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Syntheses and Crystal Structures (No Au-H Interactions) of Luminescent $[Au_2(dppm)_2][BH_3CN]_2$ and of $[Au_2(dppm)_2(I)][Au(CN)_2]$ and $[Au_2(dppm)_2(S_2CNEt_2)][BH_3CN]$

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Digold(I) complexes containing three-coordinate gold have been prepared from $[Au_2(dppm)_2][BH_3CN]_2$ (**1**) (dppm = bis(diphenylphosphino)methane). This luminescent compound, prepared by addition of BH_3CN^- to a mixture of dppm and $Au(PPh_3)NO_3$, shows no Au···H or Au···N interaction in the solid state. The reaction of **1** with NaI gave $[Au_2(dppm)_2(I)][BH_3CN]$ (**2**), which decomposed during crystallization to give the complex $[Au_2(dppm)_2(I)][Au(CN)_2]$ (**3**), containing an asymmetrically bridging iodide. The reaction of **1** with NaS_2CNEt_2 gave $[Au_2(dppm)_2(S_2CNEt_2)][BH_3CN]$ (**4**), containing a nearly symmetrically bridging dithiocarbamate ligand with long Au-S bonds. The structures of **1**, **3**, and **4** are presented. Compound **1**·$2CH_2Cl_2$ crystallized in the space group $P2_1/n$, with a = 11.959 (10) Å, b = 13.943 (8) Å, c = 17.750 (10) Å, β = 107.86 (5)°, and V = 2817 (3) Å^3. Compound **3** crystallized in the space group $P2_1/c$, with a = 15.713 (7) Å, b = 14.711 (3) Å, c = 21.888 (3) Å, β = 93.86 (3)°, and V = 5048 (3) Å^3. Compound **4** crystallized in the space group $P1$ (No. 1), with a = 11.252 (1) Å, b = 11.844 (2) Å, c = 12.165 (2) Å, α = 94.99 (1)°, β = 116.19 (1)°, γ = 106.99 (1)°, and V = 1346.4 (4) Å^3.

Introduction

Some *neutral*, binuclear gold(I) compounds, such as $[Au_2(\mu\text{-}(CH_2)_2PR_2)_2]$, R = alkyl or aryl, can be oxidized to gold(II) compounds,[1] such as $[Au_2(\mu\text{-}(CH_2)PMe_2)_2I_2]$.[2] In contrast, *dicationic*, binuclear gold(I) compounds, such as $[Au_2(dppm)_2]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$), have not been reported to give isolable gold(II) compounds. Because of the 2+ charge, such Au^I_2 compounds are expected to be harder to oxidize and easier to reduce. In an attempt to either reduce $[Au_2(dppm)_2]^{2+}$ or observe a B-H···Au interaction, BH_3CN^- was used as a counterion. The luminescence noted for the cation and some of its complexes[3] also dictated the need for additional study of this system.

Another characteristic of these dicationic binuclear compounds is that, unlike the gold ylides, they form three-coordinate gold(I) compounds. In $[Au_2(dppm)_2Cl_2]$ one chloride is associated with one of the metal atoms, forming an Au-Au-Cl angle of 97°; the other chloride forms a similar angle with the other metal atom, but on the opposite side of the Au_2P_4 plane.[4] The dibromide compound has a similar structure.[5] In $[Au_2(dppm)_2I]I$ the coordinated iodide symmetrically bridges the two metals.[5] This compound was formed serendipitously upon addition of CH_3I to $[Au_2(Ph_2PCHPPh_2)_2]$. Here we report the synthesis of two other compounds containing an associated iodide.

Side-on coordination of chloride is also found in[6] $[Au_2(Ph_2PC(=CH_2)PPh_2)_2Cl]Cl$ and in[7] $[Au_2(Ph_2PC(CH_2CH_2)PPh_2)_2Cl]Cl$, which have only one weakly coordinated chloride (Au-Au-Cl = 96 and 75°, respectively). The P-Au-P angle in these side-associated complexes is nonlinear, ranging from 155 to 171°. In $[Au_2(Ph_2PCH(CH_2OCH_3)PPh_2)_2Cl]Cl$ the coordinated chloride is in an axial position (Au-Au-Cl = 176°).[7] The coordinated chloride in these complexes interacts only weakly with the metal, as shown by the long Au···Cl distances, which range from 2.72 to 2.96 Å (Au···Cl = 2.28 Å in PPh_3AuCl and 2.50 Å in $(Ph_3P)_2AuCl$).[8] The halide is not associated with the metal in[9] $[Au_2(Me_2PCH_2PMe_2)_2]X_2{\cdot}2H_2O$ (X = Cl, Br, or I).

The only reported three-coordinate Au^I_2 compound with all bidentate ligands is $[Au_2(Me_2PCH_2PMe_2)_3][BF_4]_2$.[10] To prepare a similar complex from $[Au_2(dppm)_2]^{2+}$, we looked for a sterically nondemanding third ligand known to form strong bonds to gold. Such a ligand is diethyldithiocarbamate, $S_2CNEt_2^-$, which is flat and forms compounds such as[11] $Ph_3PAu(S_2CNEt_2)$ and $[Au_2(S_2CNEt_2)_2]$.[12]

Experimental Section

Commercial $NaBH_3CN$ (Aldrich) and dppm, because of their hygroscopic nature, were stored over $CaCl_2$. All solvents were freshly distilled before use. Experiments were carried out in oven-dried Schlenk glassware by using standard inert atmosphere techniques. Infrared spectra (Nujol mulls) were recorded on a Perkin-Elmer 783 infrared spectrophotometer (polystyrene reference film) by using CsI or KBr (200-4000 cm^{-1}) plates. NMR spectra were recorded on a Varian XL-200 Fourier transform spectrometer. Microanalysis was performed by Galbraith Laboratories, Inc.

$[Au_2(dppm)_2][BH_3CN]_2$ (1). $Ph_3PAuONO_2$ (0.05 g, 0.01 mmol) and dppm (0.04 g, 0.01 mmol) were stirred in THF (5 mL) for about 15 min at room temperature. To this stirred suspension, $NaBH_3CN$ (0.018 g, 0.03 mmol) was added in one portion. The resultant mixture was further stirred for 5 h at room temperature. A white solid was separated by filtration and washed with ether. The solid was recrystallized from CH_2Cl_2 or CH_3CN with Et_2O. The yield was 0.09 g (80%). The compound melted at 202 °C with decomposition. IR: 2340 (s), 2320 (w), 2280 (w), 2240 (w), 2179 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.50 (t, J_{H-P} = 6.4 Hz, CH_2), 7.4 and 7.7 (m, aromatic protons). ^{31}P NMR ($CDCl_3$): δ 35.91 (s). UV-vis: 293 nm. Anal. Calcd for $Au_2P_4N_2C_{52}B_2H_{50}$: C, 50.28; H, 4.03; N, 2.26. Found: C, 50.31; H, 4.10; N, 2.20.

$[Au_2(dppm)_2(I)][(BH_3CN)]$ (2). To a THF (5 mL) solution of $[Au_2(dppm)_2][BH_3CN]_2$ (0.020 g, 0.016 mmol) under inert atmosphere was added NaI (0.0024 g, 0.016 mmol). The solution immediately changed from colorless to yellow. The reaction mixture was stirred for 18 h at room temperature, at which time the THF was evaporated under vacuum, leaving a yellow solid. The solid was dissolved in CH_2Cl_2 and filtered to remove $NaBH_3CN$. After removal of solvent, the yield of yellow solid was 0.017 g (80%). This was recrystallized from CH_2Cl_2 with Et_2O. Mp: 165-166 °C. IR: 2330 (s), 2250 (w), 2220 (w), 2179

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Table I. Crystallographic Data

	1	**3**	**4**
formula	$Au_2Cl_2P_4N_2$-$C_{54}B_2H_{54}$	$Au_2P_4N_2$-$C_{52}H_{44}$	$Au_2S_2P_4N_2$-$C_{56}BH_{57}$
a, Å	11.959 (10)	15.713 (7)	11.252 (1)
b, Å	13.943 (8)	14.711 (3)	11.844 (2)
c, Å	17.750 (10)	21.888 (3)	12.165 (2)
α, deg	90	90	94.99 (1)
β, deg	107.86 (5)	93.86 (3)	116.19 (1)
γ, deg	90	90	106.99 (1)
V, $Å^3$	2817 (3)	5048 (3)	1346.4 (4)
Z	2	4	1
fw	1270.50	1541.67	1349.75
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	*P*1 (No. 1)
temp, °C	20	20	20
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71073)		
d_{calc}, g cm^{-3}	1.66	2.03	1.66
μ(Mo Kα), cm^{-1}	55.32	94.49	56.61
trans factors: max, min	0.833, 0.790	0.964, 0.572	0.832, 0.628
R, R_w[a]	0.0619, 0.0638	0.0384, 0.0338	0.0195, 0.0196
g	0.00389	0.00007	0.00029

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + |g|F_o^2]$.

(s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.60 (t, J_{H-P} = 4.41 Hz, CH_2), 7.4 and 7.7 (m, aromatic protons). Anal. Calcd for $Au_2IP_4NC_{51}BH_{47}$: C, 46.09; H, 3.54; N, 1.05. Found: C, 46.10; H, 3.50; N, 1.10.

$[Au_2(dppm)_2(S_2CNEt_2)][BH_3CN]$ (4). To a stirred solution of $[Au_2(dppm)_2][BH_3CN]_2$ (0.020 g, 0.016 mmol) in CH_2Cl_2 (5 mL) was added NaS_2CNEt_2 (0.0027 g, 0.016 mmol). The solution immediately changed from colorless to yellow. The reaction mixture was stirred for 2 h, generating a white solid, presumably $NaBH_3CN$, which was separated by filtration. The filtrate was evaporated to dryness giving a 95% yield of **4** as a yellow solid, which was recrystallized from CH_3CN with Et_2O. MP: 187–188 °C. IR: 2340 (s), 2179 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.26 (t, J_{H-H} = 7.22 Hz, CH_3 of S_2CNEt_2), 3.99 (quartet, CH_2 of S_2CNEt_2), 4.15 (s, broad, CH_2 of dppm), 7.35 and 7.77 (m, aromatic protons). ^{31}P NMR ($CDCl_3$, −30 °C): δ 30.04 (s, broad). UV-vis: 420 nm. Anal. Calcd for $Au_2S_2P_4N_2C_{56}B_1H_{57}$: C, 49.81; H, 4.25; N, 2.08. Found: C, 50.21; H, 4.30; N, 1.98.

Attempted Oxidation of $[Au_2(dppm)_2]^{2+}$. The ^1H NMR spectrum of $[Au_2(dppm)_2][BF_4]_2$ in $CDCl_3$ was obtained.[13] To the NMR tube was added excess I_2 in $CDCl_3$, giving the solution a yellow color. The chemical shift of the methylene protons did not change, and no new peaks were observed.

X-ray Crystallography. The single-crystal X-ray analyses of **3** and **4** were performed by procedures (Nicolet R3m/E diffractometer, SHELXTL (version 5.1) software) described in detail elsewhere.[1b] Crystallographic data are presented in Table I. Crystals were grown by slow diffusion of ether into a solution of acetonitrile (**4**) or CH_2Cl_2 (**3**). Each crystal was mounted on a glass fiber with epoxy. The lattice parameters were determined by using 24 high-angle reflections. The data were corrected for Lorentz and polarization effects and for intensity fluctuations in the standards; only random fluctuations were observed for **3** and **4**. Absorption corrections were made empirically on the basis of azimuthal scans. The crystal structures were determined by using Patterson and difference Fourier techniques. The final cycles of refinement were performed with hydrogen atoms placed in idealized positions (C–H and B–H = 0.96 Å). Phenyl rings were refined as rigid bodies (C–C = 1.395 Å). All non-hydrogen atoms were refined anisotropically.

Compound **4** was refined in *P*1 (No. 1) with Au(1) fixed at 0, 0, 0. The final structure contains a single noncentrosymmetric molecule in the unit cell, which could not be transformed into the centrosymmetric space group $P\bar{1}$. Initial refinement gave *R* = 0.0343 and R_w = 0.0371. Transformation to and refinement as the enantiomer gave *R* = 0.0195 and R_w = 0.0196.

The structure determination process for a crystal of **1**·$2CH_2Cl_2$ grown by diffusion of ether into a CH_2Cl_2 solution, was slightly different. The standards decreased 40% during data collection, so the lattice parameters were determined from an initial set of 10 reflections having 2θ < 15°. A numerical absorption correction (face-indexed crystal) was applied. Phenyl-ring carbon atoms were not refined anisotropically. One of the phenyl rings, C(41)–C(46), had a rotational disorder, which was modeled by the addition of atoms C(51), C(52), C(54), and C(55) in a rigid rectangle.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters ($Å^2$ × 10^3)[a] for $[Au_2(dppm)_2][BH_3CN]_2$·$2CH_2Cl_2$ (**1**)

atom	*x*	*y*	*z*	U_{iso}
Au	904 (1)	−117 (1)	−414 (1)	48 (1)[b]
Cl(1)	1524 (16)	2184 (13)	7281 (9)	260 (12)[b]
Cl(2)	1714 (19)	1908 (19)	5855 (11)	354 (17)[b]
C(3)	1910 (81)	1704 (54)	6712 (35)	401 (69)[b]
P(1)	384 (5)	1047 (4)	1391 (3)	45 (2)[b]
P(2)	2282 (5)	694 (4)	584 (3)	48 (2)[b]
B(1)	3808 (29)	3375 (15)	3279 (18)	109 (17)[b]
N(1)	4206 (22)	1505 (15)	3085 (12)	100 (12)[b]
C(1)	1924 (17)	723 (14)	1502 (11)	48 (9)[b]
C(2)	4044 (23)	2290 (13)	3169 (13)	71 (11)[b]
C(11)	684 (12)	2994 (10)	1770 (6)	69 (7)
C(12)	519 (12)	3973 (10)	1614 (6)	84 (8)
C(13)	−103 (12)	4287 (10)	855 (6)	82 (8)
C(14)	−559 (12)	3622 (10)	252 (6)	81 (8)
C(15)	−393 (12)	2643 (10)	408 (6)	64 (7)
C(16)	228 (12)	2329 (10)	1167 (6)	41 (5)
C(21)	−908 (12)	795 (12)	2404 (8)	84 (8)
C(22)	−1092 (12)	798 (12)	3143 (8)	105 (10)
C(23)	−145 (12)	921 (12)	3828 (8)	83 (8)
C(24)	986 (12)	1042 (12)	3774 (8)	81 (8)
C(25)	1170 (12)	1039 (12)	3035 (8)	84 (8)
C(26)	223 (12)	916 (12)	2350 (8)	47 (6)
C(31)	1995 (12)	2262 (9)	−413 (7)	56 (6)
C(32)	2112 (12)	3221 (9)	−602 (7)	85 (8)
C(33)	2712 (12)	3861 (9)	−13 (7)	74 (8)
C(34)	3197 (12)	3543 (9)	765 (7)	81 (8)
C(35)	3080 (12)	2584 (9)	953 (7)	84 (8)
C(36)	2479 (12)	1944 (9)	364 (7)	39 (5)
C(41)	3851 (20)	−631 (17)	372 (12)	87 (17)
C(42)	4905 (20)	−1141 (17)	574 (12)	88 (17)
C(43)	5816 (20)	−893 (17)	1250 (12)	115 (11)
C(44)	5672 (20)	−136 (17)	1726 (12)	63 (13)
C(45)	4618 (20)	374 (17)	1525 (12)	64 (13)
C(46)	3708 (20)	126 (17)	848 (12)	63 (6)
C(51)	3814 (35)	−845 (29)	1015 (29)	77 (15)
C(52)	4900 (44)	−1305 (28)	1196 (37)	121 (23)
C(54)	5812 (48)	188 (49)	1015 (77)	275 (60)
C(55)	4726 (59)	649 (28)	838 (39)	124 (22)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å) and Angles (deg)[a] for $[Au_2(dppm)_2][BH_3CN]_2$·$2CH_2Cl_2$ (**1**)

Au–P(2)	2.312 (5)	Au–Au′	2.982 (2)
Cl(1)–C(3)	1.403 (83)	Cl(2)–C(3)	1.494 (67)
P(1)–C(1)	1.846 (22)	P(1)–C(16)	1.829 (15)
P(1)–C(26)	1.781 (17)	P(1)–Au′	2.328 (5)
P(2)–C(1)	1.809 (23)	P(2)–C(36)	1.817 (14)
P(2)–C(46)	1.806 (23)	B(1)–C(2)	1.562 (29)
N(1)–C(2)	1.130 (28)	C(43)–C(52)	1.214 (57)
C(43)–C(54)	1.564 (82)	C(46)–C(51)	1.383 (46)
C(46)–C(55)	1.425 (71)		
P(2)–Au–Au′	91.3 (2)	P(2)–Au–P(1′)	175.2 (2)
Au′–Au–P(1′)	90.8 (2)	Cl(1)–C(3)–Cl(2)	131.2 (55)
C(1)–P(1)–C(16)	107.1 (8)	C(1)–P(1)–C(26)	105.6 (8)
C(16)–P(1)–C(26)	105.9 (7)	C(1)–P(1)–Au′	110.8 (6)
C(16)–P(1)–Au′	112.5 (4)	C(26)–P(1)–Au′	114.4 (6)
Au–P(2)–C(1)	113.0 (7)	Au–P(2)–C(36)	114.4 (4)
C(1)–P(2)–C(36)	104.7 (8)	Au–P(2)–C(46)	112.3 (7)
C(1)–P(2)–C(46)	104.0 (10)	C(36)–P(2)–C(46)	107.6 (9)
P(1)–C(1)–P(2)	114.4 (9)	B(1)–C(2)–N(1)	179.4 (28)
P(1)–C(16)–C(11)	119.6 (4)	P(1)–C(16)–C(15)	120.4 (4)
P(1)–C(26)–C(21)	118.0 (5)	P(1)–C(26)–C(25)	121.6 (5)
P(2)–C(36)–C(31)	118.4 (4)	P(2)–C(36)–C(35)	121.6 (4)
C(52)–C(43)–C(54)	120.4 (33)	P(2)–C(46)–C(41)	117.1 (7)
P(2)–C(46)–C(45)	122.7 (7)	P(2)–C(46)–C(51)	120.1 (23)
P(2)–C(46)–C(55)	121.0 (25)	C(51)–C(46)–C(55)	118.7 (31)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Atomic coordinates and equivalent isotropic thermal parameters for **1**, **3**, and **4** are presented in Tables II, IV, and VI, respectively. Bond distances and angles are presented in Tables III, V, and VII, respectively.

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(13) Wang, J. C.; Khan, M. N. I.; King, C.; Fackler, J. P., Jr. *Acta Crystallogr.*, in press.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Au_2(dppm)_2I][Au(CN)_2]$ (**3**)

	x	*y*	*z*	U_{iso}[a]
Au	4939 (1)	2754 (1)	1075 (1)	105 (1)
C(3)	5657 (14)	2781 (12)	447 (7)	139 (10)
N(3)	6033 (9)	2632 (10)	41 (7)	115 (7)
C(4)	4097 (10)	2708 (11)	1755 (7)	88 (8)
N(4)	3625 (10)	2617 (9)	2088 (6)	107 (7)
Au(1)	1275 (1)	6000 (1)	6593 (1)	46 (1)
Au(2)	2453 (1)	6594 (1)	7633 (1)	48 (1)
I	673 (1)	5454 (1)	7893 (1)	63 (1)
P(1)	603 (2)	7395 (3)	6504 (2)	44 (1)
P(2)	2023 (2)	4640 (2)	6538 (2)	41 (1)
P(3)	3238 (2)	5257 (2)	7631 (2)	42 (1)
P(4)	1867 (2)	8038 (2)	7556 (2)	42 (1)
C(1)	765 (7)	8021 (8)	7227 (5)	40 (5)
C(2)	2595 (8)	4338 (8)	7266 (5)	41 (5)
C(11)	667 (6)	9046 (8)	5900 (4)	73 (7)
C(12)	914	9626	5439	99 (9)
C(13)	1432	9302	4994	87 (9)
C(14)	1703	8398	5009	87 (8)
C(15)	1456	7819	5470	64 (7)
C(16)	938	8143	5915	44 (6)
C(21)	2351 (6)	8346 (6)	8757 (5)	63 (6)
C(22)	2380	8816	9311	87 (8)
C(23)	1847	9563	9380	72 (7)
C(24)	1286	9839	8895	65 (7)
C(25)	1257	9369	8340	64 (7)
C(26)	1790	8622	8271	47 (6)
C(31)	2975 (7)	3783 (6)	5679 (5)	64 (7)
C(32)	3575	3753	5238	93 (9)
C(33)	4000	4543	5081	91 (9)
C(34)	3825	5364	5366	78 (8)
C(35)	3225	5395	5807	63 (7)
C(36)	2800	4604	5964	42 (5)
C(41)	1478 (6)	2827 (7)	6593 (4)	76 (7)
C(42)	942	2111	6402	80 (8)
C(43)	260	2264	5973	74 (8)
C(44)	113	3134	5735	90 (8)
C(45)	649	3851	5926	72 (7)
C(46)	1332	3697	6354	47 (6)
C(51)	4560 (8)	6188 (7)	7128 (5)	87 (9)
C(52)	5314	6268	6830	102 (10)
C(53)	5719	5493	6626	90 (9)
C(54)	5370	4636	6719	91 (9)
C(55)	4616	4555	7017	67 (7)
C(56)	4210	5331	7221	43 (5)
C(61)	3300 (7)	5303 (7)	8896 (5)	115 (9)
C(62)	3546	5004	9487	148 (12)
C(63)	4036	4218	9571	77 (8)
C(64)	4281	3731	9065	106 (9)
C(65)	4035	4030	8475	117 (10)
C(66)	3544	4816	8390	43 (5)
C(71)	2988 (8)	8396 (7)	6657 (6)	94 (9)
C(72)	3458	8958	6293	111 (10)
C(73)	3397	9901	6346	117 (11)
C(74)	2867	10280	6764	143 (13)
C(75)	2397	9718	7129	114 (10)
C(76)	2457	8775	7075	45 (6)
C(81)	−1051 (8)	7045 (7)	6854 (4)	77 (8)
C(82)	−1937	7008	6761	83 (8)
C(83)	−2333	7266	6198	102 (10)
C(84)	−1843	7561	5728	150 (13)
C(85)	−956	7598	5821	103 (9)
C(86)	−560	7340	6384	43 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Bond Lengths (Å) and Angles (deg) for $[Au_2(dppm)_2I][Au(CN)_2]$ (**3**)

Au–C(3)	1.836 (19)	Au–C(4)	2.058 (16)
C(3)–N(3)	1.122 (24)	C(4)–N(4)	1.082 (22)
Au(1)–Au(2)	2.967 (1)	Au(1)–I	3.161 (1)
Au(1)–P(1)	2.311 (4)	Au(1)–P(2)	2.327 (4)
Au(2)–P(3)	2.321 (4)	Au(2)–P(4)	2.317 (4)
P(1)–C(1)	1.834 (12)	P(1)–C(16)	1.800 (11)
P(1)–C(86)	1.831 (12)	P(2)–C(2)	1.830 (11)
P(2)–C(36)	1.811 (11)	P(2)–C(46)	1.792 (11)
P(3)–C(2)	1.840 (12)	P(3)–C(56)	1.827 (14)
P(3)–C(66)	1.818 (11)	P(4)–C(1)	1.829 (12)
P(4)–C(26)	1.798 (11)	P(4)–C(76)	1.810 (12)
C(3)–Au–C(4)	177.8 (8)	Au–C(3)–N(3)	166.3 (16)
Au–C(4)–N(4)	173.7 (14)	Au(2)–Au(1)–I	66.0 (1)
Au(2)–Au(1)–P(1)	93.5 (1)	I–Au(1)–P(1)	98.0 (1)
Au(2)–Au(1)–P(2)	90.1 (1)	I–Au(1)–P(2)	90.7 (1)
P(1)–Au(1)–P(2)	171.3 (1)	Au(1)–Au(2)–P(3)	93.1 (1)
Au(1)–Au(2)–P(4)	89.4 (1)	P(3)–Au(2)–P(4)	170.0 (1)
Au(1)–P(1)–C(1)	109.7 (4)	Au(1)–P(1)–C(16)	116.7 (4)
C(1)–P(1)–C(16)	106.3 (5)	Au(1)–P(1)–C(86)	114.7 (4)
C(1)–P(1)–C(86)	103.0 (5)	Au(1)–P(2)–C(2)	112.6 (4)
Au(1)–P(2)–C(36)	115.3 (3)	C(2)–P(2)–C(36)	106.4 (5)
Au(1)–P(2)–C(46)	112.1 (4)	C(2)–P(2)–C(46)	105.2 (5)
Au(2)–P(3)–C(2)	110.3 (4)	Au(2)–P(3)–C(56)	114.4 (4)
C(2)–P(3)–C(56)	106.4 (5)	Au(2)–P(3)–C(66)	114.1 (4)
C(2)–P(3)–C(66)	103.8 (5)	Au(2)–P(4)–C(1)	112.2 (4)
Au(2)–P(4)–C(26)	115.1 (3)	C(1)–P(4)–C(26)	103.4 (5)
Au(2)–P(4)–C(76)	112.1 (4)	C(1)–P(4)–C(76)	106.7 (6)
P(1)–C(1)–P(4)	114.8 (6)	P(2)–C(2)–P(3)	115.0 (6)
P(1)–C(16)–C(11)	119.7 (4)	P(1)–C(16)–C(15)	120.3 (4)
P(4)–C(26)–C(21)	116.6 (3)	P(4)–C(26)–C(25)	123.2 (3)
P(2)–C(36)–C(31)	119.9 (3)	P(2)–C(36)–C(35)	120.1 (3)
P(2)–C(46)–C(41)	123.0 (3)	P(2)–C(46)–C(45)	116.9 (3)
P(3)–C(56)–C(51)	118.4 (3)	P(3)–C(56)–C(55)	121.6 (3)
P(3)–C(66)–C(61)	118.2 (4)	P(3)–C(66)–C(65)	121.8 (4)
P(4)–C(76)–C(71)	119.5 (4)	P(4)–C(76)–C(75)	120.5 (4)
P(1)–C(86)–C(81)	120.3 (3)	P(1)–C(86)–C(85)	119.7 (3)

Results and Discussion

A solution of $[Au_2(dppm)_2][BF_4]_2$ was neither readily oxidized nor decomposed by addition of iodine, confirming that the complex is more difficult to oxidize than is $[Au_2((CH_2)_2PR_2)_2]$.

The reaction between $Ph_3PAuONO_2$, dppm, and $NaBH_3CN$ in THF or THF/MeOH produced $[Au_2(dppm)_2][BH_3CN]_2$ (**1**) in 80% yield when short reaction times (3–5 h) were used. Longer reaction times in these solvents produced an unidentified brown solid. Complex **1** is a white, air-stable solid, soluble in CH_2Cl_2, $CHCl_3$, and CH_3CN. The BH_3CN^- ion was shown to be present by IR spectroscopy (ν(C≡N) 2179 cm^{-1}, ν(BH) 2340 cm^{-1}). The IR bands are nearly identical with those of $NaBH_3CN$,[14] indicating that there is very little interaction between anion and dication.

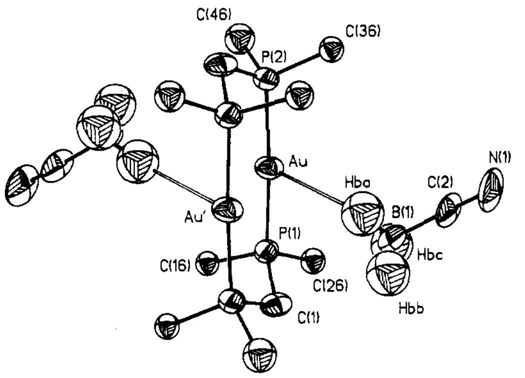

Figure 1. Structure of $[Au_2(dppm)_2][BH_3CN]_2$ (**1**). The open bond connects Au to the nearest hydride. Only the ipso carbons of the phenyl rings are shown.

Molecules of **1** in the crystal structure contain a center of symmetry (Figure 1). The Au–Au^1 separation is 2.982 (2) Å. The structure of this compound is striking for what is not observed. The atom in BH_3CN^- closest to a gold atom is a hydride, which is 2.96 (8) Å away. There is no indication of a tendency for the gold(I) atom to become three-coordinate by associating with either the hydride or nitrogen of BH_3CN^-.[15] Further, the gold is not

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[14] Berschied, J. R.; Purcell, K. F. *Inorg. Chem.* **1970**, *9*, 624–629.

[15] Crystals of **1** without CH_2Cl_2 were obtained from CH_3CN: space group $P\bar{1}$ (No. 2) with a = 13.725 (4) Å, b = 14.689 (3) Å, c = 12.435 (4) Å, α = 94.77 (2)°, β = 97.04 (2)°, γ = 83.80 (2)°, V = 2467 (1) Å^3. Although three of the phenyl rings were disordered, similar metal–metal and Au···BH_3CN distances were observed.

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)[a] for $[Au_2(dppm)_2(S_2CNEt_2)][BH_3CN]$ (**4**)

atom	*x*	*y*	*z*	U_{iso}[b]
Au(1)	10000	10000	10000	33 (1)
Au(2)	6892 (1)	9242 (1)	8962 (1)	33 (1)
P(1)	6339 (2)	7760 (2)	7268 (2)	33 (1)
P(2)	9578 (2)	8754 (2)	8159 (2)	30 (1)
P(4)	10536 (2)	11733 (2)	11433 (2)	31 (1)
P(3)	7342 (2)	11212 (2)	9968 (2)	30 (1)
S(1)	7233 (3)	8453 (2)	11013 (2)	52 (1)
S(2)	9772 (3)	8052 (2)	11006 (2)	53 (1)
C(1)	7925 (14)	7413 (11)	7538 (12)	41 (6)
C(2)	8959 (12)	11710 (10)	11540 (10)	23 (5)
C(3)	8454 (10)	7738 (7)	11415 (7)	41 (4)
C(11)	10697 (5)	7104 (5)	7531 (5)	53 (5)
C(12)	11810 (5)	6713 (5)	7711 (5)	66 (6)
C(13)	13153 (5)	7310 (5)	8772 (5)	61 (7)
C(14)	13384 (5)	8298 (5)	9654 (5)	54 (5)
C(15)	12271 (5)	8689 (5)	9475 (5)	44 (5)
C(16)	10927 (5)	8092 (5)	8413 (5)	36 (4)
C(21)	8005 (7)	13621 (5)	9723 (4)	45 (5)
C(22)	8230 (7)	14520 (5)	9091 (4)	69 (8)
C(23)	8094 (7)	14203 (5)	7898 (4)	64 (6)
C(24)	7734 (7)	12987 (5)	7338 (4)	54 (5)
C(25)	7509 (7)	12088 (5)	7970 (4)	38 (4)
C(26)	7645 (7)	12405 (5)	9163 (4)	36 (4)
C(31)	9469 (7)	10679 (5)	7049 (4)	52 (5)
C(32)	9327 (7)	11280 (4)	6087 (4)	70 (7)
C(33)	9117 (7)	10679 (4)	4941 (4)	59 (6)
C(34)	9048 (7)	9478 (4)	4755 (4)	83 (9)
C(35)	9189 (7)	8877 (4)	5717 (4)	74 (7)
C(36)	9400 (7)	9478 (4)	6863 (4)	34 (4)
C(41)	5411 (5)	5703 (5)	8039 (5)	50 (5)
C(42)	4418 (5)	4612 (5)	7941 (5)	72 (7)
C(43)	3079 (5)	4100 (5)	6859 (5)	70 (6)
C(44)	2734 (5)	4680 (5)	5874 (5)	65 (6)
C(45)	3727 (5)	5772 (5)	5972 (5)	57 (5)
C(46)	5066 (5)	6283 (5)	7054 (5)	35 (4)
C(51)	5653 (7)	7483 (5)	4712 (5)	52 (5)
C(52)	5104 (7)	7775 (5)	3547 (5)	68 (6)
C(53)	4524 (7)	8679 (5)	3395 (5)	75 (7)
C(54)	4492 (7)	9293 (5)	4408 (5)	86 (7)
C(55)	5041 (7)	9001 (5)	5573 (5)	65 (6)
C(56)	5621 (7)	8096 (5)	5725 (5)	37 (4)
C(61)	11467 (5)	11026 (5)	13682 (5)	48 (5)
C(62)	12465 (5)	11071 (5)	14902 (5)	71 (7)
C(63)	13847 (5)	11941 (5)	15475 (5)	67 (6)
C(64)	14230 (5)	12766 (5)	14828 (5)	64 (6)
C(65)	13232 (5)	12720 (5)	13608 (5)	48 (5)
C(66)	11851 (5)	11850 (5)	13035 (5)	39 (4)
C(71)	6140 (6)	11508 (7)	11517 (5)	58 (5)
C(72)	5124 (6)	11739 (7)	11764 (5)	85 (7)
C(73)	3954 (6)	11887 (7)	10802 (5)	69 (7)
C(74)	3799 (6)	11804 (7)	9592 (5)	80 (8)
C(75)	4815 (6)	11573 (7)	9344 (5)	69 (6)
C(76)	5986 (6)	11425 (7)	10306 (5)	45 (5)
C(81)	11464 (7)	14264 (5)	11999 (5)	53 (5)
C(82)	11901 (7)	15406 (5)	11770 (5)	63 (6)
C(83)	12058 (7)	15500 (5)	10702 (5)	75 (7)
C(84)	11778 (7)	14452 (5)	9864 (5)	71 (7)
C(85)	11341 (7)	13311 (5)	10093 (5)	53 (5)
C(86)	11184 (7)	13217 (5)	11160 (5)	31 (4)
C(4)	7254 (11)	6544 (8)	12455 (9)	55 (6)
C(5)	9469 (12)	6357 (10)	12619 (10)	66 (7)
C(6)	6003 (13)	5417 (11)	11537 (12)	93 (7)
C(7)	10683 (12)	7066 (12)	13861 (10)	88 (7)
N(1)	8380 (8)	6929 (6)	12106 (7)	43 (4)
N(2)	7228 (14)	5219 (10)	4898 (9)	94 (7)
C(9)	7773 (12)	4599 (9)	4723 (10)	59 (6)
B(1)	8599 (16)	3889 (14)	4555 (16)	95 (9)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\boldsymbol{u}_{ij}$ tensor.

Table VII. Bond Lengths (Å) and Angles (deg)[a] for $[Au_2(dppm)_2(S_2CNEt_2)][BH_3CN]$ (**4**)

Au(1)–Au(2)	2.949 (1)	Au(1)–P(2)	2.344 (2)
Au(1)–P(4)	2.311 (2)	Au(1)–S(2)	2.703 (3)
Au(2)–P(1)	2.305 (2)	Au(2)–P(3)	2.338 (2)
Au(2)–S(1)	2.648 (3)	P(1)–C(1)	1.843 (17)
P(1)–C(46)	1.818 (6)	P(1)–C(56)	1.821 (6)
P(2)–C(1)	1.837 (12)	P(2)–C(16)	1.828 (7)
P(2)–C(36)	1.821 (6)	P(4)–C(2)	1.828 (15)
P(4)–C(66)	1.815 (5)	P(4)–C(86)	1.815 (6)
P(3)–C(2)	1.850 (9)	P(3)–C(26)	1.824 (6)
P(3)–C(76)	1.822 (8)	S(1)–C(3)	1.733 (11)
S(2)–C(3)	1.717 (13)	C(3)–N(1)	1.337 (12)
C(4)–C(6)	1.505 (12)	C(4)–N(1)	1.472 (17)
C(5)–C(7)	1.463 (12)	C(5)–N(1)	1.494 (16)
N(2)–C(9)	1.145 (22)	C(9)–B(1)	1.486 (25)
Au(2)–Au(1)–P(2)	89.0 (1)	Au(2)–Au(1)–P(4)	94.3 (1)
P(2)–Au(1)–P(4)	159.9 (1)	Au(2)–Au(1)–S(2)	85.8 (1)
P(2)–Au(1)–S(2)	89.4 (1)	P(4)–Au(1)–S(2)	110.6 (1)
Au(1)–Au(2)–P(1)	94.3 (1)	Au(1)–Au(2)–P(3)	86.9 (1)
P(1)–Au(2)–P(3)	154.1 (1)	Au(1)–Au(2)–S(1)	87.4 (1)
P(1)–Au(2)–S(1)	113.8 (1)	P(3)–Au(2)–S(1)	92.1 (1)
Au(2)–P(1)–C(1)	110.1 (4)	Au(2)–P(1)–C(46)	114.2 (2)
C(1)–P(1)–C(46)	102.6 (5)	Au(2)–P(1)–C(56)	116.4 (2)
C(1)–P(1)–C(56)	107.5 (6)	C(46)–P(1)–C(56)	105.0 (2)
Au(1)–P(2)–C(1)	110.3 (6)	Au(1)–P(2)–C(16)	114.0 (2)
C(1)–P(2)–C(16)	103.4 (6)	Au(1)–P(2)–C(36)	115.4 (2)
C(1)–P(2)–C(36)	106.5 (5)	C(16)–P(2)–C(36)	106.3 (4)
Au(1)–P(4)–C(2)	110.5 (3)	Au(1)–P(4)–C(66)	112.9 (2)
C(2)–P(4)–C(66)	104.8 (4)	Au(1)–P(4)–C(86)	119.1 (2)
C(2)–P(4)–C(86)	103.8 (5)	C(66)–P(4)–C(86)	104.4 (2)
Au(2)–P(3)–C(2)	109.5 (4)	Au(2)–P(3)–C(26)	116.7 (2)
C(2)–P(3)–C(26)	105.8 (4)	Au(2)–P(3)–C(76)	117.2 (2)
C(2)–P(3)–C(76)	104.1 (5)	C(26)–P(3)–C(76)	102.4 (4)
Au(2)–S(1)–C(3)	110.9 (4)	Au(1)–S(2)–C(3)	113.0 (3)
P(1)–C(1)–P(2)	114.9 (8)	P(4)–C(2)–P(3)	112.4 (7)
S(1)–C(3)–S(2)	123.1 (5)	S(1)–C(3)–N(1)	117.9 (9)
S(2)–C(3)–N(1)	118.9 (8)	P(2)–C(16)–C(11)	122.4 (1)
P(2)–C(16)–C(15)	117.3 (1)	P(3)–C(26)–C(21)	120.9 (2)
P(3)–C(26)–C(25)	119.1 (2)	P(2)–C(36)–C(31)	117.3 (2)
P(2)–C(36)–C(35)	122.7 (2)	P(1)–C(46)–C(41)	118.6 (2)
P(1)–C(46)–C(45)	121.3 (2)	P(1)–C(56)–C(51)	121.7 (3)
P(1)–C(56)–C(55)	118.3 (3)	P(4)–C(66)–C(61)	118.7 (2)
P(4)–C(66)–C(65)	121.3 (2)	P(3)–C(76)–C(71)	121.3 (2)
P(3)–C(76)–C(75)	118.6 (2)	P(4)–C(86)–C(81)	119.4 (2)
P(4)–C(86)–C(85)	120.5 (2)	C(6)–C(4)–N(1)	113.4 (11)
C(7)–C(5)–N(1)	113.4 (11)	C(3)–N(1)–C(4)	123.5 (9)
C(3)–N(1)–C(5)	122.4 (10)	C(4)–N(1)–C(5)	114.1 (9)
N(2)–C(9)–B(1)	175.0 (11)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

reduced and the purified material is stable enough for crystals to be grown over several days. Experiments have suggested that BH_3CN^- reduces some metals, such as Ag^I, Hg^{II}, and Cu^{III}, by an inner-sphere mechanism that requires coordination of nitrogen to the metal.[14] Such coordination has been observed for several transition-metal ions.[16] The gold atoms in **1** do not interact with the nitrogen and, consistent with that mechanism, are not reduced.

Compound **1** was used as a starting material for the synthesis of $[Au_2(dppm)_2I]^+$. Addition of 1 equiv of NaI to **1** in THF gave a precipitate of $NaBH_3CN$ and a yellow solution from which $[Au_2(dppm)_2I][BH_3CN]$ (**2**) was obtained as a yellow powder. The IR spectrum again shows no interaction between BH_3CN^- and the cation.

We attempted to grow crystals of **2** for X-ray analysis, but decomposition occurred during the several days necessary for crystallization, and the crystal chosen for analysis was found to consist of $[Au_2(dppm)_2I][Au(CN)_2]$ (**3**) (Figure 2). The shortest distance between $Au(CN)_2^-$ and gold or iodide in the cation is 4.914 (1) Å (Au···Au(2)). The CN$^-$ may have resulted from hydrolysis of BH_3CN^- to $H_2BO_3^-$, HCN, and H_2. This reaction limits the utility of BH_3CN^- as a counterion.

Unlike the symmetrically bridging iodide in $[Au_2(dppm)_2I]I$ (Au–I = 3.127 (2) and 3.196 (2) Å; Au–Au–I = 66°), the iodide in **3** is asymmetrically bridging with Au–I distances of 3.161 (3)

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(16) Holah, D. G.; Hughes, A. N.; Maciaszek, S.; Magnuson, V. R.; Parker, K. O. *Inorg. Chem.* **1985**, *24*, 3956–3962 and references therein.

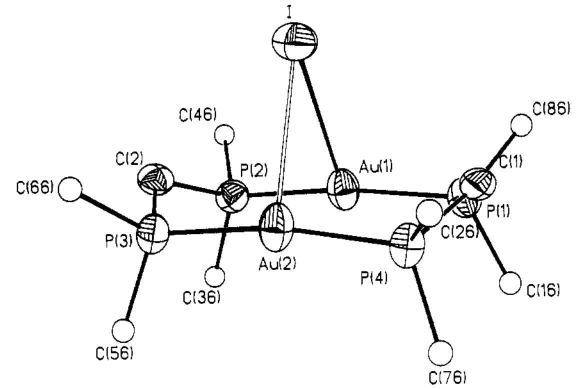

Figure 2. Structure of the cation of $[Au_2(dppm)_2(I)][Au(CN)_2]$ (**3**). Only the ipso carbons are shown for the phenyl rings.

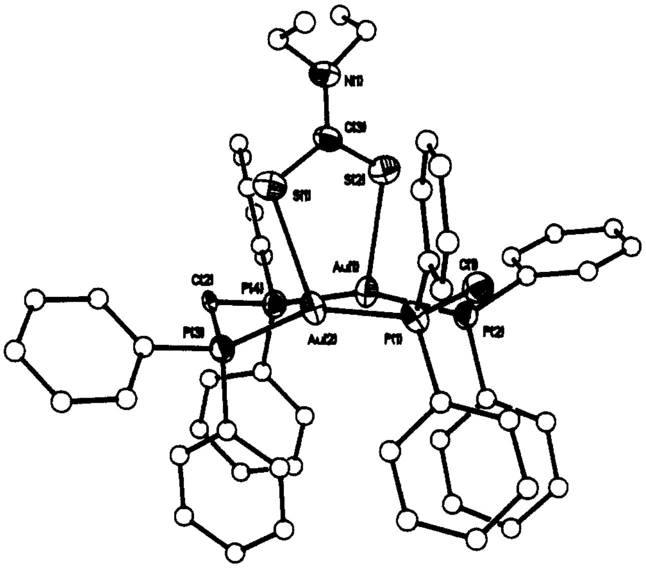

Figure 3. Structure of the cation of $[Au_2(dppm)_2(S_2CNEt_2)][BH_3CN]$ (**4**), showing the bridging dithiocarbamate ligand.

and 3.342 (3) Å and Au-Au-I = 73°. This difference must be due to different packing forces in the two compounds. Although the Au-I separation of 3.16 Å is long compared to 2.529 Å in AuI_2^-,[17] the P-Au-P angles (170 and 171°) are perturbed somewhat from linearity. The yellow color of **2** in solution indicates that the iodide does not completely dissociate. Also, the addition of iodide changes the ^1H NMR chemical shift of the methylene group from δ 4.50 to δ 4.60, and $^2J_{HCP}$ changes from 6.4 to 4.4 Hz.

The reaction between **1** and 1 equiv of NaS_2CNEt_2 gave, after precipitation of $NaBH_3CN$, a yellow solution from which a yellow powder of $[Au_2(dppm)_2(S_2CNEt_2)][BH_3CN]$ (**4**) was obtained in a 95% yield. IR spectroscopy shows the presence of BH_3CN^- as an unassociated counterion. The crystal structure (Figure 3) shows that $S_2CNEt_2^-$ bridges the two gold atoms by forming two Au-S bonds. The Au-S bond lengths, 2.648 (3) and 2.703 (3) Å, are longer than those in $Ph_3PAu^I(S_2CNEt_2)$, 2.34 Å,[11] and $(Ph_3P)_2Au^I(SCN)$, 2.47 Å.[18] However, the Au-S interaction is stronger than the Au-I interaction, as judged by the greater deviation from linearity of the P-Au-P angles, which are 160 and 154° in this Au-S compound. The average Au-P distance, 2.324 Å, is nearly the same as that found in **3**, 2.319 Å. The Au···Au separation in $Au_2(S_2CNEt_3)_2$ is a short 2.782 Å,[11] but in **4**, with just one $S_2CNEt_2^-$ ligand, it is 2.949 (1) Å, which is typical for $[Au_2(dppm)_2]^{2+}$ compounds.

The $[Au_2(dppm)_2(S_2CNEt_2)]^+$ cation remains at least partially intact in solution as shown by the yellow color (λ = 420 nm) of **4** in solution and by the changes in the NMR spectra. The ^1H NMR signal of the dppm methylene, δ 4.15, has shifted from δ 4.50 in **1**, and the ^{31}P NMR signal, δ 30.0, has shifted from δ 35.9. These NMR signals are broad at room temperature, which could be due to a conformational change; the $Au_2(dppm)_2$ unit is in a boat conformation in crystals of **3** and **4** and in a chain conformation in crystals of **1**. However, ligand dissociation and reassociation could also cause the broadening.

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Registry No. **1**, 120205-41-6; **1**·$2CH_2Cl_2$, 120229-26-7; **2**, 120205-43-8; **3**, 120205-44-9; **4**, 120205-46-1; $[AuPPh_3]NO_3$, 14897-32-6; $[Au_2(dppm)_2][BF_4]_2$, 120205-47-2.

Supplementary Material Available: For **1**, **3**, and **4**, tables of crystallographic data, anisotropic parameters, and hydrogen coordinates and thermal parameters (12 pages); tables of F_o, F_c, and $\sigma(F)$ (77 pages). Ordering information is given on any current masthead page.

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Photophysical Properties of $M(CO)_4(\alpha,\alpha'$-diimine) (M = Mo, W) Complexes

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Electronic absorption, emission, and excitation spectra and emission lifetimes have been recorded from a series of $M(CO)_4(\alpha,\alpha'$-diimine) complexes [M = Mo, W; α,α'-diimine = a substituted 1,10-phenanthroline (phen) ligand] in EPA glasses at 80 K and benzene at 293 K. Corresponding data have also been obtained from $M(CO)_4(en)$ complexes (M = Mo, W; en = ethylenediamine). The $M(CO)_4(phen)$ complexes exhibit a broad low-energy absorption band that comprises three metal to ligand charge-transfer (MLCT) transitions ($b_2 \rightarrow b_2^*$, $a_1 \rightarrow b_2^*$, $a_2 \rightarrow b_2^*$). A band is also observed at higher energy containing both MLCT ($a_2 \rightarrow a_2^*$) and ligand field (LF) transitions. Obtained emission and excitation data at 80 K identify radiative transitions from each of the ^{3}MLCT and ^{3}LF components. In solution at 293 K all of the ^{3}MLCT levels are in thermal equilibrium; however, the ^{3}LF level remains nonequilibrated. In comparison, $W(CO)_4(en)$ emits only at 80 K, apparently from a single ^{3}LF level. Further details of the emission assignments and excited-state dynamics of the $M(CO)_4(\alpha,\alpha'$-diimine) system are discussed within.

Introduction

Photophysical characteristics of transition-metal complexes are in many ways very different from those of organic molecules. For example, in metal complexes a wide variety of excited states may occur, including transitions that are metal-centered, intraligand, or charge-transfer between the metal and ligands. Furthermore,

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