2,4,6-Trinitrophenylgold(I) Complexes. *X*-Ray Crystal Structures of $[Au(SbPh_3)_4]$ $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]\cdot Et_2O$ and $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}(dmphen)]$ (dmphen = 2,9-dimethyl-1,10-phenanthroline)‡

Jose Vicente* and Aurelia Arcas
Departamento de Quimica Inorganica, Facultad de Ciencias Quimicas, Universidad de Murcia, Campus de Espinardo, 30.171 Espinardo, Murcia, Spain
Peter G. Jones*,† and Jürgen Lautner
Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, Federal Republic of Germany

The reaction of $[PPh_3(CH_2Ph)]$ $[AuCl_2]$ in refluxing acetone with $[Hg\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$ (1 : 0.55) and excess of NMe_4Cl affords $NMe_4[HgCl_3]$ and $[PPh_3(CH_2Ph)]$ $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}Cl]$ (**1**). Complex (**1**) reacts with excess of both $NaClO_4\cdot H_2O$ and tetrahydrothiophene (tht) at room temperature to give $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}(tht)]$ (**2**) which reacts with $SbPh_3$ (1 : 2) or with excess of 2,9-dimethyl-1,10-phenanthroline (dmphen) to give $[Au(SbPh_3)_4][Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$ (**3**) or $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}(dmphen)]$ (**4**), respectively. Crystal structures were determined for complexes (**3**) and (**4**). That of (**3**) [space group $P2_1/n$, a = 12.320 5(18), b = 35.802(6), c = 19.759(3) Å, β = 102.24(2)°, and Z = 4; R = 0.053, R' = 0.051] consists of tetrahedral $[Au(SbPh_3)_4]^+$ cations (mean Au–Sb bond length 2.651 Å), linear $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]^-$ anions (Au–C 2.015 and 2.041 Å), and diethyl ether of crystallization. The nitro groups display high thermal motion or disorder. The crystal structure of complex (**4**) [space group $P2_1/c$, a = 7.165 8(8), b = 16.976 3(18), c = 16.471 8(24) Å, β = 99.80(2)°, and Z = 4; R = R' = 0.023] consists of neutral molecules with geometry intermediate between two- and three-co-ordination (Au–C 2.000, Au–N 2.136, 2.573 Å; C–Au–N 168.4°). Both complexes show *ipso* C–C–C angles much less than the ideal 120°.

The only 2,4,6-trinitrophenyl complexes of transition elements are $[Pt\{C_6H_2(NO_2)_3\text{-}2,4,6\}(NPh_2)(PPh_3)_2]$,[1] obtained by treating $[Pt(PPh_3)_4]$ with $Ph_2N\text{–}N\{C_6H_2(NO_2)_3\text{-}2,4,6\}$, and some palladium derivatives we have recently reported[2] by using $[Hg\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$ as transmetallating agent.

The use of organomercury compounds in the synthesis of carbon–metal σ-bonded organometallics has several advantages over the classical organolithium and Grignard reagents; the main one is the possibility of preparing functionalized derivatives. We have shown this by obtaining aryl derivatives of gold-(I) and -(III),[3–5] palladium(II),[2,6,7] platinum(II),[8] rhodium(III),[9] tin(IV),[10] and thallium(III)[11] most of which could not be obtained by other methods.

An additional advantage is the selectivity of the transmetallation reaction. Thus, it is very difficult to prepare partially arylated or mixed diaryl complexes using lithium or magnesium reagents. Nevertheless we have been able to synthesize[2–11] mono- or (homo- and hetero-)diaryl complexes using organomercury reagents.

In this paper we report the application of the 'organomercury route' to the synthesis of gold(I) complexes. We have previously used it to prepare *o*-, *m*-, and *p*-nitrophenylgold(I) complexes.[5a] Our interest in developing the chemistry of arylgold complexes prompted us to obtain 2,4,6-trinitrophenylgold(I) derivatives, which were expected to be even more stable than the *o*-nitrophenyl derivatives.

Results and Discussion

The compound $[Hg\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$ reacts with $[PPh_3(CH_2Ph)][AuCl_2]$ (1 : 1) in refluxing acetone to give the complex $[PPh_3(CH_2Ph)][Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}Cl]$ (**1**) [equation (1)]. However, this reaction seems to be an equilibrium that always leaves unreacted mercurial, which is very difficult to separate from (**1**) and, in addition, some decomposition to metallic gold occurs. All these problems lead to low yields of complex (**1**) (≈36%).

$$[HgR_2] + Q[AuCl_2] \longrightarrow [HgR(Cl)] + Q[AuR(Cl)] \qquad (1)$$

The most convenient way of preparing complex (**1**) is to use the same reagents in the presence of excess of NMe_4Cl. In this way the decomposition to metallic gold is not observed and, in addition, only 50% of the mercury compound is needed [equation (2)]. In practice, a 1 : 0.55 molar ratio is used and the yield is almost quantitative. This reduction in the required amount of the mercury compound is due to the symmetrization of the by-product $[Hg\{C_6H_2(NO_2)_3\text{-}2,4,6\}Cl]$ by NMe_4Cl [equation (3)].

$$\tfrac{1}{2}[HgR_2] + Q[AuCl_2] \xrightarrow{+\frac{1}{2}Cl^-} Q[AuR(Cl)] + \tfrac{1}{2}[HgCl_3]^- \qquad (2)$$

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† *Present address:* Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig, Federal Republic of Germany.

‡ Tetrakis(triphenylstibine)gold(I) bis(2,4,6-trinitrophenyl)aurate(I)–diethyl ether (1/1) and (2,9-dimethyl-1,10-phenanthroline)(2,4,6-trinitrophenyl)gold(I).

Supplementary data available: further details of the crystal structure determination have been deposited with the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, whence they may be obtained by quoting the deposition number CSD 53776, the names of the authors, and the journal reference.

$$[\mathrm{HgR(Cl)}] + \tfrac{1}{2}\mathrm{Cl}^- \longrightarrow \tfrac{1}{2}[\mathrm{HgR}_2] + \tfrac{1}{2}[\mathrm{HgCl}_3]^- \quad (3)$$

Complex (**1**) reacts with excess of both tetrahydrothiophene (tht) and $NaClO_4 \cdot H_2O$ to give $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}(tht)]$ (**2**). The related complex[5b] $[Au(C_6H_4NO_2\text{-}2)(tht)]$ could not be isolated although its solutions could be used to prepare other *o*-nitrophenyl complexes. Other complexes [AuR(tht)][12] (R = C_6F_5, C_6Cl_5, or $C_6F_3H_2$) containing polyhalogenophenyl groups decompose slowly at room temperature. Complex (**2**) melts with decomposition at 143 °C and it is stable in air at room temperature.

The greater stability of complex (**2**) could reasonably be explained by the presence of both *ortho* substituents in the aryl group, which could exert a protective effect (kinetic *ortho* effect) greater than the less bulky Cl or F substituents in the polyhalogenoaryl complexes and also greater than the unique nitro group in $[Au(C_6H_4NO_2\text{-}2)(tht)]$. In addition, the Au–C bond may be strengthened by the three electron-withdrawing NO_2 groups (thermodynamic *ortho* effect).

Tetrahydrothiophenegold(I) complexes have been used as starting compounds in the synthesis of organometallic[12,13] and co-ordination compounds[12,14] because of the facile replacement of tetrahydrothiophene. We have used it to prepare complexes of formula $[AuR(X)]^-$ (R = C_6F_5, X = C_6F_5, Cl, or Br;[12a,b] R = $C_6H_4NO_2$-2, X = CN[5b]), [AuR(L)] (R = C_6F_5[12c] or $C_6H_4NO_2$-2[5b], L = PPh_3 or $AsPh_3$), and $[AuRL_2]$ [R = C_6F_5, L = $SbPh_3$, L_2 = 1,10-phenanthroline (phen), *o*-phenylenebis(dimethylarsine) (pdma);[12c] R = $C_6H_4NO_2$-2, L = $SbPh_3$, $AsPh_3$, or phen[5b]]. We are interested in complexes of the last general formula because they could contain three-co-ordinate gold [a rare situation in the chemistry of gold(I)] and no crystal structure of an organogold complex having this co-ordination number is known. In addition, some $[AuRL_2]$ complexes with L = $SbPh_3$ (R = C_6Cl_5[12d] or $C_6H_4NO_2$-2[5b]) or $AsPh_3$ (R = $C_6H_4NO_2$-2[5b]) behave in solution as if they were in equilibrium with species $[AuL_4][AuR_2]$. Indeed, the crystal structure of the complex with L = $SbPh_3$, R = C_6F_5 reveals its ionic nature.[15]

Addition of $SbPh_3$ to a diethyl ether solution of complex (**2**) (2:1) leads to immediate precipitation of a yellow complex of stoicheiometry '$Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}(SbPh_3)_2$' (**3**) (87% yield) whose acetone solutions conduct slightly. However, even if the formula $[Au(SbPh_3)_4][Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$ is assumed, the molar conductivity (46 Ω^{-1} cm^2 mol^{-1}) is lower than expected for a 1:1 electrolyte (*ca.* 100 Ω^{-1} cm^2 mol^{-1}) and can be interpreted in terms of an equilibrium between the ionic form and some neutral species.

Addition of excess of 2,9-dimethyl-1,10-phenanthroline (dmphen) to an acetone solution of complex (**2**) gives a red precipitate of $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}(dmphen)]$ (**4**) (87% yield) which is non-conducting in acetone.

I.R. and N.M.R. Data.—Complexes (**1**)—(**4**) show bands at around 1 530vs and 1 330vs cm^{-1}, corresponding to $\nu(NO_2)$ modes. The absence of any band at around 1 270 cm^{-1} means that there is no significant interaction between the metal centre and oxygen atoms of the nitro groups.[6–9] The band corresponding to ν(AuCl) in (**1**) appears at 325m cm^{-1}, which is slightly higher than the usual values reported (290—310 cm^{-1})[5a,12] for such a bond *trans* to an aryl ligand.

Proton n.m.r. spectra of complexes (**1**)—(**4**) show a signal corresponding to both equivalent protons of the nitroaryl ligand in the range δ 8.6—8.9 with respect to $SiMe_4$. In addition, complex (**1**) exhibits a doublet (at δ 4.79) corresponding to the methylene protons of the cation, (**2**) presents two multiplets (centred at δ 3.41 and 2.22) corresponding to protons of tht, and (**3**) shows a triplet and a quartet corresponding to the presence of diethyl ether. Finally, complex (**4**) shows resonances due to the ligand dmphen appearing as an AB system (centred at δ 7.94) corresponding to protons bonded to carbon atoms C(22), C(23), C(32), and C(33) (see Figure 2) and two singlets due to protons bonded to C(26) and C(36) (δ 7.77) and to methyl groups (δ 2.99).

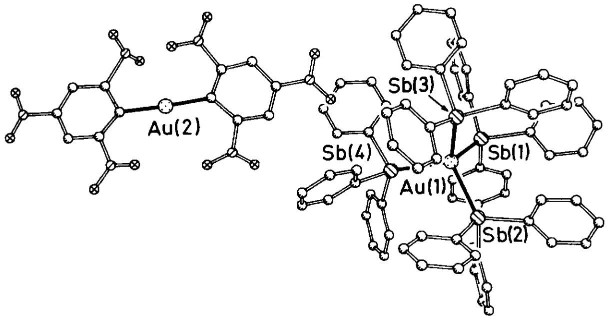

Figure 1. The formula unit of complex (**3**) in the crystal (excluding solvent of crystallization). Radii are arbitrary. For the sake of clarity, H atoms are omitted and only Au and Sb atoms are labelled. Only one orientation of the disordered nitro group is shown; the nitro group positions should be interpreted with caution (see text)

Crystal Structures of Complexes (**3**) *and* (**4**).—Complex (**3**) (Figure 1) consists in the solid state of $[Au(SbPh_3)_4]^+$ cations and $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]^-$ anions; one molecule of diethyl ether per formula unit is observed. The cation shows tetrahedral co-ordination at the gold atom, with Au–Sb bond lengths 2.647—2.655(1), av. 2.651 Å, and Sb–Au–Sb angles 107.8—111.0(1)°. The average Au–Sb bond length in $[Au(SbPh_3)_4][Au(C_6F_5)_2]$[15] is 2.640 Å. In the anion the Au–C bond lengths of 2.041(13) and 2.015(12) Å are slightly shorter than normally observed for the Au–C_6F_5 bond,[12c,15–17] although the precision of Au–C bond lengths is necessarily limited. The co-ordination geometry is essentially linear [C–Au–C 176.7(5)°]. The aromatic rings are rotated by 44° with respect to each other; they display considerable distortions, especially of bond angle, and it might seem reasonable to ascribe this to the problems in refinement (see below). However, the *ipso* C–C–C angles [108.9(11), 113.4(13)°] are much smaller than ideal sp^2 values, which is consistent with the observation of a mean *ipso* C–C–C angle of 114.7° in Au–C_6F_5 complexes[17] and also with the value of 112.9(3)° found[2] in *cis*-$[PdCl_2\{C_6H_2(NO_2)_3\text{-}2,4,6\}\{S(O)Me_2\}]^-$. The electron-withdrawing groups concentrate *p* character in the ring bonds and thus more *s* character in the Au–C bonds.

The co-ordination geometry of complex (**4**) (Figure 2) can be described as intermediate between two- and three-co-ordination; such geometry can be regarded as a compromise between the marked tendency of gold(I) to two-co-ordination and the presence of a rigid bidentate ligand.[16] The Au–N bond lengths are 2.136(3) Å to N(4) and 2.573(3) Å to N(5). The C–Au–N(4) bond angle shows considerable deviation from linearity at 168.4(1)°. Complex (**4**) is the first quasi-three-co-ordinate organogold(I) complex for which a crystal structure has been determined. A similar structure, but one closer to three-co-ordination, is that of $[Au(PPh_3)(bipy)]^+$ (bipy = 2,2′-bipyridyl)[18] which displays less unequal Au–N lengths (2.166 and 2.403 Å) and greater deviation from linearity (N–Au–P 157.1°).

Notwithstanding the increase in formal co-ordination number, the Au–C bond in (**4**) [2.000(3) Å] is shorter than those in complex (**3**). This may be due to the weaker *trans* influence of the nitrogen ligand, although the different charges of (**3**) and (**4**) could also play a role. Since this is the first crystal structure of an arylgold(I) complex with a nitrogen donor ligand, it is difficult to be more specific.

The *ipso* C–C–C bond of the aromatic ring is [as in (**3**)] much smaller than the ideal 120°; the observed value is 111.1(3)°. The comments made for (**3**) also apply here.

The Au $\cdots$ O contacts [the shortest is Au $\cdots$ O(12) 2.905 Å] are too long for any appreciable interaction [*cf.* normal Au^I–O bond lengths of about 2.05 Å [16,19]], although distances as long as 2.775(5), 2.821(5) [5b] or 2.961(4) Å [20] have been taken to indicate weak interactions. The mean N–O bond length is 1.212 Å and the mean C–N (nitro) bond length is 1.481 Å. The average values found in mono-co-ordinate *o*-nitrophenyl complexes are N–O 1.216(14) (10 values) and C–N 1.470(30) (five values), while values in chelating *o*-nitrophenyl complexes are N–O 1.217(16) (four values), N–O(M) 1.269(12) (five values), and C–N 1.405(19) (four values).[5b,6,8a,9,21] In the complex *cis*-$[PdCl_2\{C_6H_2(NO_2)_3\text{-}2,4,6\}\{S(O)Me_2\}]^-$ the av. N–O and C–N bond lengths are 1.217(7) and 1.477(5) Å, respectively.[2]

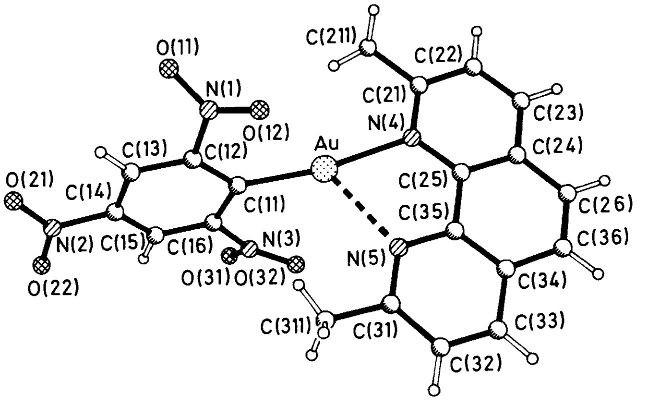

Figure 2. The molecule of complex (**4**) in the crystal, showing the atom numbering scheme. Radii are arbitrary. One H atom at C(211) is eclipsed. The longer Au–N contact is indicated by a broken bond

Experimental

Recording of i.r. spectra, the C, H, and N analyses, conductance measurements, melting point determinations, and n.m.r. spectra [at 80 MHz for (**1**), (**2**), and (**4**) and at 300 MHz for (**3**) on a Brucker AM-300 spectrometer] were performed as described elsewhere.[22] Reactions were carried out at room temperature with magnetic stirring and without special precautions against light or atmospheric moisture except where otherwise stated. Proton n.m.r. data (δ) are referenced to $SiMe_4$.

Preparations.—$[PPh_3(CH_2Ph)][Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}Cl]$ (**1**). A mixture of $[PPh_3(CH_2Ph)][AuCl_2]$ (381.4 mg, 0.61 mmol) and $[Hg\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$[23] (198.8 mg, 0.31 mmol) and NMe_4Cl (122 mg, 1.11 mmol) was refluxed in acetone (10 cm^3) for 5 h. The suspension was then concentrated to dryness and dichloromethane (10 cm^3) added. After 15 min of refluxing the suspension was filtered and the resulting solution concentrated (to 5 cm^3). Addition of ethanol (15 cm^3) gave yellow crystals of complex (**1**) (91% yield) (Found: C, 46.35; H, 3.10; Au, 25.30; N, 5.20. Calc. for $C_{31}H_{24}AuClN_3O_6P$: C, 46.65; H, 3.05; Au, 24.70; N, 5.25%). M.p. 168 °C, $\Lambda_M = 94\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^1H N.m.r. (in $CDCl_3$): δ 4.79 [d, CH_2, ^2J(H–P) 14 Hz], 7.63 (m, Ph), and 8.58 [s, $H_2C_6(NO_2)_3$].

$[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}(tht)]$ (**2**). To solid complex (**1**) (300 mg, 0.37 mmol) a solution (1.2 cm^3) of tetrahydrothiophene (1.81 mmol) in tetrahydrofuran (133.2 mg cm^{-3}) and solid $NaClO_4 \cdot H_2O$ (109.2 mg, 0.78 mmol) were added. After 30 min, diethyl ether (20 cm^3) was added, the suspension filtered, and the resulting solution concentrated (to 3 cm^3) to give yellow crystals of complex (**2**) (70% yield) (Found: C, 24.95; H, 1.95; Au,

Table 1. Details of data collection and structure refinement

Complex	(3)	(4)
Formula	$C_{88}H_{74}Au_2N_6O_{13}Sb_4$*	$C_{20}H_{14}AuN_5O_6$
M	2 304.5*	617.3
Space group	$P2_1/n$	$P2_1/c$
a/Å	12.320 5(18)	7.165 8(8)
b/Å	35.802(6)	16.976 3(18)
c/Å	19.759(3)	16.471 8(24)
β/°	102.24(2)	99.80(2)
U/Å^3	8 517	1 974.5
Z	4	4
D_c/g cm^{-3}	1.80	2.07
F(000)	4 440	1 184
μ/mm^{-1}	4.7	7.5
Crystal size (mm)	0.5 × 0.35 × 0.15	0.65 × 0.2 × 0.12
Habit	Yellow tablet	Red needle
Transmission	0.50—0.99	0.65—0.99
$2\theta_{max.}$/°	45	50
Reflections		
measured	11 209	9 287
unique	11 113	3 461
R_{int}	0.016	0.017
observed [$F > 4\sigma(F)$]	8 191	3 193
R	0.053	0.023
R'	0.051	0.023
g	0.0003	0.0001
Parameters	347	289
S	1.8	1.7
Max. shift/error	0.08	0.002
Max. electron density difference e Å^{-3}	1.6	1.2

* Including $1Et_2O$.

Table 2. Atomic co-ordinates (× 10^4) for compound (**3**)

Atom	*x*	*y*	*z*
Au(1)	5 265.1(4)	1 507.0(1)	3 937.3(2)
Au(2)	283.2(5)	623.6(2)	8 366.1(3)
Sb(1)	4 190.9(6)	1 937.4(2)	2 924.7(4)
Sb(2)	6 638.6(6)	1 056.7(2)	3 462.4(4)
Sb(3)	6 406.0(6)	1 948.2(2)	4 913.5(4)
Sb(4)	3 771.5(6)	1 110.4(2)	4 418.7(4)
C(112)	2 507(7)	1 368(3)	2 210(4)
C(113)	1 869	1 169	1 659
C(114)	1 954	1 249	982
C(115)	2 678	1 527	855
C(116)	3 316	1 726	1 406
C(111)	3 230	1 646	2 084
C(122)	4 895(6)	2 633(2)	2 201(4)
C(123)	5 538	2 836	1 829
C(124)	6 459	2 670	1 644
C(125)	6 737	2 302	1 833
C(126)	6 094	2 098	2 205
C(121)	5 173	2 264	2 389
C(132)	1 962(7)	2 354(2)	2 680(4)
C(133)	1 211	2 625	2 800
C(134)	1 529	2 884	3 332
C(135)	2 598	2 873	3 744
C(136)	3 349	2 602	3 625
C(131)	3 031	2 342	3 093
C(212)	8 714(6)	652(2)	4 315(4)
C(213)	9 299	446	4 874
C(214)	8 752	308	5 372
C(215)	7 621	377	5 311
C(216)	7 036	583	4 752
C(211)	7 583	721	4 254
C(222)	8 061(7)	1 169(2)	2 361(4)
C(223)	8 911	1 325	2 086
C(224)	9 631	1 586	2 469
C(225)	9 502	1 690	3 128
C(226)	8 652	1 534	3 403
C(221)	7 932	1 273	3 020
C(232)	4 912(7)	715(2)	2 304(5)
C(233)	4 493	479	1 747
C(234)	5 151	192	1 575
C(235)	6 229	141	1 960
C(236)	6 648	376	2 516
C(231)	5 990	663	2 688
C(312)	7 706(6)	2 348(2)	3 979(3)
C(313)	8 514	2 582	3 811
C(314)	9 275	2 761	4 335
C(315)	9 227	2 705	5 027
C(316)	8 418	2 470	5 195
C(311)	7 658	2 292	4 671
C(322)	8 049(7)	1 406(2)	5 755(3)
C(323)	8 630	1 216	6 336
C(324)	8 472	1 310	6 994
C(325)	7 731	1 594	7 070
C(326)	7 150	1 784	6 488
C(321)	7 309	1 690	5 831
C(332)	5 616(7)	2 740(2)	5 156(4)
C(333)	4 931	3 007	5 367
C(334)	4 114	2 896	5 717
C(335)	3 981	2 519	5 856
C(336)	4 665	2 252	5 645
C(331)	5 483	2 363	5 294
C(412)	1 641(7)	754(2)	3 559(4)
C(413)	1 020	494	3 112
C(414)	1 547	192	2 871
C(415)	2 695	150	3 079
C(416)	3 316	410	3 526
C(411)	2 789	712	3 766
C(422)	5 149(6)	925(2)	5 851(4)
C(423)	5 415	742	6 488
C(424)	4 818	426	6 605
C(425)	3 956	293	6 085
C(426)	3 691	476	5 448
C(421)	4 288	792	5 331
C(432)	2 329(6)	1 791(2)	4 542(4)
C(433)	1 448	1 988	4 714
C(434)	719	1 808	5 058
C(435)	871	1 431	5 230
C(436)	1 751	1 234	5 058
C(431)	2 481	1 414	4 714
C(511)	−691(11)	323(4)	8 884(7)
C(512)	−591(11)	−38(4)	9 086(7)
C(513)	−1 290(11)	−227(4)	9 452(7)
C(514)	−2 069(12)	−25(4)	9 661(8)
C(515)	−2 246(13)	332(5)	9 536(8)
C(516)	−1 544(14)	520(5)	9 131(9)
C(521)	1 255(10)	943(3)	7 899(6)
C(522)	1 677(10)	847(3)	7 305(6)
C(523)	2 362(10)	1 054(3)	6 990(6)
C(524)	2 721(10)	1 384(4)	7 287(7)
C(525)	2 354(11)	1 514(4)	7 871(7)
C(526)	1 645(11)	1 283(4)	8 124(7)
N(2)	234(12)	−273(4)	8 863(7)
O(21)	1 021(11)	−137(4)	8 681(7)
O(22)	250(13)	−607(4)	8 964(8)
N(4)	−2 851(12)	−223(4)	10 066(7)
O(41)	−2 585(11)	−533(4)	10 188(7)
O(42)	−3 513(11)	−32(4)	10 225(7)
N(6)	−1 726(15)	980(5)	8 977(11)
O(61)	−1 416(17)	1 112(6)	9 516(11)
O(62)	−2 229(17)	976(6)	8 426(11)
N(22)	1 353(10)	479(3)	6 944(7)
O(221)	1 126(15)	217(4)	7 244(7)
O(222)	1 351(11)	464(4)	6 338(7)
N(24)	3 521(10)	1 612(4)	7 007(7)
O(241)	3 708(10)	1 522(3)	6 455(6)
O(242)	3 893(9)	1 891(3)	7 327(6)
N(26)	1 310(14)	1 459(5)	8 735(9)
O(26A)*	888(24)	1 758(7)	8 637(14)
O(26B)*	1 311(23)	1 265(7)	9 211(13)
O(26C)*	1 964(17)	1 602(7)	9 176(12)
O(26D)*	333(17)	1 458(9)	8 725(15)
O(100)	5 602(19)	1 085(6)	9 531(13)
C(101)	4 711(24)	957(8)	8 980(16)
C(102)	5 038(24)	923(8)	8 378(16)
C(103)	5 587(36)	1 104(12)	10 321(25)
C(104)	6 367(34)	1 360(11)	10 578(20)

* Occupancy factor 0.5.

39.80; N, 7.55. Calc. for $C_{10}H_{10}AuN_3O_6S$: C, 24.15; H, 2.05; Au, 39.60; N, 8.45%). M.p. 143 °C (decomp.), $\Lambda_M = 0$. ^{1}H N.m.r. (in $CDCl_3$): δ 2.22, 3.41 (m, CH_2, tht), and 8.91 [s, $H_2C_6(NO_2)_3$].

[Au($SbPh_3$)$_4$][Au{$C_6H_2(NO_2)_3$-2,4,6}$_2$]. Et_2O (**3**). To a solution of $SbPh_3$ (57.5 mg, 0.16 mmol) in diethyl ether (5 cm^3), solid complex (**2**) (40.5 mg, 0.08 mmol) was added. The resulting yellow precipitate was filtered off and recrystallized (dichloromethane–diethyl ether) to give single crystals of complex (**3**) (87% yield) suitable for *X*-ray diffraction study (Found: C, 45.90; H, 3.20; Au, 17.15; N, 3.70. Calc. for $C_{88}H_{74}Au_2N_6O_{13}Sb_4$: C, 45.85; H, 3.25; Au, 17.10; N, 3.65%). M.p. 190 °C (decomp.), $\Lambda_M = 46\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^{1}H N.m.r. [in $(CD_3)_2CO$]: δ 8.73 [s, $H_2C_6(NO_2)_3$].

[Au{$C_6H_2(NO_2)_3$-2,4,6}(dmphen)] (**4**). To a solution of complex (**2**) (76 mg, 0.15 mmol) in acetone (8 cm^3) a solution of dmphen (101.3 mg, 0.49 mmol) in diethyl ether (15 cm^3) was slowly added and the precipitate filtered off and washed with acetone–diethyl ether (1:4) to give complex (**4**) as a red solid (87% yield). Single crystals suitable for *X*-ray diffraction study were obtained by slow diffusion of a diethyl ether solution of the ligand in excess into a solution of complex (**2**) in acetone (Found: C, 38.70; H, 2.10; Au, 32.05; N, 10.35. Calc. for $C_{20}H_{14}AuN_5O_6$: C, 38.90; H, 2.30; Au, 31.90; N, 11.35%). M.p. 200 °C (decomp.), $\Lambda_M = 1\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^{1}H N.m.r. (in $CDCl_3$): 2.99 (s, CH_3), 7.59, 7.69, 8.20, 8.30 [AB system, C(22)H, C(23)H, C(32)H, C(33)H; δ(A) 7.65, δ(B) 8.24, ^3J(H–H) 8.2 Hz], 7.77 [s, C(26)H, C(36) H], and 8.83 [s, $H_2C_6(NO_2)_3$].

Crystal Structure Determinations of Complexes (**3**) *and* (**4**).—Profile-fitted data [24] were collected on a Stoe–Siemens four-circle diffractometer using monochromated Mo-K_α radiation. Absorption corrections were based on ψ scans. Cell constants were refined from 2θ values of selected strong reflections in the range 20—24°.

Table 3. Atomic co-ordinates (× 10^4) for compound (**4**)

Atom	*x*	*y*	*z*
Au	1 815.6(2)	299.8(1)	2 844.7(1)
N(5)	3 288(4)	1 290(2)	3 954(2)
C(31)	3 818(5)	2 033(2)	3 902(3)
C(311)	3 972(7)	2 331(3)	3 062(3)
C(32)	4 228(6)	2 512(3)	4 607(3)
C(33)	4 109(6)	2 213(3)	5 354(3)
C(34)	3 575(5)	1 416(3)	5 429(2)
C(35)	3 151(5)	981(2)	4 701(2)
N(4)	2 069(4)	−251(2)	4 024(2)
C(21)	1 574(6)	−1 012(2)	4 067(2)
C(211)	1 131(8)	−1 475(3)	3 292(3)
C(22)	1 484(6)	−1 372(3)	4 827(2)
C(23)	1 917(5)	−955(3)	5 537(2)
C(24)	2 487(5)	−163(2)	5 510(2)
C(25)	2 569(5)	168(2)	4 741(2)
N(1)	3 937(5)	−128(2)	1 267(2)
O(11)	4 287(5)	−550(2)	718(2)
O(12)	4 807(6)	−146(3)	1 946(2)
N(2)	79(6)	1 440(2)	−856(2)
O(21)	1 096(5)	1 180(2)	−1 326(2)
O(22)	−1 187(6)	1 917(3)	−1 046(2)
N(3)	−1 680(6)	1 361(2)	1 855(3)
O(31)	−3 340(6)	1 435(3)	1 522(3)
O(32)	−1 127(6)	1 518(3)	2 564(2)
C(11)	1 233(5)	631(2)	1 664(2)
C(12)	2 311(5)	420(2)	1 058(2)
C(13)	1 981(6)	665(2)	247(2)
C(14)	468(6)	1 143(2)	1(2)
C(15)	−760(6)	1 354(2)	521(2)
C(16)	−315(5)	1 099(2)	1 330(2)
C(26)	2 972(6)	300(3)	6 240(3)
C(36)	3 479(6)	1 052(3)	6 202(2)

Table 4. Selected bond lengths (Å) and angles (°) for complex (**3**)

Au(1)–Sb(1)	2.647(1)	Au(1)–Sb(2)	2.649(1)
Au(1)–Sb(3)	2.653(1)	Au(1)–Sb(4)	2.655(1)
Au(2)–C(511)	2.041(13)	Au(2)–C(521)	2.015(12)
Sb(1)–C(111)	2.101(9)	Sb(1)–C(121)	2.119(8)
Sb(1)–C(131)	2.110(9)	Sb(2)–C(211)	2.115(8)
Sb(2)–C(221)	2.120(8)	Sb(2)–C(231)	2.108(9)
Sb(3)–C(311)	2.107(8)	Sb(3)–C(321)	2.127(8)
Sb(3)–C(331)	2.104(9)	Sb(4)–C(411)	2.122(8)
Sb(4)–C(421)	2.113(8)	Sb(4)–C(431)	2.108(8)
Sb(2)–Au(1)–Sb(1)	109.9(1)	Sb(3)–Au(1)–Sb(1)	107.8(1)
Sb(3)–Au(1)–Sb(2)	109.9(1)	Sb(4)–Au(1)–Sb(1)	108.0(1)
Sb(4)–Au(1)–Sb(2)	110.2(1)	Sb(4)–Au(1)–Sb(3)	111.0(1)
C(521)–Au(2)–C(511)	176.7(5)	C(111)–Sb(1)–Au(1)	114.6(2)
C(121)–Sb(1)–Au(1)	116.8(2)	C(121)–Sb(1)–C(111)	99.5(3)
C(131)–Sb(1)–Au(1)	121.8(2)	C(131)–Sb(1)–C(111)	100.3(3)
C(131)–Sb(1)–C(121)	100.2(3)	C(211)–Sb(2)–Au(1)	112.1(2)
C(221)–Sb(2)–Au(1)	121.0(2)	C(221)–Sb(2)–C(211)	99.8(3)
C(231)–Sb(2)–Au(1)	119.4(2)	C(231)–Sb(2)–C(211)	102.8(3)
C(231)–Sb(2)–C(221)	98.5(3)	C(311)–Sb(3)–Au(1)	118.9(2)
C(321)–Sb(3)–Au(1)	117.4(2)	C(321)–Sb(3)–C(311)	99.9(3)
C(331)–Sb(3)–Au(1)	115.9(2)	C(331)–Sb(3)–C(311)	98.4(3)
C(331)–Sb(3)–C(321)	103.1(3)	C(411)–Sb(4)–Au(1)	119.4(2)
C(421)–Sb(4)–Au(1)	119.2(2)	C(421)–Sb(4)–C(411)	100.7(3)
C(431)–Sb(4)–Au(1)	116.3(2)	C(431)–Sb(4)–C(411)	98.5(3)
C(431)–Sb(4)–C(421)	98.7(3)	C(526)–C(521)–C(522)	108.9(11)
C(516)–C(511)–C(512)	113.4(13)		

Table 5. Bond lengths (Å) and angles (°) for complex (**4**)

Au–N(5)	2.573(3)	Au–N(4)	2.136(3)	C(24)–C(25)	1.397(5)	C(24)–C(26)	1.429(6)
Au–C(11)	2.000(3)	N(5)–C(31)	1.323(5)	N(1)–O(11)	1.213(5)	N(1)–O(12)	1.185(5)
N(5)–C(35)	1.358(5)	C(31)–C(311)	1.494(6)	N(1)–C(12)	1.485(5)	N(2)–O(21)	1.232(5)
C(31)–C(32)	1.408(6)	C(32)–C(33)	1.348(7)	N(2)–O(22)	1.217(6)	N(2)–C(14)	1.479(5)
C(33)–C(34)	1.418(6)	C(34)–C(35)	1.397(5)	N(3)–O(31)	1.228(5)	N(3)–O(32)	1.198(5)
C(34)–C(36)	1.427(6)	C(35)–C(25)	1.446(5)	N(3)–C(16)	1.480(6)	C(11)–C(12)	1.407(6)
N(4)–C(21)	1.345(5)	N(4)–C(25)	1.373(4)	C(11)–C(16)	1.398(5)	C(12)–C(13)	1.382(5)
C(21)–C(211)	1.487(6)	C(21)–C(22)	1.404(6)	C(13)–C(14)	1.359(5)	C(14)–C(15)	1.377(6)
C(22)–C(23)	1.357(6)	C(23)–C(24)	1.408(6)	C(15)–C(16)	1.385(5)	C(26)–C(36)	1.331(7)
N(5)–Au–N(4)	71.3(1)	N(5)–Au–C(11)	120.0(1)	C(35)–C(25)–N(4)	119.4(3)	C(35)–C(25)–C(24)	118.8(3)
N(4)–Au–C(11)	168.4(1)	Au–N(5)–C(31)	131.6(3)	N(4)–C(25)–C(24)	121.7(3)	O(11)–N(1)–O(12)	123.1(4)
Au–N(5)–C(35)	107.8(2)	C(31)–N(5)–C(35)	119.6(3)	O(11)–N(1)–C(12)	116.8(3)	O(12)–N(1)–C(12)	120.0(4)
N(5)–C(31)–C(311)	116.8(4)	N(5)–C(31)–C(32)	121.2(4)	O(21)–N(2)–O(22)	124.8(4)	O(21)–N(2)–C(14)	116.3(4)
C(311)–C(31)–C(32)	122.0(4)	C(31)–C(32)–C(33)	119.9(4)	O(22)–N(2)–C(14)	118.9(4)	O(31)–N(3)–O(32)	123.2(5)
C(32)–C(33)–C(34)	120.0(4)	C(33)–C(34)–C(35)	116.9(4)	O(31)–N(3)–C(16)	117.1(4)	O(32)–N(3)–C(16)	119.6(4)
C(33)–C(34)–C(36)	123.1(4)	C(35)–C(34)–C(36)	120.0(4)	Au–C(11)–C(12)	124.7(3)	Au–C(11)–C(16)	124.2(3)
N(5)–C(35)–C(34)	122.3(3)	N(5)–C(35)–C(25)	118.4(3)	C(12)–C(11)–C(16)	111.1(3)	N(1)–C(12)–C(11)	120.0(3)
C(34)–C(35)–C(25)	119.2(3)	Au–N(4)–C(21)	119.1(2)	N(1)–C(12)–C(13)	114.3(3)	C(11)–C(12)–C(13)	125.8(3)
Au–N(4)–C(25)	121.7(2)	C(21)–N(4)–C(25)	119.0(3)	C(12)–C(13)–C(14)	117.7(4)	N(2)–C(14)–C(13)	119.9(4)
N(4)–C(21)–C(211)	118.8(3)	N(4)–C(21)–C(22)	121.2(3)	N(2)–C(14)–C(15)	118.0(3)	C(13)–C(14)–C(15)	122.1(3)
C(211)–C(21)–C(22)	120.0(4)	C(21)–C(22)–C(23)	120.2(4)	C(14)–C(15)–C(16)	116.8(4)	N(3)–C(16)–C(11)	120.0(3)
C(22)–C(23)–C(24)	119.7(4)	C(23)–C(24)–C(25)	118.1(3)	N(3)–C(16)–C(15)	113.6(3)	C(11)–C(16)–C(15)	126.3(4)
C(23)–C(24)–C(26)	121.9(4)	C(25)–C(24)–C(26)	119.9(4)	C(24)–C(26)–C(36)	121.2(4)	C(34)–C(36)–C(26)	120.8(4)

The structures were solved by the heavy-atom method and subjected to full-matrix least-squares refinement on *F*. Hydrogen atoms were included using a riding model. For complex (**4**) all non-H atoms were anisotropic. For (**3**), only Au and Sb were anisotropic; phenyl rings were refined as rigid groups with idealized geometry. The nitro groups displayed high thermal motion [or, at N(26) disorder] and appropriate constraints were employed. This disorder reduces the reliability of the structure determination as regards the light-atom positions. One ordered molecule of ether was located. Weighting schemes of the form $w^{-1} = \sigma^2(F) + gF^2$ were employed. Further details of the individual data collections and refinements are given in Table 1; atom co-ordinates and derived bond lengths and angles are given in Tables 2—5.

Additional material available from the Cambridge Crystallographic Data Centre comprises the atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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