)$_3$ (**3**)]. To a dichloromethane solution (40 cm^3) of [{Au(mes)}$_5$] (0.316 g, 0.2 mmol) was added L [1 mmol; L = PPh$_3$, 0.262 g; PPh$_2$Me, 0.193 g; or P(OPh)$_3$, 0.316 g] and the mixture was stirred for 15 min at room temperature. The solution was concentrated to 5 cm^3 and addition of n-hexane (30 cm^3) gave [Au(mes)(PPh$_3$)] (70% yield), (**2**) [86%, ^{1}H n.m.r. 7.48 (m, 10 H, Ph), 6.94 (s, 2 H), 2.60 (s, 6 H, *o*-Me), 2.28 (s, 3 H, *p*-Me), and 2.12 (d, 3 H, *p*-Me)], or (**3**) (66%) as white solids.

[{Au(PPh$_3$)}$_2$(μ-mes)]ClO$_4$ (**4**). This complex can be obtained in two ways.

(*a*) A mixture of [{Au(PPh$_3$)}$_2$(μ-Cl)]ClO$_4$[7] (1.053 g, 1 mmol) and [{Ag(mes)}$_4$] (0.250 g, 0.27 mmol) in tetrahydrofuran (50 cm^3) was stirred for 2 h at room temperature. The precipitated AgCl was filtered off and the solution was evaporated to *ca.* 5 cm^3. Addition of diethyl ether (30 cm^3) precipitated complex (**4**) (84% yield) [^{1}H n.m.r. 7.3 (m, 32 H, Ph), 2.74 (s, 6 H, *o*-Me), and 2.51 (s, 3 H, *p*-Me)] as a white solid.

(*b*) To a freshly prepared diethyl ether solution (50 cm^3) of [Au(OClO$_3$)(PPh$_3$)][17] (1 mmol) was added [Au(mes)(PPh$_3$)] (0.578 g, 1 mmol). After 2 h of stirring at room temperature complex (**4**) was filtered off (64% yield).

Q[Au(mes)(C$_6$F$_5$)] [Q = NEt$_4$ (**5**) *or* NBu$_4$ (**6**)], NEt$_4$[Au-(mes)Cl] (**7**), *or* [N(PPh$_3$)$_2$][(mes)Au(CN)Au(mes)] (**8**). These complexes can be obtained in the following ways.

(*a*) A mixture of NEt$_4$[Au(C$_6$F$_5$)Cl][18] (0.530 g, 1 mmol), NBu$_4$[Au(C$_6$F$_5$)Br][18] (0.686 g, 1 mmol) or NEt$_4$[AuCl$_2$] (0.398 g, 1 mmol) and [{Ag(mes)}$_4$] (0.250 g, 0.27 mmol) in tetrahydrofuran (80 cm^3) was stirred for 5 h at room temperature. The AgCl was filtered off and the solution was evaporated to dryness. The white complexes (**5**) (72% yield) [^{1}H n.m.r. 6.73 (s, 2 H), 2.77 (q, 8 H, CH$_2$ of Et), 2.45 (s, 6 H, *o*-Me), 2.15 (s, 3 H, *p*-Me), and 0.95 (t, 12 H, CH$_3$ of Et)], (**6**) (78% yield) [^{1}H n.m.r.

Table 2. Atomic co-ordinates (× 10^4) for complex (**7**)

Atom	x	y	z
Au	1 157.3(3)	906.3(2)	3 704.4(2)
Cl	455(2)	−503(2)	2 961(2)
C(21)	−898(9)	2 039(6)	4 862(5)
C(41)	2 607(12)	4 938(7)	5 555(7)
C(61)	4 279(8)	2 346(7)	3 788(5)
C(1)	1 663(7)	2 163(5)	4 311(4)
C(2)	598(8)	2 567(6)	4 767(4)
C(3)	898(9)	3 445(6)	5 147(5)
C(4)	2 264(11)	3 983(6)	5 098(6)
C(5)	3 286(9)	3 590(7)	4 657(5)
C(6)	3 052(8)	2 694(6)	4 262(4)
N	4 462(6)	1 408(4)	6 898(3)
C(7)	4 613(9)	826(5)	6 156(5)
C(8)	3 340(10)	74(6)	5 892(6)
C(9)	4 366(10)	788(6)	7 632(5)
C(10)	5 681(9)	42(6)	7 853(5)
C(11)	2 982(8)	2 007(5)	6 694(5)
C(12)	2 673(10)	2 692(7)	7 339(6)
C(13)	5 948(8)	2 036(5)	7 125(5)
C(14)	6 178(10)	2 784(7)	6 508(6)

Table 3. Selected bond lengths (Å) and angles (°) for complex (**7**)

Au–Cl	2.328(2)	Au–C(1)	2.018(7)
C(21)–C(2)	1.506(11)	C(41)–C(4)	1.527(13)
C(61)–C(6)	1.500(11)	C(1)–C(2)	1.403(10)
C(1)–C(6)	1.411(10)	C(2)–C(3)	1.374(11)
C(3)–C(4)	1.399(12)	C(4)–C(5)	1.353(13)
C(5)–C(6)	1.404(12)		
Cl–Au–C(1)	176.9(2)	Au–C(1)–C(2)	120.9(5)
Au–C(1)–C(6)	121.8(5)	C(2)–C(1)–C(6)	117.2(6)
C(21)–C(2)–C(1)	120.6(7)	C(21)–C(2)–C(3)	118.3(7)
C(1)–C(2)–C(3)	121.1(7)	C(2)–C(3)–C(4)	122.3(8)
C(41)–C(4)–C(3)	121.3(9)	C(41)–C(4)–C(5)	122.3(8)
C(3)–C(4)–C(5)	116.4(8)	C(4)–C(5)–C(6)	124.0(8)
C(61)–C(6)–C(1)	122.5(7)	C(61)–C(6)–C(5)	118.5(7)
C(1)–C(6)–C(5)	119.0(7)		

Table 4. Atomic co-ordinates (× 10^4) for complex (**8**)

Atom	x	y	z
Au	996.7(1)	278.5(2)	2 622.2(2)
C(11)	1 816(3)	433(5)	2 800(4)
C(12)	1 916(4)	−276(5)	2 366(5)
C(13)	2 501(5)	−172(7)	2 546(6)
C(14)	3 003(4)	580(7)	3 144(6)
C(15)	2 908(4)	1 275(6)	3 581(5)
C(16)	2 317(3)	1 231(6)	3 393(5)
C(17)	1 387(4)	−1 125(6)	1 683(6)
C(18)	3 673(5)	625(8)	3 401(8)
C(19)	2 236(4)	2 053(6)	3 849(6)
X(1)	215(3)	158(4)	2 515(5)
P	4 378(1)	1 062(1)	1 480(1)
N	5 000	1 505(5)	2 500
C(21)	4 478(3)	−316(4)	1 288(4)
C(22)	4 864(4)	−495(5)	1 113(6)
C(23)	4 989(5)	−1 559(7)	1 033(7)
C(24)	4 724(4)	−2 408(6)	1 108(6)
C(25)	4 331(4)	−2 246(6)	1 282(5)
C(26)	4 210(3)	−1 199(5)	1 376(4)
C(31)	4 285(3)	1 922(4)	682(4)
C(32)	3 834(3)	1 648(5)	−253(4)
C(33)	3 738(3)	2 332(6)	−862(4)
C(34)	4 086(3)	3 313(6)	−549(5)
C(35)	4 527(3)	3 591(6)	366(5)
C(36)	4 630(3)	2 902(5)	988(5)
C(41)	3 571(3)	1 146(4)	1 135(3)
C(42)	3 516(3)	1 853(6)	1 600(5)
C(43)	2 881(4)	1 978(7)	1 300(5)
C(44)	2 318(3)	1 393(7)	556(5)
C(45)	2 375(3)	718(6)	89(5)
C(46)	2 995(3)	595(6)	365(5)

Table 5. Selected bond lengths (Å) and angles (°) for complex (**8**)

Au–C(11)	2.035(11)	Au–X(1)	2.021(11)
C(11)–C(12)	1.407(15)	C(11)–C(16)	1.400(8)
C(12)–C(13)	1.387(18)	C(12)–C(17)	1.506(9)
C(13)–C(14)	1.364(11)	C(14)–C(15)	1.393(18)
C(14)–C(18)	1.524(20)	C(15)–C(16)	1.388(16)
C(16)–C(19)	1.501(16)	X(1)–X(1a)	1.146(23)
P–N	1.579(3)	P–C(21)	1.807(6)
P–C(31)	1.805(8)	P–C(41)	1.802(8)
C(11)–Au–X(1)	177.0(3)	Au–C(11)–C(12)	121.8(5)
Au–C(11)–C(16)	120.5(8)	C(12)–C(11)–C(16)	117.7(9)
C(11)–C(12)–C(13)	119.6(7)	C(11)–C(12)–C(17)	121.2(10)
C(13)–C(12)–C(17)	119.2(10)	C(12)–C(13)–C(14)	123.3(12)
C(13)–C(14)–C(15)	117.1(12)	C(13)–C(14)–C(18)	122.9(12)
C(15)–C(14)–C(18)	119.9(8)	C(14)–C(15)–C(16)	121.6(7)
C(11)–C(16)–C(15)	120.6(9)	C(11)–C(16)–C(19)	121.3(10)
C(15)–C(16)–C(19)	118.2(7)	Au–X(1)–X(1a)	175.3(5)
N–P–C(21)	114.9(3)	N–P–C(31)	108.2(2)
C(21)–P–C(31)	107.4(4)	N–P–C(41)	111.9(2)
C(21)–P–C(41)	107.9(3)	C(31)–P–C(41)	106.1(3)
P–N–P(b)	139.5(5)		

Symmetry operators: (a) $-x, y, 0.5 - z$; (b) $1 - x, y, 0.5 - z$.

6.74 (s, 2 H), 2.98 (m, 8 H, CH_2N), 2.53 (s, 6 H, *o*-Me), 2.15 (s, 3 H, *p*-Me), 1.35 (m, 16 H, CH_2), and 0.92 (t, 12 H, CH_3)] or, respectively, (**7**) (37%) [^{1}H n.m.r. 6.70 (s, 2 H), 3.24 (q, 8 H, CH_2 of Et), 2.40 (s, 6 H, *o*-Me), 2.12 (s, 3 H, *p*-Me), and 1.24 (t, 12 H, CH_3 of Et)] were recrystallized from dichloromethane–diethyl ether or acetone–diethyl ether.

(*b*) To a diethyl ether solution (50 cm^3) of [{Au(mes)}$_5$] (0.316 g, 0.2 mmol) was added [NEt_4]Cl (0.166 g, 1 mmol) or [$N(PPh_3)_2$]CN (0.279 g, 0.5 mmol). The mixture was stirred for 5 h at room temperature. The white precipitate was filtered off and recrystallized from acetone–diethyl ether to give complex (**7**) (80% yield) or (**8**) (65%) [^{1}H n.m.r. 7.45 (m, 30 H, Ph), 6.76 (s, 4 H), 2.44 (s, 12 H, *o*-Me), and 2.20 (s, 6 H, *p*-Me)].

X-Ray Structure Determination of Complex (**7**).—*Crystal data* $C_{17}H_{31}AuCN$, $M_r = 481.9$, monoclinic, space group $P2_1/n$, $a = 8.526(1)$, $b = 13.917(2)$, $c = 16.457(2)$ Å, $\beta = 101.14(1)°$, $U = 1\,915.8$ Å^3, $Z = 4$, $D_c = 1.67$ Mg m^{-3}, λ(Mo-K_α) = 0.710 69 Å, $\mu = 7.8$ mm^{-1}, $F(000) = 944$, colourless prism, 0.5 × 0.3 × 0.2 mm.

Data collection and reduction. 4 388 Profile-fitted intensities[19] were registered to $2\theta_{max.}$ 50° on a Stoe–Siemens four-circle diffractometer using monochromated Mo-K_α radiation. Absorption corrections were applied using ψ scans, with transmissions 0.75—0.99. Merging equivalents gave 3 356 unique reflections (R_{int} 0.022), of which 2 656 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX, modified by its author Professor G. M. Sheldrick). Cell constants were refined from 2θ values of 78 reflections in the range 20—25°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on *F*. Hydrogen atoms were included using a riding model. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.000\,35F^2$. An extinction correction of the form $F_{corr.} = F_c/(1 + xF^2/\sin 2\theta)^{0.25}$ was applied, where x refined to 3(1) × 10^{-7}. The final R was 0.038, with R' 0.038; 182 parameters; S 1.4; maximum Δ/σ 0.001; maximum $\Delta\rho$ 0.8 e Å^{-3}. Final atomic co-ordinates are presented in Table 2, selected bond lengths and angles in Table 3.

X-Ray Structure Determination of Complex (**8**).—*Crystal data.* $C_{55}H_{52}Au_2N_2P_2$, M_r = 1 197; monoclinic, space group $C2/c$, a = 27.702(8), b = 12.318(4), c = 20.501(6) Å, β = 135.61(1)°, U = 4 894 Å^3, Z = 4, D_c = 1.62 Mg m^{-3}, μ(Mo-K_α) = 6.1 mm^{-1}, $F(000)$ = 2 336, crystal size 0.6 × 0.4 × 0.2 mm.

Data collection and reduction. As for complex (**7**), with the following differences: 6 159 intensities, 4 283 unique ($R_{int.}$ 0.030), 3 576 observed. Transmissions 0.47—0.99. 74 Reflections used for cell constant refinement.

Structure solution and refinement. As for complex (**7**), with the following differences. The disordered C/N site was refined as C with a site occupation factor of 13/12. R 0.037, R' 0.038; 277 parameters; x 1.0(2) × 10^{-7}; S 1.5; max. Δ/σ 0.001. Final atomic co-ordinates are presented in Table 4, selected bond lengths and angles in Table 5.

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