Some Attempts to Prepare Five-co-ordinated Gold(III) Complexes. Crystal and Molecular Structures of $[Au(C_6H_4CH_2NMe_2\text{-}2)(phen)(PPh_3)][BF_4]_2\cdot CH_2Cl_2$, $[Au(C_6H_4CH_2NMe_2\text{-}2)(NC_9H_6O)]BF_4$, and $[Au(C_6H_4CH_2NMe_2\text{-}2)(H_2NC_6H_4S)]ClO_4$†

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Complexes $[Au(dmp)(phen)]X_2$ [dmp = 2-(dimethylaminomethyl)phenyl, phen = 1,10-phenanthroline, X = BF_4 or ClO_4] react (*i*) with PR_3 (R = Ph or C_6H_4OMe-*p*) (1:1) to give the five-co-ordinated complexes $[Au(dmp)(phen)(PR_3)][BF_4]_2$, (*ii*) with KCN (1:1) to give $[Au(dmp)(CN)(phen)]BF_4$, and (*iii*) with KCN and 1,2-bis(diphenylphosphino)ethane (dppe) to give $[Au(dmp)(CN)(dppe)]ClO_4$, which in turn reacts with [AuCl(tht)] (tht = tetrahydrothiophene) to form the gold(I)–gold(III) complex $[Au(dmp)(CN)(dppe)AuCl]ClO_4$. Complexes $[Au(dmp)(py)_2]X_2$ (py = pyridine) react with 8-hydroxyquinoline (NC_9H_6OH) or 2-aminothiophenol ($H_2NC_6H_4SH$) to form $[Au(dmp)(NC_9H_6O)]BF_4$ or $[Au(dmp)(H_2NC_6H_4S)]ClO_4$ respectively; the crystal structures of these latter complexes show square-planar co-ordination of the gold atom with the phenyl group of dmp *trans* to oxygen or nitrogen respectively. The crystal structure of $[Au(dmp)(phen)(PPh_3)][BF_4]_2\cdot CH_2Cl_2$ shows a distorted square-pyramidal co-ordination, with the basal plane containing Au and the donor atoms of dmp, PPh_3, and one phen N atom; the other N atom occupies a more distant axial position [Au–N 2.151(12), 2.154(8), and 2.627(10) Å].

Most gold(III) complexes display square-planar co-ordination. Some have been shown to possess distorted octahedral or distorted square-pyramidal geometries;[1] however, four of the donor atoms then usually adopt an almost square-planar co-ordination around the gold atom and the two or one additional axial donor atoms are at appreciably greater distances from the metal atom.

Most five-co-ordinated gold(III) complexes are of the general formula $[AuX_3(L\text{–}L)]$, where X = Cl or Br and L–L is a sterically demanding bidentate nitrogen ligand such as 2,2′-biquinolyl,[2] 2,9-dimethyl-1,10-phenanthroline,[3] or 2-(2′-pyridyl)quinoline.[4] With this type of ligand, a square-planar geometry would be possible only with a severe distortion, as has been observed[5] for (η^3-allyl)(8,8′-dimethyl-2,2′-biquinolyl)-palladium(II) perchlorate in which the palladium atom lies 1.1 Å out of the plane of the neutral ligand. In contrast, the gold atom prefers to co-ordinate the three X ligands and one of the nitrogen atoms in a plane perpendicular to that of the neutral ligand. Steric effects are thus minimized because only one halide ligand is in the plane of the bidentate ligand. If the bidentate ligand is rigid, *e.g.* 2,2′-biquinolyl or some phenanthroline derivatives, co-ordination of one N atom necessarily brings the second one within bond distance of the gold centre. However, five-co-ordination is also observed in $[AuX_3(L\text{–}L)]$ complexes where L–L is a flexible ligand such as 2-(2′-pyridyl)quinoline.[4]

We have described[6] the synthesis and crystal structure of $[Au(C_4Ph_4)(phen)Cl]$ (phen = 1,10-phenanthroline, C_4Ph_4 = 1,2,3,4-tetraphenylbuta-1,3-diene-1,4-diyl), which shows a distorted square-pyramidal geometry with a normal in-plane Au–N bond distance [2.184(4) Å] and a long axial Au–N bond [2.755(4) Å]. We have also prepared the four-co-ordinated $[Au(C_4Ph_4)(phen)]^+$ and similar complexes with 2,2′-bipyridine, 2,2′-biquinolyl, *etc.* which suggests that no steric hindrance exists between the C_4Ph_4 group and, in particular, 1,10-phenanthroline.

We thus conclude that five-co-ordination is not inevitable even when a sterically demanding bidentate ligand is used, but for gold(III) it seems that such a ligand promotes five-co-ordination even when the ligand is flexible and consistent with four-co-ordination. Further, gold(III) complexes with two strong chelating ligands (such as phen and C_4Ph_4 in the above example) can be viewed as precursors of five-co-ordinated complexes.

We have recently reported[7] the synthesis of several [2-(dimethylaminomethyl)phenyl]gold(III) complexes, including the first dicationic organogold(III) complexes $[Au(dmp)L_2]X_2$, by using the corresponding organomercurial $[Hg(dmp)_2]$ [dmp = 2-(dimethylaminomethyl)phenyl].[8] In this paper we report some attempts to prepare five-co-ordinated gold(III) complexes starting from $[Au(dmp)(phen)]X_2$ (X = ClO_4 or BF_4). We chose this complex because (*i*) the dmp group is strongly chelated to the gold centre,[7] (*ii*) phen is a rigid chelating ligand, and (*iii*) because of the high charge, neutral and anionic ligands could easily give 1:1 adducts. We also describe several attempts to prepare five-co-ordinated complexes starting from $[Au(dmp)(NC_9H_6O)]^+$ (NC_9H_6O = 8-hydroxyquinolinate) or $[Au(dmp)(H_2NC_6H_4S)]^+$ ($H_2NC_6H_4S$ = 2-aminothiophenolate).

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† [2-(Dimethylaminomethyl)phenyl-C^1,*N*](1,10-phenanthroline)(triphenylphosphine)gold(III) bis(tetrafluoroborate)–dichloromethane (1/1), [2-(dimethylaminomethyl)phenyl-C^1,*N*](8-hydroxyquinolinato-*N*,*O*)gold(III) tetrafluoroborate, and (2-aminothiophenolato-*N*,*S*)[2-(dimethylaminomethyl)phenyl-C^1,*N*]gold(III) perchlorate respectively.

Supplementary data available: further details of the crystal structure determinations have been deposited with the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, whence they may be obtained by quoting the deposition number CSD-51742, the names of the authors, and the journal reference.

Results and Discussion

Reactions of $[Au(dmp)(phen)]^{2+}$ *with Neutral Ligands.*—Addition of PPh_3 or $P(C_6H_4OMe\text{-}p)_3$ to suspensions of $[Au(dmp)(phen)][BF_4]_2$ (1:1) in acetone or dichloromethane leads instantaneously to the formation of solutions from which complexes $[Au(dmp)(phen)L][BF_4]_2$ [L = PPh_3 (**1**) or $P(C_6H_4OMe\text{-}p)_3$ (**2**)] can be isolated. The reaction between the perchlorate salt and PPh_3 gives the same cationic complex (by i.r.). If PPh_3 is added (1:1) to a solution of (**1**) no reaction is observed. We have already reported[8] several unsuccessful attempts to prepare $[Au(dmp)(PPh_3)_2]^{2+}$. The present result confirms our observation on the difficulty of co-ordinating two mutually *cis* PPh_3 ligands to a gold(III) cation.

The addition of pyridine (py) to $[Au(dmp)(phen)][BF_4]_2$ (13:1) has no effect. This is not unexpected since the complex was prepared from $[Au(dmp)(py)_2][BF_4]_2$[8] (1:1).

Reactions of $[Au(dmp)(phen)]^{2+}$ *with Anionic Ligands.*—Reactions between $[Au(dmp)(phen)]X_2$ (X = ClO_4 or BF_4) and $[PPh_3(CH_2Ph)]Cl$ (1:1) in dichloromethane do not give the expected $[Au(dmp)(phen)Cl]X$ (elemental analyses show less nitrogen than expected). Another attempt to prepare this complex by reacting $[Au(dmp)Cl(tht)]ClO_4$ (tht = tetrahydrothiophene) with 1,10-phenanthroline gave a product with elemental analyses approximately as expected, but still not analytically pure.

The reaction of $[Au(dmp)(phen)]^{2+}$ with KCN (1:1) leads to the adduct $[Au(dmp)(CN)(phen)]BF_4$ (**3**). It also reacts with KCN and 1,2-bis(diphenylphosphino)ethane (dppe) (1:1:1) giving the cationic $[Au(dmp)(CN)(dppe)]ClO_4$ (**4**). Reaction of (**4**) with [AuCl(tht)] leads to the gold(I)–gold(III) complex $[Au(dmp)(CN)(dppe)AuCl]ClO_4$ (**5**).

Synthesis and Reactivity of $[\overline{Au(dmp)(NC_9H_6O})]^+$ *and* $[\overline{Au(dmp)(H_2NC_6H_4S})]^+$.—Reactions between $[Au(dmp)(py)_2]X_2$ and 8-hydroxyquinoline or 2-aminothiophenol give complexes $[\overline{Au(dmp)(NC_9H_6O})]BF_4$ (**6**) and $[\overline{Au(dmp)(H_2NC_6H_4S})]ClO_4$ (**7**) respectively and the corresponding [Hpy]X salts.

No reaction between (**6**) or (**7**) and neutral or anionic ligands led to a new pure isolable complex; PPh_3 reacts with both complexes but mixtures were obtained that we could not separate. The same is observed with (**6**) and $[NMe_4]Cl$. Complex (**7**) does not react with $P(C_6H_{11})_3$ and its reaction with KBr leads to decomposition.

Table 1 presents analytical and other data for complexes (**1**)—(**7**).

Structures of Complexes (**1**), (**6**), *and* (**7**).—*X*-Ray structure determinations of complexes (**1**), (**6**), and (**7**) were carried out (see Experimental section). The structure of (**1**) (Figure 1) is not essentially different from that of other known five-co-ordinated complexes (see Introduction); Au, P, N(2), N(1), and C(21) form a planar unit (all deviations less than 0.1 Å) with an additional axial long Au–N bond. The mutually *trans* Au–N(2) and Au–C(21) bond lengths [2.154(8) and 2.033(11) Å respectively] are very similar to those in the complex[8] $[Au(dmp)(py)_2]^{2+}$ [2.155(9) and 2.028(11) Å respectively]. This is further evidence for minimal perturbation of the square-planar system by the additional distant ligand. A comparison of the Au–N(2) bond length with other equatorial Au–N bond distances in distorted square-pyramidal complexes containing phenanthroline or some of its derivatives, $[AuX_3(dmphen)]$ [2.08(1) (X = Cl); 2.09(1) (X = Br) Å; dmphen = 2,9-dimethyl-1,10-phenanthroline][3] or $[Au(C_4Ph_4)(phen)Cl]$ [2.184(4) Å],[6] suggests an order of *trans* influence Cl $\lesssim$ Br < aryl < C_4Ph_4. The axial Au–N bond length [2.627(10) Å] is similar to that in

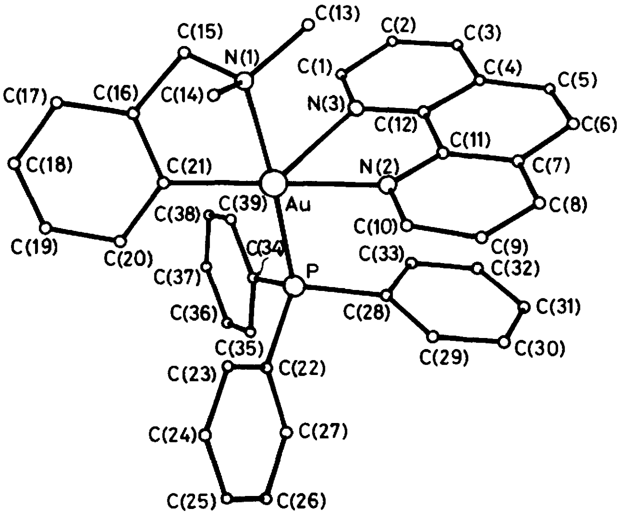

Figure 1. Perspective view of the cation of $[Au(dmp)(phen)(PPh_3)][BF_4]_2\cdot CH_2Cl_2$ (**1**) in the crystal, showing the atom-numbering scheme. Radii arbitrary; H atoms omitted for clarity

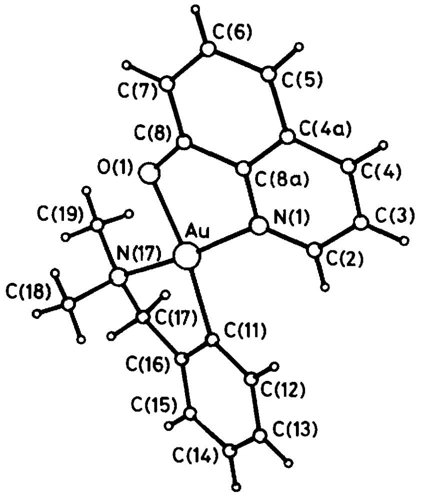

Figure 2. Perspective view of the cation of $[\overline{Au(dmp)(NC_9H_6O})]BF_4$ (**6**) in the crystal, showing the atom-numbering scheme. Radii arbitrary

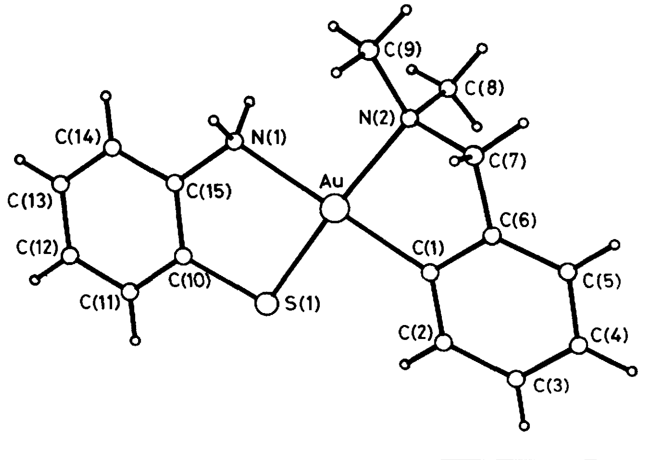

Figure 3. Perspective view of the cation of $[\overline{Au(dmp)(H_2NC_6H_4S})]ClO_4$ (**7**) in the crystal, showing the atom-numbering scheme. Radii arbitrary

Table 1. Analytical and other data for complexes (**1**)—(**7**)

Complex	M.p. (°C)	Λ_M[a]	Analysis (%)[b] C	H	N	Au	Yield (%)
(**1**) $[Au(dmp)(phen)(PPh_3)][BF_4]_2$	145	164	49.3 (49.4)	3.8 (3.7)	4.3 (4.4)	20.6 (20.8)	85
(**2**) $[Au(dmp)(phen)\{P(C_6H_4OMe\text{-}p)_3\}][BF_4]_2$	160	174	48.5 (48.6)	3.9 (4.0)	3.8 (4.0)	19.3 (19.0)	96
(**3**) $[Au(dmp)(CN)(phen)]BF_4$	125 (decomp.)	106	42.4 (42.3)	3.3 (3.2)	8.7 (9.0)	31.2 (31.6)	90
(**4**) $[Au(dmp)(CN)(dppe)]ClO_4$	170 (decomp.)	123	50.8 (50.6)	4.4 (4.2)	3.0 (3.3)	23.2 (23.0)	98
(**5**) $[Au(dmp)(CN)(dppe)AuCl]ClO_4$	120 (decomp.)	114	42.6 (42.2)	3.3 (3.5)	3.0 (2.7)	38.7 (38.4)	92
(**6**) $[Au(dmp)(NC_9H_6O)]BF_4$	190 (decomp.)	136	38.2 (38.5)	3.2 (3.2)	5.1 (5.0)	34.8 (35.0)	90
(**7**) $[Au(dmp)(H_2NC_6H_4S)]ClO_4$	185 (decomp.)	95	32.1 (32.5)	3.1 (3.3)	4.8 (5.0)	35.1 (35.5)	94

[a] In acetone solution (Ω^{-1} cm^2 mol^{-1}). [b] Calculated values are given in parentheses.

Table 2. Crystal data for $[Au(dmp)(phen)(PPh_3)][BF_4]_2 \cdot CH_2Cl_2$ (**1**), $[Au(dmp)(NC_9H_6O)]BF_4$ (**6**), and $[Au(dmp)(H_2NC_6H_4S)]ClO_4$ (**7**)

Compound	(**1**)	(**6**)	(**7**)
Formula	$C_{39}H_{35}AuB_2F_8N_3P \cdot CH_2Cl_2$	$C_{18}H_{18}AuBF_4N_2O$	$C_{15}H_{18}AuClN_2O_4S$
M	1 032.2	562.1	554.8
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	14.681(3)	8.605(3)	8.455(2)
b/Å	15.716(3)	10.799(4)	17.337(4)
c/Å	19.563(6)	11.764(4)	12.081(3)
α/°	90	105.25(2)	90
β/°	111.01(2)	109.86(2)	103.23(2)
γ/°	90	104.98(2)	90
U/Å^3	4 213	916.2	1 723.9
Z	4	2	4
D_c/g cm^{-3}	1.63	2.04	2.14
Reflections for cell constant refinement	51	46	54
Crystal form and size (mm)	Colourless prism 0.75 × 0.45 × 0.3	Yellow prism 0.35 × 0.3 × 0.1	Yellow prism 0.55 × 0.25 × 0.15
$2\theta_{max}$/°	50	50	50
μ/mm^{-1}	3.7	8.1	8.8
Transmission factors	0.60—0.95	0.53—0.95	0.51—0.97
F(000)	2 032	536	1 036
Reflections measured	8 311	3 925	3 258
Unique reflections	7 400	3 218	3 019
Observed reflections [$>4\sigma(F)$]	5 330	2 940	2 622
R	0.062	0.029	0.027
R'	0.061	0.030	0.027
g	0.0005	0.000 25	0.0002
No. of parameters	494	265	223

$[AuX_3(dmphen)]$ [2.58(1) (X = Cl); 2.61(2) (X = Br) Å][3] but shorter than reported[6] for $[Au(C_4Ph_4)(phen)Cl]$ [2.755(4) Å].

It is reasonable to propose five-co-ordination for complexes (**2**) and (**3**) on the basis of the strong chelating properties of the dmp ligand.

The diphosphine ligand in $[Au(dmp)(CN)(dppe)]ClO_4$ (**4**) is free to react with [AuCl(tht)] to give the complex $[Au(dmp)(CN)(dppe)AuCl]ClO_4$ (**5**), which shows ν(AuCl) at 330 cm^{-1} as expected for a chloro(phosphine)gold(I) complex. If the chloro-ligand were associated with the gold(III) centre ν(AuCl) should appear at 350 or 300 cm^{-1} according to the nature of the *trans* ligand.[7]

Both (**6**) and (**7**) (see Figures 2 and 3) show square-planar co-ordination of the gold atom. (Maximum deviation from mean plane of five atoms 0.08, 0.02 Å respectively.) The phenyl ring is *trans* to the oxygen atom in (**6**) and to the nitrogen atom in (**7**). By comparing the Au–NMe$_2$ bond lengths in (**1**), (**6**), (**7**), and $[Au(dmp)(py)_2]^{2+}$ [2.069(7) Å],[8] the order of *trans* influence is $-NC_9H_6O$ < py < $-SC_6H_4NH_2$ < PPh_3. The Au–C bond distances in these four complexes are relatively insensitive to the nature of the *trans* ligand [range 2.014(5)—2.033(11) Å].

Experimental

Infrared spectra were recorded over the range 4 000—200 cm^{-1} on a Perkin-Elmer 1430 spectrometer using Nujol mulls between polyethylene sheets. Conductivities were measured in 2×10^{-4}—5×10^{-4} mol dm^{-3} solutions with a Philips 9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, and N analyses were carried out by the Instituto de Química Bio-Orgánica, Barcelona (Spain). Gold was determined by ashing the samples with an aqueous solution of hydrazine. All the reactions were carried out at room temperature.

Table 3. Atom co-ordinates (× 10^4) for (**1**)

Atom	*x*	*y*	*z*
Au	4 879.8(0.3)	2 192.5(0.3)	1 918.2(0.2)
P	3 637(2)	2 241(2)	2 386(1)
N(1)	5 976(6)	2 215(6)	1 427(5)
N(2)	5 671(6)	1 298(5)	2 755(4)
N(3)	4 486(7)	626(6)	1 433(5)
C(1)	3 933(9)	312(7)	799(7)
C(2)	3 842(11)	−580(9)	668(8)
C(3)	4 312(9)	−1 115(8)	1 223(7)
C(4)	4 872(8)	−822(7)	1 907(7)
C(5)	5 371(10)	−1 314(7)	2 508(7)
C(6)	5 928(10)	−1 009(8)	3 148(7)
C(7)	6 019(8)	−95(7)	3 253(6)
C(8)	6 614(8)	264(8)	3 909(7)
C(9)	6 720(8)	1 130(8)	3 976(6)
C(10)	6 235(8)	1 603(8)	3 385(6)
C(11)	5 554(7)	440(7)	2 675(6)
C(12)	4 945(7)	88(6)	1 976(6)
C(13)	6 484(9)	1 403(8)	1 452(8)
C(14)	6 710(8)	2 874(8)	1 787(7)
C(15)	5 416(9)	2 455(8)	657(6)
C(16)	4 745(8)	3 174(8)	660(6)
C(17)	4 561(9)	3 839(9)	156(7)
C(18)	3 974(9)	4 513(8)	230(7)
C(19)	3 587(9)	4 504(7)	753(7)
C(20)	3 758(8)	3 844(6)	1 268(6)
C(21)	4 355(7)	3 177(6)	1 211(6)
C(22)	3 808(8)	3 120(6)	3 024(5)
C(23)	4 543(8)	3 716(7)	3 115(6)
C(24)	4 668(11)	4 376(8)	3 603(8)
C(25)	4 081(12)	4 414(10)	4 009(8)
C(26)	3 373(11)	3 837(9)	3 950(7)
C(27)	3 256(9)	3 172(8)	3 465(6)
C(28)	3 626(8)	1 287(7)	2 893(6)
C(29)	4 146(9)	1 254(7)	3 651(6)
C(30)	4 146(11)	501(9)	4 031(8)
C(31)	3 651(12)	−196(9)	3 667(9)
C(32)	3 139(11)	−160(8)	2 921(9)
C(33)	3 118(9)	572(8)	2 538(7)
C(34)	2 446(7)	2 266(6)	1 655(6)
C(35)	1 618(8)	2 435(9)	1 821(8)
C(36)	716(10)	2 387(12)	1 270(9)
C(37)	631(10)	2 202(9)	565(8)
C(38)	1 438(9)	2 022(8)	405(7)
C(39)	2 351(8)	2 081(8)	953(6)
C′	6 097(16)	6 586(15)	1 761(12)
Cl(1)	6 381(8)	5 480(7)	1 848(7)
Cl(2)	5 140(12)	6 115(11)	2 394(10)
B	2 495(5)	6 956(4)	99(4)
F(1)	2 915(5)	6 394(4)	−212(4)
F(2)	3 005(7)	7 011(7)	819(4)
F(3)	2 494(9)	7 723(4)	−200(7)
F(4)	1 578(5)	6 718(7)	−11(5)
B′	7 338(5)	8 831(4)	1 132(4)
F(1′)	7 114(10)	8 279(6)	578(6)
F(2′)	6 639(7)	8 815(11)	1 418(7)
F(3′)	7 413(11)	9 621(4)	903(6)
F(4′)	8 188(6)	8 614(7)	1 646(6)

Table 4. Atom co-ordinates (× 10^4) for (**6**)

Atom	*x*	*y*	*z*
Au	5 196.1(0.3)	1 908.9(0.2)	2 727.8(0.2)
O(1)	3 970(6)	1 852(5)	3 960(4)
N(1)	4 200(7)	3 387(5)	2 507(4)
C(2)	4 193(10)	4 014(7)	1 683(7)
C(3)	3 514(9)	5 077(7)	1 732(7)
C(4)	2 821(9)	5 429(7)	2 589(7)
C(4a)	2 741(7)	4 725(7)	3 428(6)
C(5)	1 965(8)	4 957(8)	4 309(7)
C(6)	1 904(9)	4 166(8)	5 043(7)
C(7)	2 565(8)	3 116(8)	4 943(6)
C(8)	3 322(8)	2 848(7)	4 100(6)
C(8a)	3 427(7)	3 684(6)	3 348(5)
C(11)	6 690(7)	1 971(6)	1 722(5)
C(12)	7 478(8)	3 078(7)	1 442(6)
C(13)	8 531(8)	2 959(8)	794(7)
C(14)	8 847(9)	1 758(9)	459(7)
C(15)	8 143(9)	661(9)	775(7)
C(16)	7 045(8)	763(7)	1 396(6)
C(17)	6 189(9)	−365(7)	1 776(6)
N(17)	5 999(7)	328(5)	2 981(5)
C(18)	7 718(10)	919(8)	4 179(6)
C(19)	4 608(10)	−729(7)	3 104(7)
B	8 869(8)	7 267(6)	2 089(5)
F(1)	8 886(16)	7 899(9)	1 264(9)
F(2)	7 289(11)	6 215(10)	1 513(10)
F(3)	8 940(13)	8 169(9)	3 165(6)
F(4)	10 183(15)	6 853(14)	2 406(14)
F(1′)	9 500(24)	6 737(19)	1 257(15)
F(2′)	7 126(11)	6 842(19)	1 421(16)
F(3′)	9 288(24)	6 749(18)	3 005(14)
F(4′)	9 701(21)	8 631(8)	2 603(18)

Table 5. Atom co-ordinates (× 10^4) for (7)

Atom	*x*	*y*	*z*
Au	1 913.5(0.2)	−80.7(0.1)	3 827.6(0.2)
Cl(1)	2 545(2)	1 002(1)	−375(1)
S(1)	1 241(2)	1 046(1)	4 555(1)
N(1)	589(5)	324(3)	2 208(4)
N(2)	2 569(5)	−1 170(2)	3 276(4)
O(1)	1 948(9)	1 674(3)	−2(5)
O(2)	2 218(7)	366(3)	276(4)
O(3)	4 237(7)	1 075(4)	−269(5)
O(4)	1 823(6)	868(3)	−1 545(4)
C(1)	3 179(6)	−466(3)	5 346(4)
C(2)	3 159(7)	−180(3)	6 413(5)
C(3)	4 104(8)	−535(3)	7 382(4)
C(4)	5 005(7)	−1 183(4)	7 284(5)
C(5)	4 992(7)	−1 481(4)	6 216(5)
C(6)	4 106(6)	−1 119(3)	5 254(4)
C(7)	4 143(7)	−1 386(3)	4 088(5)
C(8)	1 291(7)	−1 752(3)	3 392(5)
C(9)	2 765(8)	−1 186(4)	2 082(5)
C(10)	35(6)	1 455(3)	3 290(4)
C(11)	−726(7)	2 164(3)	3 344(5)
C(12)	−1 690(7)	2 468(3)	2 372(5)
C(13)	−1 951(7)	2 077(4)	1 343(5)
C(14)	−1 202(8)	1 389(4)	1 304(5)
C(15)	−215(6)	1 072(3)	2 274(4)

$[Au(dmp)(phen)(PPh_3)][BF_4]_2$ (**1**).—To a suspension of $[Au(dmp)(phen)][BF_4]_2$ (46.3 mg, 0.07 mmol) in acetone (6 cm^3) solid PPh_3 (18 mg, 0.07 mmol) was added, giving a colourless solution. After 45 min stirring, the solution was concentrated (1 cm^3) and diethyl ether (10 cm^3) added to precipitate (**1**) as a white solid, which was filtered off and washed with diethyl ether (2 × 5 cm^3). Single crystals were obtained by the liquid diffusion method, using CH_2Cl_2–light petroleum.

$[Au(dmp)(phen)\{P(C_6H_4OMe\text{-}p)_3\}][BF_4]_2$ (**2**).—To a suspension of $[Au(dmp)(phen)][BF_4]_2$ (30 mg, 0.04 mmol) in dichloromethane (6 cm^3) solid $P(C_6H_4OMe\text{-}p)_3$ (15.4 mg, 0.04 mmol) in dichloromethane was added. The resulting pale yellow

Table 6. Selected bond lengths (Å) and angles (°) for (**1**)

Au—P	2.318(4)	Au—N(1)	2.151(12)
Au—N(2)	2.154(8)	Au—N(3)	2.627(10)
Au—C(21)	2.033(11)	C(1)—N(3)	1.311(15)
C(1)—C(2)	1.424(19)	C(2)—C(3)	1.350(19)
C(3)—C(4)	1.374(18)	C(4)—C(5)	1.378(17)
C(5)—C(6)	1.317(18)	C(6)—C(7)	1.451(17)
C(7)—C(8)	1.388(16)	C(8)—C(9)	1.370(18)
C(10)—N(2)	1.305(14)	C(10)—C(9)	1.344(16)
C(11)—N(2)	1.361(14)	C(11)—C(7)	1.379(16)
C(11)—C(12)	1.448(14)	C(12)—N(3)	1.335(14)
C(12)—C(4)	1.438(16)	C(13)—N(1)	1.470(17)
C(14)—N(1)	1.478(16)	C(15)—N(1)	1.483(15)
C(15)—C(16)	1.499(19)	C(16)—C(17)	1.395(19)
C(16)—C(21)	1.391(20)	C(17)—C(18)	1.405(20)
C(18)—C(19)	1.335(23)	C(19)—C(20)	1.405(17)
C(20)—C(21)	1.397(17)	C(22)—P	1.818(11)
P–Au–N(1)	175.9(3)	P–Au–N(2)	90.4(4)
N(1)–Au–N(2)	93.7(4)	P–Au–N(3)	94.1(4)
N(1)–Au–N(3)	87.5(5)	N(2)–Au–N(3)	69.6(4)
P–Au–C(21)	94.8(5)	N(1)–Au–C(21)	81.1(5)
N(2)–Au–C(21)	169.3(4)	N(3)–Au–C(21)	119.1(4)
Au–P–C(22)	111.2(5)	Au–P–C(28)	110.7(5)
C(22)–P–C(28)	106.3(6)	Au–P–C(34)	111.2(5)
C(22)–P–C(34)	112.4(6)	C(28)–P–C(34)	104.8(6)
Au–N(1)–C(13)	115.0(10)	Au–N(1)–C(14)	109.5(9)
C(13)–N(1)–C(14)	108.5(10)	Au–N(1)–C(15)	103.0(8)
C(13)–N(1)–C(15)	110.2(11)	C(14)–N(1)–C(15)	110.4(11)
Au–N(2)–C(10)	117.7(8)	Au–N(2)–C(11)	123.1(7)
C(10)–N(2)–C(11)	118.9(10)	Au–N(3)–C(1)	132.5(8)
Au–N(3)–C(12)	108.9(7)	C(1)–N(3)–C(12)	118.6(10)
N(3)–C(1)–C(2)	121.8(12)	C(1)–C(2)–C(3)	118.7(13)
C(2)–C(3)–C(4)	122.0(13)	C(3)–C(4)–C(5)	126.3(12)
C(3)–C(4)–C(12)	115.0(11)	C(5)–C(4)–C(12)	118.6(11)
C(4)–C(5)–C(6)	124.5(12)	C(5)–C(6)–C(7)	119.3(12)
C(6)–C(7)–C(8)	121.9(11)	C(6)–C(7)–C(11)	119.7(11)
C(8)–C(7)–C(11)	118.2(11)	C(7)–C(8)–C(9)	120.3(11)
C(8)–C(9)–C(10)	117.4(11)	N(2)–C(10)–C(9)	124.8(12)
N(2)–C(11)–C(7)	120.3(10)	N(2)–C(11)–C(12)	119.8(10)
C(7)–C(11)–C(12)	119.9(11)	N(3)–C(12)–C(4)	123.8(10)
N(3)–C(12)–C(11)	118.3(10)	C(4)–C(12)–C(11)	118.0(10)
N(1)–C(15)–C(16)	108.4(11)	C(15)–C(16)–C(17)	121.6(13)
C(15)–C(16)–C(21)	117.3(11)	C(17)–C(16)–C(21)	121.1(12)
C(16)–C(17)–C(18)	117.5(14)	C(17)–C(18)–C(19)	121.1(13)
C(18)–C(19)–C(20)	122.8(13)	C(19)–C(20)–C(21)	116.9(13)
Au–C(21)–C(16)	111.4(9)	Au–C(21)–C(20)	127.7(10)
C(16)–C(21)–C(20)	120.6(11)		

solution was stirred for 1 h, concentrated (1 cm^3), and diethyl ether (19 cm^3) added to precipitate complex (**2**) as a white solid, which was filtered off and recrystallized from dichloromethane–diethyl ether.

[Au(dmp)(CN)(phen)]BF$_4$ (**3**).—To a suspension of [Au(dmp)(phen)][BF$_4$]$_2$ (60 mg, 0.1 mmol) in acetone (5 cm^3) solid KCN (6 mg, 0.1 mmol) was added. The resulting suspension was stirred for 30 min, evaporated to dryness, and the residue extracted with dichloromethane (3 × 5 cm^3). The suspension was filtered off, the solution concentrated (1 cm^3), and diethyl ether (10 cm^3) added to precipitate (**3**) as an orange solid, which was filtered off and recrystallized from acetone–diethyl ether.

Table 7. Selected bond lengths (Å) and angles (°) for (**6**)

Au–O(1)	2.067(6)	Au–N(1)	2.031(6)
Au–C(11)	2.021(7)	Au–N(17)	2.054(6)
O(1)–C(8)	1.331(10)	N(1)–C(2)	1.320(11)
N(1)–C(8a)	1.383(9)	C(2)–C(3)	1.413(13)
C(3)–C(4)	1.357(13)	C(4)–C(4a)	1.404(12)
C(4a)–C(5)	1.415(12)	C(4a)–C(8a)	1.395(10)
C(5)–C(6)	1.370(14)	C(6)–C(7)	1.389(13)
C(7)–C(8)	1.370(12)	C(8)–C(8a)	1.428(11)
C(11)–C(12)	1.391(10)	C(11)–C(16)	1.402(11)
C(12)–C(13)	1.377(12)	C(13)–C(14)	1.377(13)
C(14)–C(15)	1.386(14)	C(15)–C(16)	1.385(12)
C(16)–C(17)	1.508(11)	C(17)–N(17)	1.503(10)
N(17)–C(18)	1.484(8)	N(17)–C(19)	1.502(10)
O(1)–Au–N(1)	82.2(2)	O(1)–Au–C(11)	172.1(2)
N(1)–Au–C(11)	103.1(3)	O(1)–Au–N(17)	93.0(2)
N(1)–Au–N(17)	174.5(2)	C(11)–Au–N(17)	81.9(3)
Au–O(1)–C(8)	110.7(5)	Au–N(1)–C(2)	128.3(6)
Au–N(1)–C(8a)	111.0(5)	C(2)–N(1)–C(8a)	120.7(7)
N(1)–C(2)–C(3)	119.5(8)	C(2)–C(3)–C(4)	120.7(8)
C(3)–C(4)–C(4a)	120.4(8)	C(4)–C(4a)–C(5)	125.0(7)
C(4)–C(4a)–C(8a)	117.0(7)	C(5)–C(4a)–C(8a)	117.9(7)
C(4a)–C(5)–C(6)	119.7(8)	C(5)–C(6)–C(7)	122.1(8)
C(6)–C(7)–C(8)	120.3(8)	O(1)–C(8)–C(7)	122.9(7)
O(1)–C(8)–C(8a)	118.9(7)	C(7)–C(8)–C(8a)	118.2(7)
N(1)–C(8a)–C(4a)	121.5(7)	N(1)–C(8a)–C(8)	116.8(6)
C(4a)–C(8a)–C(8)	121.8(7)	Au–C(11)–C(12)	127.9(6)
Au–C(11)–C(16)	112.4(5)	C(12)–C(11)–C(16)	119.5(7)
C(11)–C(12)–C(13)	120.1(7)	C(12)–C(13)–C(14)	119.8(8)
C(13)–C(14)–C(15)	121.4(9)	C(14)–C(15)–C(16)	118.9(9)
C(11)–C(16)–C(15)	120.2(7)	C(11)–C(16)–C(17)	116.0(7)
C(15)–C(16)–C(17)	123.7(7)	C(16)–C(17)–N(17)	107.4(5)
Au–N(17)–C(17)	107.2(4)	Au–N(17)–C(18)	109.0(4)
C(17)–N(17)–C(18)	111.7(6)	Au–N(17)–C(19)	110.5(5)
C(17)–N(17)–C(19)	108.4(5)		

Table 8. Selected bond lengths (Å) and angles (°) for (**7**)

Au–S(1)	2.267(1)	Au–N(1)	2.138(4)
Au–N(2)	2.118(4)	Au–C(1)	2.014(5)
S(1)–C(10)	1.779(5)	N(1)–C(15)	1.475(7)
N(2)–C(7)	1.509(6)	N(2)–C(8)	1.509(8)
N(2)–C(9)	1.489(7)	C(1)–C(2)	1.386(8)
C(1)–C(6)	1.395(8)	C(2)–C(3)	1.400(7)
C(3)–C(4)	1.378(9)	C(4)–C(5)	1.387(9)
C(5)–C(6)	1.382(7)	C(6)–C(7)	1.490(8)
C(10)–C(11)	1.396(8)	C(10)–C(15)	1.369(7)
C(11)–C(12)	1.372(8)	C(12)–C(13)	1.388(9)
C(13)–C(14)	1.356(9)	C(14)–C(15)	1.387(7)
S(1)–Au–N(1)	86.9(1)	S(1)–Au–N(2)	175.6(1)
N(1)–Au–N(2)	97.1(2)	S(1)–Au–C(1)	93.5(2)
N(1)–Au–C(1)	179.4(2)	N(2)–Au–C(1)	82.4(2)
Au–S(1)–C(10)	98.9(2)	Au–N(1)–C(15)	113.0(3)
Au–N(2)–C(7)	105.8(3)	Au–N(2)–C(8)	108.8(3)
C(7)–N(2)–C(8)	108.5(4)	Au–N(2)–C(9)	114.7(3)
C(7)–N(2)–C(9)	110.4(5)	Au–C(1)–C(2)	127.7(4)
Au–C(1)–C(6)	112.8(4)	C(2)–C(1)–C(6)	119.4(4)
C(1)–C(2)–C(3)	119.6(5)	C(2)–C(3)–C(4)	120.5(5)
C(3)–C(4)–C(5)	119.8(5)	C(4)–C(5)–C(6)	120.0(6)
C(1)–C(6)–C(5)	120.6(5)	C(1)–C(6)–C(7)	117.4(4)
C(5)–C(6)–C(7)	122.0(5)	N(2)–C(7)–C(6)	109.4(5)
S(1)–C(10)–C(11)	119.3(4)	S(1)–C(10)–C(15)	121.2(4)
C(11)–C(10)–C(15)	119.4(5)	C(10)–C(11)–C(12)	119.2(5)
C(11)–C(12)–C(13)	121.3(6)	C(12)–C(13)–C(14)	118.7(5)
C(13)–C(14)–C(15)	121.0(6)	N(1)–C(15)–C(10)	119.7(4)
N(1)–C(15)–C(14)	119.9(5)	C(10)–C(15)–C(14)	120.3(5)

[Au(dmp)(CN)(dppe)]ClO$_4$ (**4**).—To a suspension of [Au(dmp)(phen)][ClO$_4$]$_2$ (40 mg, 0.06 mmol) in acetone (10 cm^3) solid KCN (3.9 mg, 0.06 mmol) and 1,2-bis(diphenylphosphino)ethane (24 mg, 0.06 mmol) were added. The resulting suspension was stirred for 3 h, and evaporated to dryness. The residue was extracted with dichloromethane, filtered off, and the solution concentrated (1 cm^3) and diethyl ether (10 cm^3) added to precipitate (**4**) as a white solid, which was filtered off and recrystallized from dichloromethane–diethyl ether.

$[\mathrm{Au(dmp)(CN)(dppe)AuCl}]\mathrm{ClO_4}$ (**5**).—To a solution of (**4**) (40 mg, 0.05 mmol) in dichloromethane (5 cm^3) solid [AuCl(tht)] (15 mg, 0.05 mmol) was added. The resulting solution was stirred for 2 h, concentrated (1 cm^3), and diethyl ether (10 cm^3) added to precipitate (**5**) as a white solid, which was filtered off and recrystallized from dichloromethane–diethyl ether.

$[\mathrm{Au(dmp)(NC_9H_6O)}]\mathrm{BF_4}$ (**6**).—To a white suspension of $[\mathrm{Au(dmp)(py)_2}][\mathrm{BF_4}]_2$ (21.3 mg, 0.03 mmol) in dichloromethane (3 cm^3) solid 8-hydroxyquinoline (4.7 mg, 0.03 mmol) was added giving a yellow solution and an orange solid. After 40 min stirring the suspension was filtered off and the resulting orange solid and yellow solution treated separately. The solid was washed with methanol (3 × 3 cm^3) and diethyl ether (3 × 5 cm^3) to give (**6**). The solution was concentrated (3 cm^3) and diethyl ether (10 cm^3) added to precipitate an orange solid which was washed with methanol (3 × 3 cm^3) and diethyl ether (3 × 5 cm^3) to give (**6**). Both fractions of (**6**) were jointly recrystallized from dichloromethane–diethyl ether. Suitable crystals for the *X*-ray diffraction study were obtained by the liquid diffusion method using dichloromethane and n-hexane.

$[\mathrm{Au(dmp)(H_2NC_6H_4S)}]\mathrm{ClO_4}$ (**7**).—To a white suspension of $[\mathrm{Au(dmp)(py)_2}][\mathrm{BF_4}]_2$ (21.3 mg, 0.03 mmol) in dichloromethane (5 cm^3) neat 2-aminothiophenol (0.05 cm^3, 0.47 mmol) was added giving a yellow suspension. After 30 min the suspension was concentrated (2 cm^3) and diethyl ether (15 cm^3) added to precipitate a yellow solid which was filtered off, washed with methanol (3 × 3 cm^3) and diethyl ether (2 × 5 cm^3) to give (**7**) as a yellow solid which was recrystallized from dichloromethane–diethyl ether. Suitable crystals for the *X*-ray diffraction study were obtained as for (**6**).

X-Ray Structure Determinations of (**1**), (**6**), *and* (**7**).—Profile-fitted[9] data were collected on a Stoe-Siemens four-circle diffractometer using monochromated Mo-K_α radiation (λ = 0.710 69 Å). Absorption corrections based on ψ-scans were applied. Cell constants were refined from $\pm 2\theta$ values of strong reflections in the range 20—23°. Structure solution by the heavy-atom method, refinement on F, program system SHELXTL (written by G. M. S.) Non-H atoms anisotropic, H atoms included using riding model with C–H 0.96 Å, H–C–H 109.5°, $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$. Crystal data are summarized in Table 2, with further details (or exceptions from the above) as follows: (**1**), $\mathrm{CH_2Cl_2}$ refined isotropically, both $\mathrm{BF_4}^-$ anions with isotropic B, B–F restrained to be equal with a weight corresponding to an e.s.d. of 0.005 Å, F···F restrained to 1.633 × B–F, e.s.d. 0.01 Å; (**6**), alternative $\mathrm{BF_4}^-$ sites (common B) refined as for (**1**) but with anisotropic major component [site occupation factor (s.o.f.) 0.7], isotropic minor component (s.o.f. 0.3, common thermal parameters for F). Final atomic co-ordinates are given in Tables 3—5, with derived bond lengths and angles in Tables 6—8.

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