Reactions of *cis*-Di-isocyanidebis(perfluorophenyl)gold(III) Complexes with Hydrazines. Crystal and Molecular Structure of *cis*-[$Au\{C(NHC_6H_4Me\text{-}p)=N\text{-}N(Ph)C(NHC_6H_4Me\text{-}p)\}(C_6F_5)_2$] †

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Addition of CNR (R = Ph or *p*-tolyl) to solutions of *cis*-[$Au(C_6F_5)_2(OEt_2)_2$]ClO_4 leads to *cis*-[$Au(C_6F_5)_2(CNR)_2$]ClO_4, which reacts (*a*) with NHPhNHPh to give the cationic complexes [$Au\{C(NHR)N(Ph)N(Ph)C(NHR)\}(C_6F_5)_2$]$ClO_4$, which readily undergo deprotonation to form [$Au\{C(=NR)N(Ph)N(Ph)C(NHR)\}(C_6F_5)_2$], and (*b*) with NH_2NHR' (R′ = H or Ph) to give [$Au\{C(NHR)=N\text{-}N(R')C(NHR)\}(C_6F_5)_2$]. The structure of [$Au\{C(NHC_6H_4Me\text{-}p)=N\text{-}N(Ph)C(NHC_6H_4Me\text{-}p)\}(C_6F_5)_2$] has been determined by *X*-ray diffraction [space group $P2_1/c$, with a = 12.230(2), b = 20.276(3), c = 13.123(2) Å, β = 101.21(2)°, R = 0.036 for 5 822 reflections].

Hydrazines have frequently been used as reductants in the synthesis of isocyanide complexes of metals in low oxidation states.[1] However, in the reaction with [$M(CNMe)_4$]$^{2+}$ (M = Pd or Pt) [2–4] or [$Fe(CNMe)_6$]$^{2+}$,[5,6] two *cis*-isocyanide ligands undergo nucleophilic attack with the formation of a metallacyclic carbene [$M\{C(NHMe)N(R)N(H)C(NHMe)\}$]$^{n+}$ (R = H, Me, or Ph), which can readily be deprotonated [2] to give [$M\{C(=NMe)N(R)N(H)C(NHMe)\}$]$^{(n-1)+}$. Analogous organogold(III) complexes were until now unknown, because of the non-existence of gold isocyanide complexes with mutually *cis* isocyanide ligands. In the present paper we describe the preparation of complexes of the form *cis*-[$Au(C_6F_5)_2(CNR)_2$]ClO_4 (R = Ph or *p*-tolyl), and their reaction with NHR′–NHR″ (R′, R″ = H or Ph), to give cationic complexes, [$Au\{C(NHR)N(Ph)N(Ph)C(NHR)\}(C_6F_5)_2$]$ClO_4$, or neutral derivatives, [$Au\{C(=NR)N(Ph)N(Ph)C(NHR)\}(C_6F_5)_2$] and [$Au\{C(NHR)=N\text{-}N(R')C(NHR)\}(C_6F_5)_2$].

Results and Discussion

Addition of $AgClO_4$ to a suspension of *cis*-[NBu_4][$Au(C_6F_5)_2Cl_2$] [7] in diethyl ether leads (after removal of the precipitated AgCl and [NBu_4]ClO_4) to colourless solutions, which are stable at room temperature, and which we assume to contain *cis*-[$Au(C_6F_5)_2(OEt_2)_2$]$^+$. Addition of CNR (R = Ph or *p*-tolyl) allows the isolation of the corresponding cationic bis(isocyanide) complexes *cis*-[$Au(C_6F_5)_2(CNR)_2$]ClO_4 [R = Ph (1) or *p*-tolyl (2)] [equation (i)].

$$cis\text{-}[NBu_4][Au(C_6F_5)_2Cl_2] + 2\ AgClO_4 \xrightarrow[-\ 2\ AgCl,\ -\ [NBu_4]ClO_4]{OEt_2}$$
$$cis\text{-}[Au(C_6F_5)_2(OEt_2)_2]ClO_4 \xrightarrow{CNR}$$
$$cis\text{-}[Au(C_6F_5)_2(CNR)_2]ClO_4 \qquad \text{(i)}$$
$$R = Ph\ (1)\ \text{or}\ p\text{-tolyl}\ (2)$$

Complexes (1) and (2) are white solids, which are air- and moisture-stable at room temperature, and are conducting in acetone solution (1 : 1 electrolytes, see Table 1). The *cis* configuration of the two C_6F_5 groups is confirmed [7,8] by the presence of two i.r. bands at 825m and 815m cm^{-1}. The ν(C–N) vibration appears also as a double band at 2 280m and 2 270m cm^{-1} for (1), and 2 290m and 2 270m cm^{-1} for (2), in accordance with the *cis* configuration of the two isocyanide ligands. Two absorptions at 1 100s, br and 620m cm^{-1} indicate the presence of the perchlorate anion.[9]

Hydrazobenzene adds to the two isocyanide groups of complexes (1) and (2) with the formation of cyclic double carbenes, as shown in equation (ii). The resulting complexes (3) and (4) are white solids, which are conducting in acetone solution. Their ionic character is also indicated by the presence of two absorptions at 1 100s, br and 620m cm^{-1} (ClO_4^-). Other vibrations at 3 250w [ν(NH)], 1 640m, 1 605m [δ(NH)], and 1 550s cm^{-1} [ν(CN)] are characteristic of carbenes.[10]

Complexes (3) and (4) can readily be deprotonated by passing a dichloromethane solution through a layer (2 cm) of alumina or by treatment with an aqueous solution of ammonia or NaOH [equation (iii)]. The resulting pale yellow complexes (5) and (6) are stable at room temperature and are non-conducting in acetone solution (Table 1).

The reaction of complexes (1) and (2) with hydrazine or phenylhydrazine takes a different course. Their addition to dichloromethane solutions of *cis*-[$Au(C_6F_5)_2(CNR)_2$]ClO_4 causes an instantaneous change of colour from colourless to yellow. The deep yellow products (7)—(10) do not contain perchlorate and are non-conducting in acetone solution (Table 1) [equation (iv)].

The structure of complex (10) has been determined by single-crystal *X*-ray diffraction methods (see later). The gold atom exhibits a distorted square-planar co-ordination, probably because of the rigidity of the five-membered ring [C(1)–Au–C(2), 77.5°]. Of the two possible structures (A) or (B) (shown below) [the latter is similar to complexes (5) and (6)] the *X*-ray structure (Figure) confirms possibility (A); of the C–N bond lengths, C(1)–N(2) [1.294(7) Å] is the shortest and C(1)–N(1) [1.360(7) Å] the longest. The Au–C distances

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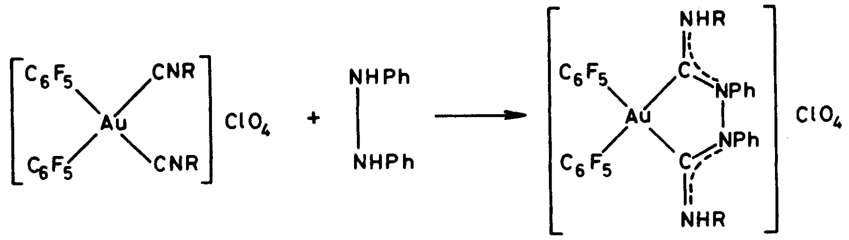
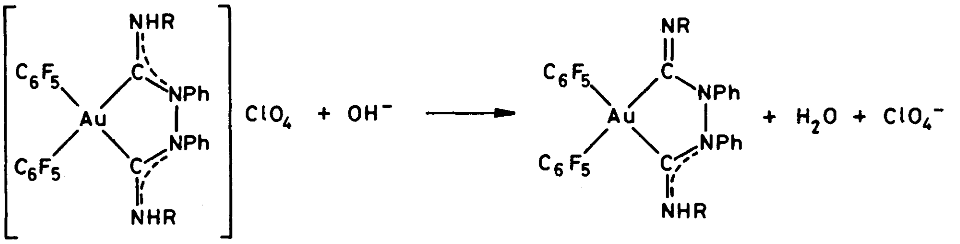
† Bis(perfluorophenyl)[3-phenyl-1,4-bis(*p*-toluidino)-2,3-diazabut-1-en-1-yl-4-ylidene]gold.

Supplementary data available (No. SUP 23986, 49 pp.): anisotropic and isotropic thermal parameters, H-atom co-ordinates, full bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



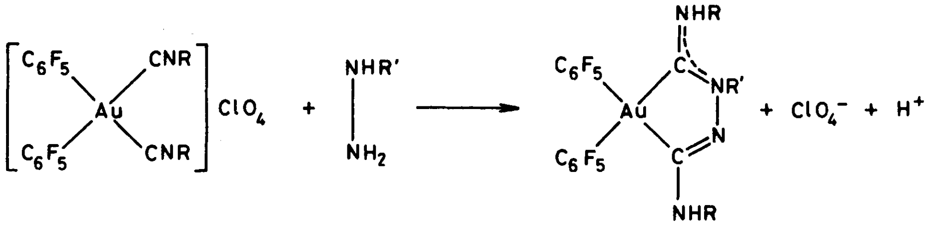
(ii)

R = Ph(3) or *p*-tolyl (4)



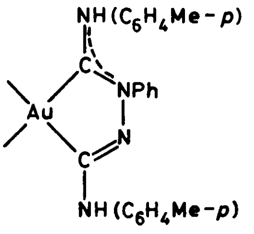
(iii)

R = Ph(5) or *p*-tolyl (6)

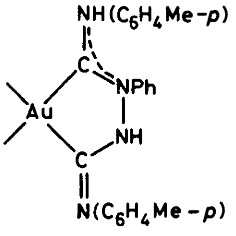


(iv)

R′ = H; R = Ph(7) or *p*-tolyl (8)
R′ = Ph; R = Ph(9) or *p*-tolyl (10)



(A)



(B)

to the C_6F_5 groups (mean 2.082 Å) are comparable with those found for other gold(III) complexes [2.085 and 2.065 Å for [Au(C_6F_5)$_3$(pdma)] [pdma = *o*-phenylenebis(dimethylarsine][11]] and marginally longer than those found for gold(I) derivatives {2.051 Å for [Au(C_6F_5)$_2$]$^-$ [12] and 2.07 Å for [Au(C_6F_5)(PPh$_3$)] [13]}. The Au–C(21) bond [2.097(5) Å] is longer than Au–C(11) [2.067(6) Å], indicating that the *trans* influence of the imidoyl C atom is stronger than that of the carbene C atom.

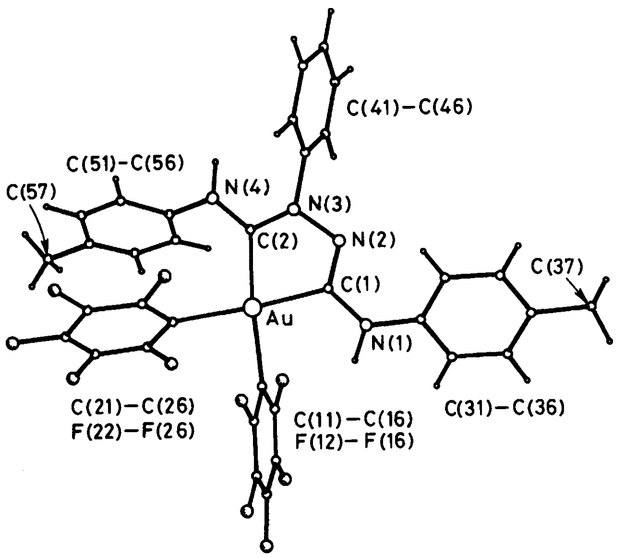


Figure. Perspective view of the molecule of (10), showing the atom-numbering scheme. Selected deviations of atoms from the mean plane of the atoms bound to Au are as follows (Å): C(31) 0.34, N(1) 0.14, C(1) 0.12, N(2) 0.37, N(3) 0.24, C(41) 0.34, C(2) −0.12, N(4) −0.38, C(51) −1.09, Au −0.07, C(11) −0.11, and C(21) 0.11

Experimental

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in *ca.* 5 × 10^{-4} mol dm^{-3} acetone solutions with a Philips 9501/01 conductimeter. Molecular weights were determined in chloroform solution with a Hitachi–Perkin-Elmer 115 osmometer. Carbon, N, and H analyses were carried out with a Perkin-Elmer 240 microanalyser, gold analyses by ashing in a crucible with aqueous hydrazine.

All reactions were run at room temperature.

Table 1. Physical data for complexes (1)—(10)

Complex	M.p. [a] (°C)	Λ_M [b] (Ω^{-1} cm^2 mol^{-1})	M [c] Found (calc.)
(1) *cis*-$[Au(C_6F_5)_2(CNPh)_2]ClO_4$	130 (d)	157	—
(2) *cis*-$[Au(C_6F_5)_2(CNC_6H_4Me\text{-}p)_2]ClO_4$	120 (d)	134	—
(3) $[Au\{C(NHPh)N(Ph)N(Ph)C(NHPh)\}(C_6F_5)_2]ClO_4$	115 (d)	115	—
(4) $[Au\{C(NHC_6H_4Me\text{-}p)N(Ph)N(Ph)C(NHC_6H_4Me\text{-}p)\}(C_6F_5)_2]ClO_4$	115 (d)	129	—
(5) $[Au\{C(=NPh)N(Ph)N(Ph)C(NHPh)\}(C_6F_5)_2]$	140 (d)	2	928 (920)
(6) $[Au\{C(=NC_6H_4Me\text{-}p)N(Ph)N(Ph)C(NHC_6H_4Me\text{-}p)(C_6F_5)_2]$	145 (d)	3	960 (949)
(7) $[Au\{C(NHPh)=N\text{-}N(H)C(NHPh)\}(C_6F_5)_2]$	190 (d)	3	780 (768)
(8) $[Au\{C(NHC_6H_4Me\text{-}p)=N\text{-}N(H)C(NHC_6H_4Me\text{-}p)\}(C_6F_5)_2]$	175	2	810 (796)
(9) $[Au\{C(NHPh)=N\text{-}N(Ph)C(NHPh)\}(C_6F_5)_2]$	190 (d)	2	820 (844)
(10) $[Au\{C(NHC_6H_4Me\text{-}p)=N\text{-}N(Ph)C(NHC_6H_4Me\text{-}p)\}(C_6F_5)_2]$	220 (d)	1	943 (872)

[a] d = Decomposition. [b] In acetone. [c] In chloroform.

Table 2. Atom co-ordinates ($\times 10^4$) for complex (10)

Atom	*X/a*	*Y/b*	*Z/c*
Au	4 874(1)	6 127(1)	3 261(1)
C(1)	6 285(4)	6 445(2)	4 254(3)
C(2)	5 944(4)	5 346(2)	3 266(3)
N(1)	6 309(3)	7 023(2)	4 782(3)
N(2)	7 192(3)	6 111(2)	4 280(3)
N(3)	6 963(3)	5 508(2)	3 713(3)
N(4)	5 763(3)	4 744(2)	2 852(3)
C(11)	3 899(4)	6 939(2)	3 422(4)
C(12)	3 338(4)	6 958(3)	4 231(4)
C(13)	2 587(5)	7 451(3)	4 329(4)
C(14)	2 404(5)	7 944(3)	3 609(5)
C(15)	2 980(5)	7 953(2)	2 812(4)
C(16)	3 704(4)	7 450(2)	2 743(4)
C(21)	3 613(4)	5 831(2)	2 026(3)
C(22)	2 545(4)	5 685(2)	2 112(4)
C(23)	1 742(4)	5 486(3)	1 287(4)
C(24)	2 021(5)	5 437(3)	332(4)
C(25)	3 069(5)	5 578(3)	208(4)
C(26)	3 845(4)	5 781(3)	1 046(4)
F(12)	3 495(3)	6 479(2)	4 956(2)
F(13)	2 022(3)	7 440(2)	5 115(3)
F(14)	1 639(3)	8 410(2)	3 668(3)
F(15)	2 815(3)	8 444(2)	2 123(3)
F(16)	4 247(3)	7 466(2)	1 928(2)
F(22)	2 241(2)	5 720(2)	3 050(2)
F(23)	718(3)	5 333(2)	1 412(3)
F(24)	1 254(3)	5 227(2)	−489(2)
F(25)	3 336(3)	5 523(2)	−743(2)
F(26)	4 884(3)	5 919(2)	892(3)
C(31)	7 218(4)	7 330(2)	5 443(4)
C(32)	6 978(5)	7 749(3)	6 207(4)
C(33)	7 834(5)	8 062(3)	6 886(5)
C(34)	8 935(5)	7 963(3)	6 819(5)
C(35)	9 153(5)	7 561(3)	6 046(5)
C(36)	8 312(4)	7 239(2)	5 359(4)
C(37)	9 872(6)	8 274(4)	7 603(6)
C(41)	7 910(4)	5 071(2)	3 817(3)
C(42)	8 478(4)	5 019(3)	3 009(4)
C(43)	9 368(5)	4 595(3)	3 109(4)
C(44)	9 683(5)	4 229(3)	3 995(5)
C(45)	9 112(5)	4 287(3)	4 794(4)
C(46)	8 210(4)	4 709(3)	4 703(4)
C(51)	4 686(4)	4 434(2)	2 575(4)
C(52)	3 993(4)	4 393(2)	3 279(4)
C(53)	2 971(5)	4 095(3)	2 996(5)
C(54)	2 600(5)	3 840(2)	2 021(4)
C(55)	3 336(5)	3 874(3)	1 330(5)
C(56)	4 361(5)	4 164(3)	1 610(4)
C(57)	1 460(5)	3 548(3)	1 687(6)

Preparation of the Complexes.—*cis*-$[Au(C_6F_5)_2(CNR)_2]ClO_4$ [R = Ph (1) *or* p-*tolyl* (2)]. To a suspension of *cis*-$[NBu_4][Au(C_6F_5)_2Cl_2]$ [7] (0.844 g, 1 mmol) in diethyl ether (20 cm^3) was added $AgClO_4$ (0.415 g, 2 mmol); the mixture was stirred for 2 h in the dark, and AgCl and $[NBu_4]ClO_4$ then filtered off. Addition of CNR [14] (R = Ph or *p*-tolyl) (2 mmol) to the filtrate precipitated the white complexes (1), yield 80% (Found: C, 36.95; H, 1.2; Au, 22.9; N, 3.6. $C_{26}H_{10}AuClF_{10}N_2O_4$ requires C, 37.3; H, 1.2; Au, 23.5; N, 3.35%) or (2), yield 82% (Found: C, 39.35; H, 2.0; Au, 22.4; N, 3.3. $C_{28}H_{14}AuClF_{10}N_2O_4$ requires C, 38.9; H, 1.65; Au, 22.7; N, 3.25%).

$[Au\{C(NHR)N(Ph)N(Ph)C(NHR)\}(C_6F_5)_2]ClO_4$ [R = Ph (3) *or* p-*tolyl* (4)]. To a solution of (1) or (2) (0.2 mmol) in dichloromethane (15 cm^3) was added hydrazobenzene (0.037 g, 0.2 mmol); the mixture was stirred for 5 d. A slight turbidity was removed by filtration through Kieselguhr (1 cm). Partial concentration to *ca.* 8 cm^3 and addition of hexane (20 cm^3) led to the precipitation of the white complexes (3), yield 49% (Found: C, 44.85; H, 2.55; Au, 19.2; N, 5.25. $C_{38}H_{22}AuClF_{10}N_4O_4$ requires C, 44.7; H, 2.15; Au, 19.3; N, 5.5%) or (4), yield 51% (Found: C, 45.95; H, 2.65; Au, 18.95; N, 4.95. $C_{40}H_{26}AuClF_{10}N_4O_4$ requires C, 45.8; H, 2.5; Au, 18.8; N, 5.35%).

$[Au\{C(=NR)N(Ph)N(Ph)C(NHR)\}(C_6F_5)_2]$ [R = Ph (5) *or* p-*tolyl* (6)]. A solution of (3) or (4) (0.2 mmol) in dichloromethane was filtered through a layer (2 cm) of alumina. Con-

Table 3. Bond lengths (Å) and angles (°) for complex (10)

Au–C(1)	2.053(5)	Au–C(2)	2.053(6)
Au–C(11)	2.067(6)	Au–C(21)	2.097(5)
C(1)–N(1)	1.360(7)	C(1)–N(2)	1.294(7)
C(2)–N(3)	1.312(7)	C(2)–N(4)	1.336(7)
N(2)–N(3)	1.431(6)	C(31)–N(1)	1.414(7)
C(41)–N(3)	1.443(7)	C(51)–N(4)	1.441(7)

C(1)–Au–C(2)	77.5(3)	C(1)–Au–C(11)	96.6(3)
C(2)–Au–C(11)	173.5(3)	C(1)–Au–C(21)	169.0(3)
C(2)–Au–C(21)	98.8(3)	C(11)–Au–C(21)	87.4(3)
Au–C(1)–N(1)	121.7(4)	Au–C(1)–N(2)	117.6(4)
N(1)–C(1)–N(2)	120.2(5)	Au–C(2)–N(3)	111.0(4)
Au–C(2)–N(4)	130.4(4)	N(3)–C(2)–N(4)	118.5(5)
C(1)–N(1)–C(31)	128.9(5)	C(1)–N(2)–N(3)	110.6(5)
C(2)–N(3)–N(2)	121.3(5)	C(2)–N(3)–C(41)	124.4(5)
N(2)–N(3)–C(41)	113.7(4)	C(2)–N(4)–C(51)	124.9(5)
Au–C(11)–C(12)	119.2(5)	Au–C(11)–C(16)	124.9(5)
Au–C(21)–C(22)	124.7(5)	Au–C(21)–C(26)	119.4(4)
N(1)–C(31)–C(32)	117.4(6)	N(1)–C(31)–C(36)	123.5(6)
N(3)–C(41)–C(42)	119.3(5)	N(3)–C(41)–C(46)	119.3(5)
N(4)–C(51)–C(52)	120.7(5)	N(4)–C(51)–C(56)	119.7(6)

centration to *ca.* 8 cm^3 and addition of hexane (20 cm^3) led to the yellow complexes (5), yield 80% (Found: C, 48.95; H, 2.3; Au, 21.0; N, 6.0. $C_{38}H_{21}AuF_{10}N_4$ requires C, 49.6; H, 2.3; Au, 21.4; N, 6.1%) or (6), yield 78% (Found: C, 50.8; H, 3.0; Au, 21.2; N, 5.4. $C_{40}H_{25}AuF_{10}N_4$ requires C, 50.65; H, 2.65; Au, 20.75; N, 5.9%).

$[\mathrm{Au}\{\overline{\mathrm{C(NHR)=N{-}N(R')C}}\mathrm{(NHR)}\}(C_6F_5)_2]$ [R′ = H; R = Ph (7) *or* p-*tolyl* (8); R′ = Ph, R = Ph (9), *or* p-*tolyl* (10)]. To a solution of (1) or (2) (0.2 mmol) in dichloromethane (15 cm^3) was added an aqueous solution of hydrazine or phenylhydrazine (0.2 mmol). The resulting yellow solution was stirred for 24 h and the slight turbidity was filtered off. The filtrate was concentrated to *ca.* 8 cm^3, and hexane was added to precipitate the yellow complexes (7), yield 45% (Found: C, 40.55; H, 2.05; Au, 24.8; N, 7.05. $C_{26}H_{13}AuF_{10}N_4$ requires C, 40.65; H, 1.7; Au, 25.65; N, 7.3%), (8), yield 30% (Found: C, 42.5; H, 2.2; Au, 22.35; N, 7.3. $C_{28}H_{17}AuF_{10}N_4$ requires C, 42.25; H, 2.15; Au, 22.35; N, 7.05%), (9), yield 39% (Found: C, 45.5; H, 2.1; Au, 24.05; N, 6.35. $C_{32}H_{17}AuF_{10}N_4$ requires C, 45.5; H, 2.05; Au, 23.3; N, 6.65%), or (10), yield 44% (Found: C, 47.1; H, 2.55; Au, 23.1; N, 6.2. $C_{34}H_{21}AuF_{10}N_4$ requires C, 46.8; H, 2.4; Au, 22.55; N, 6.4%).

Crystal Data for (10).—$C_{34}H_{21}AuF_{10}N_4$, $M = 872.52$, monoclinic, space group $P2_1/c$, $a = 12.230(2)$, $b = 20.276(3)$, $c = 13.123(2)$ Å, $\beta = 101.21(2)$°, $U = 3\,192$ Å^3, $Z = 4$, $F(000) = 1\,688$, $D_c = 1.82$ g cm^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.720\,69$ Å $\mu(\text{Mo-}K_\alpha) = 4.7$ mm^{-1}, crystal size 0.5 × 0.25 × 0.25 mm.

A Stoe-Siemens four-circle diffractometer was used to measure 7 334 profile-fitted [15] intensities in the range $7 < 2\theta < 55°$. After Lorentz polarisation and empirical absorption corrections, averaging equivalents gave 7 310 unique reflections, 5 822 of which with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL, written by G. M. S.). Cell constants were refined from 2θ values of 40 reflections in the range 20—23°.

The gold atom was located from the Patterson function and C, N, and F atoms in a subsequent difference synthesis. After anisotropic refinement of these atoms, all H atoms except those at C(45) and C(37) appeared in a difference synthesis, thus confirming the structure (A) (see above). Isotropic H atoms were included in the refinement using a riding model, with X–H (X = C or N) 0.96 Å, H–C–H 109.5°, $U(\mathrm{H}) = 1.2\,U_{\mathrm{iso}}(X)$. The final R was 0.036, with $R' = 0.034$ [weighting scheme $w^{-1} = \sigma^2(F) + 0.0002\,F^2$]. A final difference map showed no features >0.9 e Å^{-3}. Final atomic co-ordinates and derived parameters are given in Tables 2 and 3.

References

1 L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley, New York, 1969.
2 A. Burke, A. L. Balch, and J. H. Enemark, *J. Am. Chem. Soc.*, 1970, **92**, 2255.
3 W. M. Butler and J. H. Enemark, *Inorg. Chem.*, 1971, **10**, 2416.
4 G. Rouschias and B. L. Shaw, *Chem. Commun.*, 1970, 183; *J. Chem. Soc. A*, 1971, 2097.
5 A. L. Balch and J. Miller, *J. Am. Chem. Soc.*, 1972, **94**, 417.
6 D. H. Cuatecontzi and J. D. Miller, *Inorg. Chim. Acta*, 1980, **38**, 157.
7 R. Usón, A. Laguna, J. García, and M. Laguna, *Inorg. Chim. Acta*, 1979, **37**, 201.
8 R. Usón, J. Forniés, P. Espinet, F. Martínez, and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1981, 463.
9 B. J. Hathaway and A. F. Underhill, *J. Chem. Soc.*, 1961, 3091.
10 R. Usón, A. Laguna, J. Vicente, J. García, B. Bergareche, and P. Brun, *Inorg. Chim. Acta*, 1978, **28**, 237.
11 R. Usón, A. Laguna, M. Laguna, E. Fernandez, P. G. Jones, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1982, 1971.
12 R. Usón, A. Laguna, J. Vicente, J. García, P. G. Jones, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 655.
13 R. W. Baker and P. Pauling, *J. Chem. Soc., Dalton Trans.*, 1972, 2264.
14 W. P. Weber, G. W. Gokel, and I. K. Ugi, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 530.
15 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

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