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Reactions of Cationic Gold Clusters with Lewis Bases. Preparation and X-ray Structure Investigation of $[Au_8(PPh_3)_7](NO_3)_2 \cdot 2CH_2Cl_2$ and $Au_6(PPh_3)_4[Co(CO)_4]_2$

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The compound $[Au_8(PPh_3)_7](NO_3)_2 \cdot 2CH_2Cl_2$ has been prepared and well characterized by a variety of physical measurements, including a complete X-ray structure analysis. It crystallizes in space group $P2_1/n$ with $Z = 4$ and the following unit cell dimensions: $a = 25.444$ (6) Å, $b = 17.332$ (6) Å, $c = 28.795$ (6) Å, $\beta = 97.66$ (3)°, $V = 12584.9$ Å^3. The cation consists of a central gold atom surrounded by seven peripheral Au–PPh$_3$ moieties in an icosahedrally derived structure, with the following important distance ranges: Au$_{centr}$–Au$_{per}$ = 2.63–2.72 Å, Au$_{per}$–Au$_{per}$ = 2.71–2.94 Å, and Au–P = 2.24–2.36 Å. Reaction of the coordinatively unsaturated $[Au_8(PPh_3)_7](NO_3)_2$ with $Li[Co(CO)_4]$ results in the formation of the heterometallic $Au_6(PPh_3)_4[Co(CO)_4]_2$, on which a complete X-ray structure determination has been performed. This compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$ and the following unit cell dimensions: $a = 13.672$ (6) Å, $b = 13.524$ (4) Å, $c = 14.160$ (5) Å, $\alpha = 119.72$ (2)°, $\beta = 118.83$ (3)°, $\gamma = 71.32$ (2)°, $V = 1980.6$ Å^3. The centrosymmetric molecule contains a Au skeleton, which can be described as two tetrahedrons with one common edge, with the Au atoms being bonded either to a phosphine or to a Co(CO)$_4$ group. Important distance ranges are Au–Au = 2.62–2.81 Å, Au–P = 2.28–2.37 Å, and Au–Co = 2.46 Å.

Introduction

The reactivity of $[Au_9L_8]^{3+}$ (L = PPh$_3$) toward Lewis bases has been an important issue of research in our laboratory during the last few years, not only as a method for the synthesis of new gold cluster compounds but also as a model for the interaction of a substrate with a metal surface.

Thus far the reaction of $[Au_9L_8]^{3+}$ with L or X$^-$ (X$^-$ = Cl$^-$ or SCN$^-$) has been reported.[1] Preliminary X-ray results have been reported on $[Au_8L_8]^{2+}$,[2,3] prepared from the reaction of $[Au_9L_8]^{3+}$ with 2 equiv of L, according to eq 1. Although

$$[Au_9L_8]^{3+} + 2L \rightarrow [Au_8L_8]^{2+} + [AuL_2]^+ \qquad (1)$$

this reaction seems rather simple, the question arises how the bulky phosphine can react with the starting material $[Au_9L_8]^{3+}$, which is almost spherically screened by triphenylphosphine ligands. This dissociative mechanism is reasonable, resulting in the formation of an intermediate, which can be held responsible for the remarkable reactivity of the $[Au_9L_8]^{3+}$ cluster.

Here we give a detailed report describing this intermediate $[Au_8L_7]^{2+}$ and the reaction thereof with $[Co(CO)_4]^-$ leading to the heterometallic $Au_6L_4[Co(CO)_4]_2$. Both compounds have already been announced in preliminary communications.[4,5]

Experimental Section

a. Instruments. C, H, and N analyses were carried out in the microanalytical department of this university.

The other elemental analyses were performed by Dr. A. Bernhardt, Elbach über Engelskirchen, West Germany.

Conductivity measurements were performed with a Metrohm Konduktoskop and a Philips PR 9510/00 conductivity cell at 25 °C. Λ_0 (Ω^{-1} cm^2 equiv^{-1}) values were obtained by extrapolation of Λ vs. $C^{1/2}$ data.

$^{31}P\{^1H\}$ NMR spectra were recorded with a Varian XL-100FT spectrometer. Infrared spectra were recorded with a Perkin-Elmer 283 spectrometer.

The ^{197}Au Mössbauer spectra were recorded at 4.2 K with the apparatus described earlier.[6,7]

b. Preparation (See Table I). $[RhCl(C_8H_{14})_2]_2$ has been prepared according to the literature.[10]

$[Au_9(PPh_3)_8](NO_3)_3$.[8] An 8.60-g amount of $Au(PPh_3)NO_3$[9] was suspended in 200 mL of technical 96% ethanol. To this suspension was slowly added 156 mg of NaBH$_4$ (mole ratio 4:1) in 200 mL of 100% ethanol, added, whereupon the solution immediately turned red. After 1 h this solution is filtered and evaporated to dryness,and the solid is dissolved again in a minimal volume of CH$_2$Cl$_2$. To remove any inorganic salts like borates, this solution is filtered and evaporated to dryness and the residue is dissolved in THF, whereupon immediately the dark green $[Au_9(PPh_3)_8](NO_3)_3$ begins to deposit from the red solution. After 1 day the solution is practically colorless and the pure compound can be isolated by filtration and subsequent washing with THF and hexane; yield 4.70 g (70%).

$[Au_8(PPh_3)_8](NO_3)_2$. A 4.40-g amount of $[Au_9(PPh_3)_8](NO_3)_3$ and a 10-fold excess of PPh$_3$ (2.84 g) are mixed in about 20 mL of CH$_2$Cl$_2$. After 30 min the red product is precipitated with 200 mL toluene, isolated by filtration, and subsequently washed with toluene and hexane; yield 3.40 g (83%).

$[Au_8(PPh_3)_7](NO)_2$. A 2.46-g amount of $[Au_8(PPh_3)_8](NO_3)_2$ is dissolved in 25 mL of CH$_2$Cl$_2$, and 116 mg of $[RhCl(C_8H_{14})_2]_2$ (mole ratio 4:1) is added as a solid, whereupon the clear red solution immediately turns red-brown. After 10 min a light brown product is precipitated with 200 mL of toluene. This precipitate can be isolated by filtration and subsequent washing with toluene and hexane. The crude product always contains some $[Au_9(PPh_3)_8](NO_3)_3$ and $[Au_8(PPh_3)_8](NO_3)_2$ in minor amounts as can be shown in $^{31}P\{^1H\}$ NMR spectra. Purification is achieved by washing with a small volume of ethanol, whereupon the pure dark red-brown $[Au_8(PPh_3)_7](NO_3)_2$, which remains on the filter, can be washed with hexane; yield 1.70 g (74%). Crystals suitable for X-ray determination can be obtained by slow diffusion of diethyl ether into a methylene chloride solution.

$Li[Co(CO)_4]$ was prepared from Co$_2$(CO)$_8$ and LiBEt$_3$H in THF according to the literature.[11]

$Au_6(PPh_3)_4[Co(CO)_4]_2$. A 690-mg amount of $[Au_8(PPh_3)_7](NO_3)_2$ was mixed with 75 mg of $Li[Co(CO)_4]$ (mole ratio 1:2) in 20 mL of THF. A red-brown solution results within 1/2 h. This solution is filtered and precipitated with 50 mL of hexane. The Crude product is extracted with toluene (20 mL), and from the filtrate a brown product is precipitated with hexane (50 mL). A very small amount of air-stable dark red-brown crystals, suitable for X-ray structure determination, was obtained by the diffusion of *n*-hexane into a toluene solution. All solvents were carefully dried before use, and the reaction

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(1) F. A. Vollenbroek, J. J. Bour, and J. W. A. van der Velden, *Recl. Trav. Chim. Pays-Bas*, **99**, 137 (1980).

(2) F. A. Vollenbroek, W. P. Bosman, J. J. Bour, J. H. Noordik, and P. T. Beurskens, *J. Chem. Soc., Chem. Commun.*, 387 (1979).

(3) M. Manassero, L. Naldini, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 385 (1979).

(4) J. W. A. van der Velden, J. J. Bour, W. P. Bosman, and J. H. Noordik, *J. Chem. Soc., Chem. Commun.*, 1218 (1981).

(5) J. W. A. van der Velden, J. J. Bour, B. F. Otterloo, W. P. Bosman, and J. H. Noordik, *J. Chem. Soc., Chem. Commun.*, 583 (1981).

(6) M. P. A. Viegers and J. M. Trooster, *Phys. Rev. B: Solid State*, **15**, 72 (1977).

(7) M. P. A. Viegers, Ph.D. Thesis, University of Nijmegen, Nijmegen, The Netherlands, 1976.

(8) P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 1423 (1971).

(9) L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Coord. Chem. Rev.*, **1**, 255 (1966).

(10) A van der Ent and A. L. Onderdelinden, *Inorg. Synth.*, **14**, 94 (1973).

(11) J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker, and J. C. Selover, *Inorg. Chem.*, **18**, 553 (1979).

(12) T. L. Bundell and H. M. Powell, *J. Chem. Soc. A*, 1685 (1971).

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Table I. Experimental Data of the Gold Clusters

	$[Au_9(PPh_3)_8](NO_3)_3$[a]	$[Au_8(PPh_3)_8](PF_6)_2\cdot 2CH_2Cl_2$	$[Au_8(PPh_3)_7](NO_3)_2$	$Au_6(PPh_3)_4[Co(CO)_4]_2$
formula	$C_{144}H_{120}Au_9N_3O_9P_8$	$C_{145}H_{122}Au_8Cl_2F_{12}P_{10}$	$C_{126}H_{105}Au_8N_2O_6P_7$	$C_{80}H_{60}Au_6Co_2O_8P_4$
M_r	4057.078	4048.973	3535.811	2572.929
$\delta(^{31}P)$[b]	−54.8	−53.0	−56.6	−52.8
elemental anal.[c]				
C	41.5 (42.6)	43.95 (43.01)	42.72 (42.80)	
H	2.7 (2.9)	3.23 (3.04)	3.06 (2.99)	
N/F	1.0 (1.0)	5.60 (5.63)	0.76 (0.79)	
Au	43.8 (43.7)	39.03 (38.92)	44.41 (44.57)	
P			6.03 (6.13)	
type of electrolyte[d]	1:3	1:2	1:2	
^{197}Au Mössbauer parameters, mm/s				
peripheral Au QS	6.6	6.7	6.9	
peripheral Au IS[e]	2.1	1.9	2.4	
central Au IS	*f*	2.4	*f*	

[a] The first report on this compound was given in ref 8. [b] Relative to TMP ($O{=}P(OMe)_3$) in CD_2Cl_2, all singlets apart from the septet of PF_6. [c] Theoretical values are given within parentheses. [d] Measured in methanol at 25 °C. [e] Isomer shift with respect to ^{197}Pt source. [f] Central Au signal not observed separately.

Table II. Crystal Data of $[Au_8(PPh_3)_7](NO_3)_2$ and $Au_6(PPh_3)_4[Co(CO)_4]_2$

	$Au_8C_{126}H_{105}N_2O_6P_7\cdot 2CH_2Cl_2$	$Au_6C_{80}Co_2H_{60}P_4O_8$
M_r	3705.677	2572.929
space group	$P2_1/n$	$P\bar{1}$
a, Å	25.444 (6)	13.672 (6)
b, Å	17.332 (6)	13.524 (4)
c, Å	28.795 (6)	14.160 (5)
α, deg	90.0	119.72 (3)
β, deg	97.66 (3)	118.83 (3)
γ, deg	90.0	71.32 (3)
V, Å^3	12584.9	1980.6
Z	4	2
δ(calcd), g cm^{-3}	2.053	1.470
μ(Cu Kα), cm^{-1}	108.51	
μ(Mo Kα), cm^{-1}		11.25

Table III. Fractional Coordinates (×10^4) and Isotropic Thermal Parameters (×100, Å^2) for $[Au_8(PPh_3)_7](NO_3)_2\cdot 2CH_2Cl_2$[a]

	x	y	z	U_{eq}
Au(1)	2888 (1)	909 (2)	29 (1)	4.24 (2)
Au(2)	2551 (1)	2192 (2)	423 (1)	5.29 (3)
Au(3)	2068 (1)	1661 (2)	−481 (1)	5.48 (3)
Au(4)	3015 (1)	967 (2)	961 (1)	5.42 (3)
Au(5)	3060 (1)	2250 (2)	−420 (1)	5.27 (3)
Au(6)	2855 (1)	759 (2)	−898 (1)	4.95 (2)
Au(7)	3360 (1)	−340 (2)	−269 (1)	4.99 (3)
Au(8)	2699 (1)	−392 (2)	446 (1)	4.99 (3)
P(2)	2197 (8)	3350 (13)	615 (7)	4.79 (5)
P(3)	1193 (8)	1391 (14)	−657 (7)	6.68 (7)
P(4)	3272 (8)	959 (14)	1765 (6)	5.85 (5)
P(5)	3682 (8)	3151 (13)	−571 (7)	5.43 (4)
P(6)	2737 (9)	750 (13)	−1726 (6)	6.14 (5)
P(7)	3924 (8)	−1326 (14)	−377 (7)	5.94 (5)
P(8)	2248 (8)	−1362 (14)	724 (7)	6.57 (6)

[a] Esd's are in parentheses for x, y, z, and U_{eq}; $U_{eq} = {}^1/_3\Sigma_i\Sigma_j a_i^* a_j^* a_i \cdot a_j U_{ij}$.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[Au_8(PPh_3)_7](NO_3)_2$

Au(1)–Au(2)	2.688 (6)	Au(4)–Au(8)	2.842 (5)
Au(1)–Au(3)	2.720 (3)	Au(5)–Au(6)	2.942 (6)
Au(1)–Au(4)	2.663 (5)	Au(6)–Au(7)	2.817 (5)
Au(1)–Au(5)	2.724 (6)	Au(7)–Au(8)	2.829 (5)
Au(1)–Au(6)	2.673 (5)	Au(2)–P(2)	2.30 (3)
Au(1)–Au(7)	2.672 (5)	Au(3)–P(3)	2.27 (2)
Au(1)–Au(8)	2.629 (5)	Au(4)–P(4)	2.32 (2)
Au(2)–Au(3)	2.879 (5)	Au(5)–P(5)	2.31 (3)
Au(2)–Au(4)	2.796 (5)	Au(6)–P(6)	2.36 (2)
Au(2)–Au(5)	2.901 (5)	Au(7)–P(7)	2.28 (3)
Au(3)–Au(5)	2.706 (5)	Au(8)–P(8)	2.24 (3)
Au(3)–Au(6)	2.923 (6)		

P(2)–Au(2)–Au(1)	168.9 (6)	Au(3)–Au(1)–Au(5)	59.6 (2)
P(3)–Au(3)–Au(1)	133.0 (6)	Au(3)–Au(1)–Au(6)	65.6 (2)
P(4)–Au(4)–Au(1)	170.3 (6)	Au(3)–Au(1)–Au(7)	124.0 (2)
P(5)–Au(5)–Au(1)	145.6 (6)	Au(3)–Au(1)–Au(8)	118.9 (2)
P(6)–Au(6)–Au(1)	172.4 (6)	Au(4)–Au(1)–Au(5)	116.2 (2)
P(7)–Au(7)–Au(1)	165.7 (5)	Au(4)–Au(1)–Au(6)	173.8 (3)
P(8)–Au(8)–Au(1)	160.0 (6)	Au(4)–Au(1)–Au(7)	110.9 (2)
Au(2)–Au(1)–Au(3)	64.3 (2)	Au(4)–Au(1)–Au(8)	65.0 (2)
Au(2)–Au(1)–Au(4)	63.0 (2)	Au(5)–Au(1)–Au(6)	66.0 (2)
Au(2)–Au(1)–Au(5)	64.8 (2)	Au(5)–Au(1)–Au(7)	115.6 (2)
Au(2)–Au(1)–Au(6)	122.2 (2)	Au(5)–Au(1)–Au(8)	178.4 (2)
Au(2)–Au(1)–Au(7)	171.2 (3)	Au(6)–Au(1)–Au(7)	63.6 (2)
Au(2)–Au(1)–Au(8)	115.4 (2)	Au(6)–Au(1)–Au(8)	112.9 (2)
Au(3)–Au(1)–Au(4)	120.5 (2)	Au(7)–Au(1)–Au(8)	64.5 (2)

and crystallization were carried out under an N_2 atmosphere, with use of Schlenk apparatus.

The infrared spectrum shows—besides bands attributable to coordinated phosphine—ν(CO)'s at 2010, 1940, and 1885 cm^{-1}, lying at lower values than those in $PPh_3Au[Co(CO)_4]$[11] (2045, 1975, and 1945 cm^{-1}). Due to the small amount of product no other physical measurements have been performed. When not mentioned, all solvents were of Merck p.A. grade.

Structure Determination of $Au_8(PPh_3)_7(NO_3)_2\cdot 2CH_2Cl_2$

Collection and Reduction of Crystallographic Data. Single crystals of $Au_8(PPh_3)_7(NO_3)_2\cdot 2CH_2Cl_2$ rapidly lose the solvent molecules and, hence, their crystallinity. Therefore, a crystal was mounted in a sealed capillary and X-ray data were measured on a Nonius CAD4 diffractometer, with monochromated Cu Kα radiation. The unit cell dimensions were calculated from the setting angles of 25 reflections having 16° < 2θ < 50°. The crystal data are listed in Table II.

The data were collected by the ω–2θ mode with a variable scan speed, with a maximum of 45 s/reflection. A total of 11 212 reflections with 2° < θ < 27.5° were recorded ($\pm h,\pm k,\pm l$). Three standard reflections were measured after every 1800 s of X-ray exposure time, whose intensities decreased to 50% of the initial values, due to decomposition of the crystal. After averaging of equivalent reflections ($R_{av} = [(\sum||I| - |\bar{I}||)/\sum|I|] = 0.056$, including all reflections) 2829 reflections remained of which 2180 had $I > 3\sigma(I)$ ($\sigma(I)$ based on counting statistics). The intensity data of the remaining 2829 reflections were corrected for Lorentz and polarization effects and then reduced to $|F_o|$ values. Correction of the data for absorption was not done.

Solution and Refinement of the Structure. The structure was solved by using a Patterson synthesis to find the position of the gold atoms. The remaining non-hydrogen atoms were positioned by the DIRDIF procedure[13] and by difference Fourier maps. All of the 2829 observed reflections were used in the refinement by full-matrix least-squares methods, allowing anisotropic vibrations for gold and phosphorus, with constrained phenyl rings (including H atoms), nitrate ions, and dichloromethane. The weight w for each reflection was calculated

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[13] P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, T. E. M. van den Hark, and P. A. J. Prick, Technical Report 1980/1, Crystallography Laboratory, University of Nijmegen, The Netherlands.

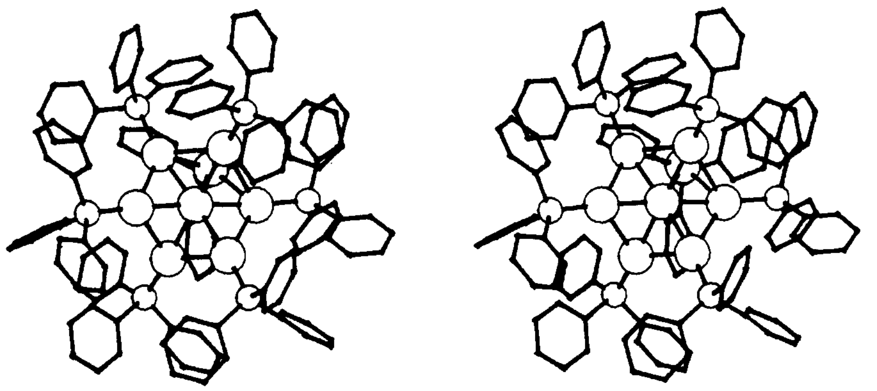

Figure 1. Stereoview of the $[Au_8(PPh_3)_7]^{2+}$ cluster.

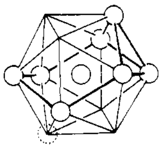

Figure 2. Au skeleton of the $[Au_8(PPh_3)_7]^{2+}$ cluster in relation to the regular icosahedron. The dotted circle represents the extra Au atom in $[Au_9(PPh_3)_8]^{3+}$.

according to the formula $w = [(\sigma_0{}^2 + 0.03F_o)^2]^{-1}$. The refinement converged to an R value $(=\sum(|F_o| - |F_c|)/\sum|F_o|)$ of 0.056 and R_w value $(=[\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2})$ of 0.077. The atomic scattering factors were taken from Table 2.2.B of ref 14. All crystallographic calculations were executed with use of the XRAY-76 programs.[15] Positional parameters are listed in Table III and selected bond distances and angles in Table IV.

Description of the Structure of $[Au_8(PPh_3)_7](NO_3)_2 \cdot 2CH_2Cl_2$

Overall Molecular Configuration and Packing. The crystal consists of cationic gold clusters $[Au_8(PPh_3)_7]^{2+}$ (Figure 1) packed together with nitrate anions and CH_2Cl_2 molecules. An inspection of all nonbonding interactions within each molecule and between different molecules does not reveal unusually short contacts. The $[Au_8(PPh_3)_7]^{2+}$ cation is totally asymmetric, not only as the whole molecule but also in the Au–P and Au skeletons. The nitrate ions and methylene chloride molecules were constrained to an ideal model. RMS deviation from an ideal phenyl ring and the ideal nitrate ion is 0.1 Å.

The Metal Atom Cluster. The Au skeleton can be described as being derived from the regular icosahedral Au_{13} cluster,[16,17] by removing two and three gold atoms, respectively, above and below the centered hexagon, a common feature of all gold clusters containing 8, 9, 11, or 13 Au atoms (Figure 2).

In terms of coordination numbers, the central Au atom is seven-coordinated, exclusively so by Au atoms. The peripheral Au atoms are all five-coordinated, with the exception of Au(4), Au(7), and Au(8) with the coordination number 4 (Figure 3).

The mean center-to-periphery gold distance is 2.68 Å (see also Table IV), a value very near those of $[Au_8(PPh_3)_8]^{2+}$ (2.70 Å),[2,3] $[Au_9(P(p\text{-}MeC_6H_4)_3)_8]^{3+}$ (2.71 Å),[8] and $Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$ (2.68 Å).[18a] The shortest center-to-periphery gold distance is Au(1)–Au(8) = 2.63 Å. The mean peripheral gold distance is 2.85 Å, which is a normal value for the above-mentioned centered Au clusters, where this distance lies between 2.81 and 2.98 Å. As can be seen from these figures, the peripheral gold distances are generally larger than the center-to-periphery (or radial) distances. In contrast to this, $[Au_8(PPh_3)_7]^{2+}$ contains one very short peripheral distance Au(3)–Au(5) = 2.706 (5) Å.

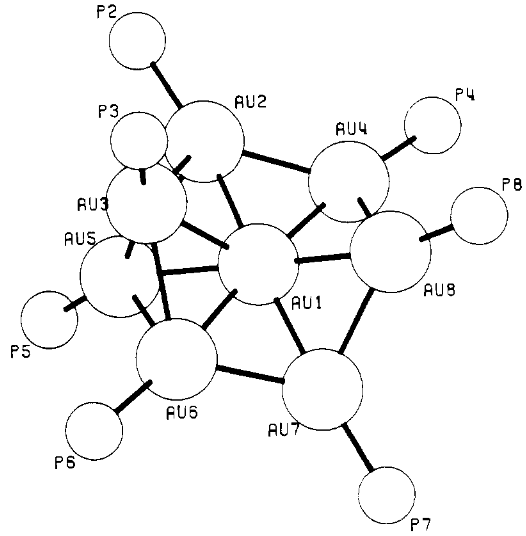

Figure 3. Au–P skeleton of $[Au_8(PPh_3)_7]^{2+}$ with the numbering scheme. Phenyl rings have been omitted for clarity.

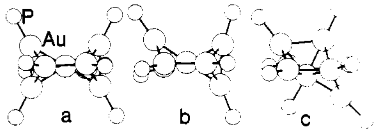

Figure 4. Au–P skeleton of $[Au_9(P(p\text{-}CH_3C_6H_4)_3)_8]^{3+}$ (a), $[Au_8(PPh_3)_7]^{2+}$ (b), and $[Au_8(PPh_3)_8]^{2+}$ (c).

The Metal–Ligand System. Every peripheral gold atom has one bonded triphenylphosphine ligand (Figure 3). In contrast with $[Au_8L_8]^{2+}$ (L = PPh_3) the Au(1) in the center of the hexagon has no phosphine bonded to itself, so it is rather exposed. Most of the Au–P vectors point approximately toward this central gold atom ($\angle P\text{–}Au_{per}\text{–}Au(1)$ = 160–172°) with the remarkable exception of $\angle P(3)\text{–}Au(3)\text{–}Au(1)$ = 133.0 (6)° and $\angle P(5)\text{–}Au(5)\text{–}Au(1)$ = 145.6 (6)°. In most centered gold clusters the $P\text{–}Au_{per}\text{–}Au_{centr}$ moieties are essentially linear,

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(14) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1977.

(15) J. M. Stewart, Ed., "The X-ray system, version of 1976", Technical Report TN-446, Computer Science Center, University of Maryland, College Park, MD.

(16) J. W. A. van der Velden, F. A. Vollenbroek, J. J. Bour, P. T. Beurskens, J. M. M. Smits, and W. P. Bosman, *Recl. Trav. Chim. Pays-Bas*, **100**, 148 (1981).

(17) C. E. Briant, B. R. C. Theobald, J. W. White, L. K. Bell, D. M. P. Mingos, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 201 (1981).

(18) (a) P. L. Bellow, M. Manassero, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 1481 (1972). (b) We assume that $[Au_9L_8]^{3+}$ is isostructural with $[Au_9(P(p\text{-}CH_3C_6H_4)_3)_8]^{3+}$, an assumption based on similar chemical, analytical, and spectral properties.

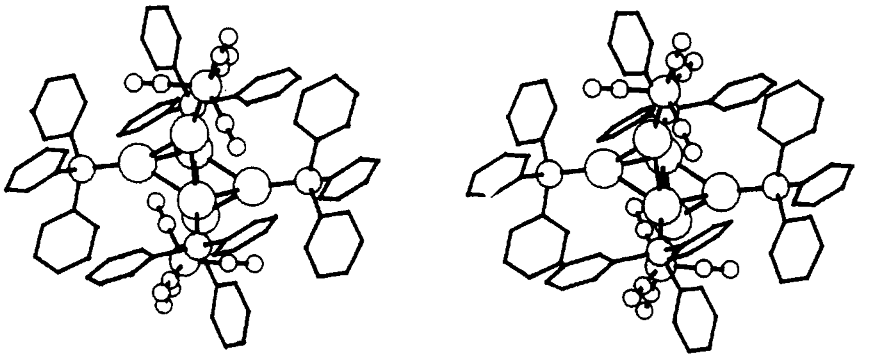

Figure 5. Stereoview of the $Au_6(PPh_3)_4[Co(CO)_4]_2$ cluster.

with the exception of $[Au_9(P(p\text{-}CH_3C_6H_4)_3)_8]^{3+}$, where two sets of four equivalent angles are present at 150 and 180°.[8]

In $[Au_8L_8]^{2+}$ the peripheral Au–P distances are in the range 2.29 (3)–2.33 (3) Å, in contrast to the considerably longer Au(1)–P distance, 2.42 (3) Å (Figure 4c). This fact suggested that the use of 1 equiv of phosphine abstractor might lead to the abstraction of the phosphine ligand from the central gold atom. Indeed, the formed $[Au_8L_7]^{2+}$ has no phosphine attached to the central Au atom, but the overall Au–P skeleton differs as well from the starting material $[Au_8L_8]^{2+}$. The change in structure consists mainly of a shift of the Au(3)–P(3) entity, from right above the Au(1)–P(1) axis toward an icosahedral gold position (c → b in Figure 4). By doing so, the overall Au–P skeleton shows a strong similarity to that of $[Au_9L_8]^{3+}$,[18b] from which it can be obtained by abstraction of an $[AuL]^+$ ion (a → b in Figure 4). This is in agreement with the proposed dissociative equilibrium of $[Au_9L_8]^{3+}$ in solution, resulting in the formation of $[Au_8L_7]^{2+}$ and $[AuL]^+$. As was already pointed out in the text above, the P–Au_{per}–Au(1) angles in $[Au_8L_8]^{2+}$ are essentially linear (mean value 173°), while there are two sets of angles in $[Au_9L_8]^{3+}$. It is remarkable that in $[Au_8L_7]^{2+}$ for the same groups as in $[Au_9L_8]^{3+}$ similar sets of angles can be observed ($\angle$P(*n*)–Au(*n*)–Au(1): *n* = 3, 5, and 8, mean value 146°; *n* = 2, 4, 6, and 7, mean value 169°). It should also be remarked that the shortest peripheral Au distance occurs at the atoms with the strongest deviation from linearity in pointing Au–P vectors, at Au(3) and Au(5).

Another intriguing resemblance to the $[Au_9L_8]^{3+}$ cluster can be found in the ^{197}Au Mössbauer spectra of both compounds, which show only one quadrupole doublet, with similar Mössbauer parameters in the range normally found for peripheral gold atoms bonded to phosphines.[19] In contrast with all other centered gold clusters, where a single resonance line could be observed for the central atom, no separate signal could be seen in either of these two compounds, suggesting that the Mössbauer parameters of Au_{centr} are almost the same as those of the peripheral gold atoms or that their intensity might be too low to be detected separately.

Structure Determination of $Au_6C_{80}Co_2H_{60}P_4O_8$

Collection and Reduction of Crystallographic Data. Crystallographic data of a crystal 0.1 × 0.1 × 0.1 mm were collected on a single-crystal CAD4 diffractometer using Mo Kα radiation (λ = 0.71073 Å), monochromated with a graphite-crystal monochromator. The unit cell dimensions were calculated from the setting angles of 25 reflections having 11° < 2θ < 22°. The crystal data are listed in Table II.

The data were collected by the ω–2θ mode with a variable scan speed, with a maximum of 45 s/reflection. A total of 5443 reflections with 1.5° < θ < 18° were recorded ($\pm h, \pm k, \pm l$). Three standard reflections were measured after every 1800 s of X-ray exposure time. Their intensities decreased to 75% of the initial values, due to the decomposition of the crystal. After averaging of equivalent reflections ($R_{av} = (\sum||I| - |\bar{I}||)/\sum|I|$ = 0.06, including all reflections) 2723 reflections remained, of which 1240 had $I > 3\sigma(I)$ ($\sigma(I)$ based on counting statistics). The intensity data of the remaining 2723 reflections were corrected for Lorentz and polarization effects and then reduced to $|F_o|$ values. Correction of the data for absorption has not been done.

Table V. Fractional Coordinates (×10⁴) and Isotropic Thermal Parameters (×100, Å²) for $Au_6(PPh_3)_4[Co(CO)_4]_2$[a]

	x	*y*	*z*	U_{eq}
Au(1)	4922 (3)	5056 (3)	5919 (3)	5.8 (2)
Au(2)	5922 (3)	3041 (3)	4636 (3)	7.7 (3)
Au(3)	3728 (3)	3455 (3)	3672 (3)	7.2 (3)
Co	1960 (10)	2500 (10)	2120 (10)	12.0 (1)
P(1)	4870 (20)	5170 (20)	7570 (20)	8.6 (2)
P(2)	7570 (20)	1850 (20)	4830 (20)	6.8 (2)

[a] Esd's are in parentheses for *x*, *y*, *z*, and U_{eq}; $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j a_i \cdot a_j U_{ij}$.

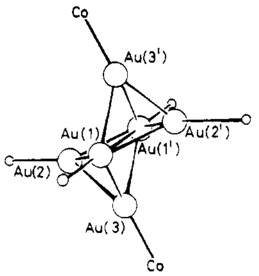

Figure 6. $Au_6P_4[Co(CO)_4]_2$ skeleton. Phenyl rings have been omitted for clarity.

Solution and Refinement of the Structure. The structure was solved by using a Patterson synthesis to find the position of the gold atoms. The remaining non-hydrogen atoms were positioned by the DIRDIF procedure[13] and by difference Fourier maps.

All of the 1240 observed reflections were used in the refinement by the full-matrix least-squares method. We allowed anisotropic vibration for gold, cobalt, and phosphorus atoms, with constrained phenyl rings and carbonyls. The weight *w* for each reflections was calculated according to the formula $w = [\sigma_o^2 + (0.005F_o)^2]^{-1}$. The refinement converged to an *R* value ($=\sum(|F_o| - |F_c|)/\sum|F_o|$) of 0.078 and $R_w = (=[\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$ = 0.105.

The relatively high *R* value is the result of a disorder in the phenyl groups. No attempts have been made to solve the disorder problem, since the conformation of the backbone of the molecule was our main interest. The atomic scattering factors were taken from Table 2.2B of ref 14. All crystallographic calculations were executed with use of the X-RAY-76 programs.[15] Positional parameters are listed in Table V and selected bond distances and angles in Table VI.

Description of the Structure of $Au_6L_4[Co(CO)_4]_2$ (L = PPh_3)

Overall Molecular Configuration and Packing. The crystal is composed of neutral molecules $Au_6L_4[Co(CO)_4]_2$ (Figure 5). An inspection of all nonbonding interactions within each molecule and between different molecules does not reveal

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(19) F. A. Vollenbroek, J. W. A. van der Velden, J. J. Bour, and J. M. Trooster, *Recl. Trav. Chim. Pays-Bas*, **100**, 375 (1981).

Table VI. Bond Distances (Å) and Angles (deg) for $Au_6(PPh_3)_4[Co(CO)_4]_2$

Au(1)-Au(2)	2.773 (6)	Au(2)-Au(3)	2.621 (7)
Au(1)-Au(3)	2.811 (5)	Au(3)-Co	2.460 (16)
Au(1)-Au(1′)	2.655 (9)	Au(1)-P(1)	2.282 (42)
Au(1)-Au(2′)	2.801 (8)	Au(2)-P(2)	2.368 (24)
Au(1)-Au(3′)	2.823 (9)		
Au(2)-Au(1)-Au(3)	56.0 (2)	Au(1)-Au(3)-Au(1′)	56.2 (2)
Au(2)-Au(1)-Au(1′)	62.1 (2)	Au(2)-Au(3)-Au(1′)	61.8 (2)
Au(2)-Au(1)-Au(2′)	123.0 (3)	Au(1)-Au(3)-Co	151.1 (6)
Au(2)-Au(1)-Au(3′)	96.7 (3)	Au(2)-Au(3)-Co	143.0 (4)
Au(3)-Au(1)-Au(1′)	62.1 (2)	Au(1′)-Au(3)-Co	139.7 (7)
Au(3)-Au(1)-Au(2′)	96.4 (2)	Au(2)-Au(1)-P(1)	120.0 (7)
Au(3)-Au(1)-Au(3′)	123.8 (3)	Au(3)-Au(1)-P(1)	119.2 (8)
Au(1′)-Au(1)-Au(2′)	61.0 (2)	Au(1′)-Au(1)-P(1)	178.6 (9)
Au(1′)-Au(1)-Au(3′)	61.7 (3)	Au(2′)-Au(1)-P(1)	118.9 (7)
Au(2′)-Au(1)-Au(3′)	55.6 (2)	Au(3′)-Au(1)-P(1)	117.1 (8)
Au(1)-Au(2)-Au(3)	62.7 (2)	Au(1)-Au(2)-P(2)	139.6 (7)
Au(1)-Au(2)-Au(1′)	56.9 (2)	Au(3)-Au(2)-P(2)	155.7 (6)
Au(3)-Au(2)-Au(1′)	62.6 (2)	Au(1′)-Au(2)-P(2)	132.8 (10)
Au(1)-Au(3)-Au(2)	61.3 (2)		
Au(3)-Co-C(1)	82 (2)	Au(3)-Co-C(3)	174 (2)
Au(3)-Co-C(2)	78 (2)	Au(3)-Co-C(4)	76 (2)

unusually short contacts. The molecule itself is centrosymmetric. Figure 6 shows the labeling scheme used.

The Metal Atom Cluster. In describing the octanuclear Au_6Co_2 skeleton, it is feasible to separate the Au and Co atoms, since the $Co(CO)_4$ groups are coordinated to one Au atom each on the periphery of the gold skeleton. In this way it might be argued that $Co(CO)_4$ functions only as a ligand.

The Au skeleton itself can be described as two tetrahedrons with one common edge, which deviates from the squeezed octahedron in $[Au_6(P(p\text{-}CH_3C_6H_4)_3)_6]^{2+}$.[20] Tetrahedral constructions are, however, favored for small noncentered gold clusters, as they have been reported in three instances: $[Au_5(PPh_2CH_2PPh_2)_3(PPh_2CHPPh_2)]^{2+}$,[21,22] $Au_4(PPh_3)_4(\mu\text{-}I)_2$,[23] and $[Au_6(PPh_2(CH_2)_3PPh_2)_4]^{2+}$.[24] The mean Au–Au distance is 2.76 Å, ranging from 2.62 to 2.81 Å. The distances Au(1)–Au(1′) (2.66 Å) and Au(2)–Au(3) (2.62 Å) are among the shortest ever found for gold clusters. Considering the $[Co(CO)_4]$ groups as anions, the charge on the Au skeleton can be regarded as 2+, a similar value as for the other above-mentioned Au_6 clusters.

The Metal–Ligand System. Four gold atoms (1, 1′, 2, 2′) are bonded to phosphine ligands, while the two apical gold atoms are coordinated to tetracarbonylcobalt (Figure 6). All Au–P distances are equal (2.29 (3) Å), at a normal value for gold phosphine clusters. The phosphines bonded to Au(1) and Au(1′) lie in the same plane as the four gold atoms of any of the two Au_4 diamonds and form an almost linear P–Au(1)–Au(′)–P moiety (∠P–Au(1)–Au(1′) = 178.6 (9)°). The other two phosphines, which are coordinated to Au(2) and Au(2′), respectively, are tilted, one above and one below the plane, their P–Au vectors pointing toward the center of the nearest tetrahedron (Figure 6). Also the Au–Co vectors point inwards toward the tetrahedrons. The Au–Co distances (2.46 Å) are identical with that in $PPh_3Au[Co(CO)_4]$,[11] with the $[Co(CO)_4]$ group having the same slightly distorted trigonal bipyramidal coordination. In accordance with this, the IR spectra of both compounds show similar bands in the ν(CO) region, although there is a significant lowering of 35–60 cm^{-1}. This lowering should be attributed to the higher electron density on the metal skeleton in the cluster, resulting in a larger π-back-donation into the π* MO's of the carbonyls.

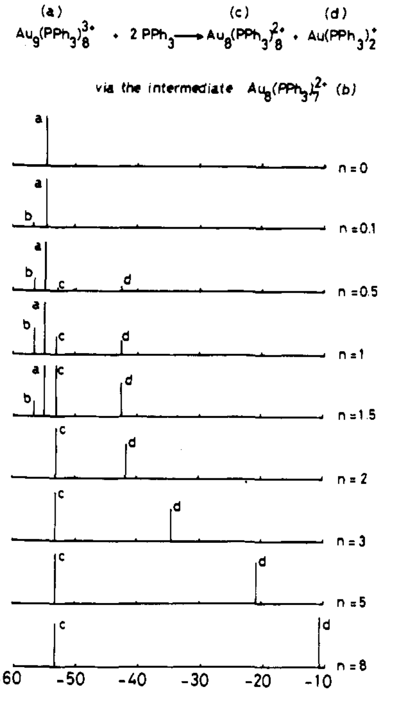
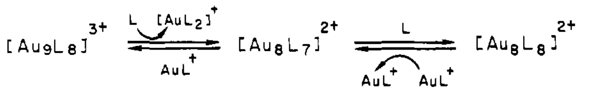


Figure 7. $^{31}P\{^1H\}$ NMR stick spectra, corresponding to $[Au_9L_8]^{3+} + nL$ (L = PPh_3, $0 \le n \le 8$; all compounds giving singlets; a = $[Au_9L_8]^{3+}$, b = $[Au_8L_7]^{2+}$, c = $[Au_8L_8]^{2+}$, and d = $[AuL_2]^+$, measured in CH_2Cl_2, with initial concentration $[[Au_9L_8]^{3+}] = 10^{-2}$ mol/L.

Scheme I



Discussion

We have indicated in a preliminary communication[4] that the reported reactivity of $[Au_9L_8]^{3+}$ (L = PPh_3) toward Lewis bases can be ascribed to the formation of an active species by a dissociative in solution:

$$[Au_9L_8]^{3+} \rightleftarrows [Au_8L_7]^{2+} + [AuL]^+ \qquad (2)$$

Since both compounds on the right hand side of eq 2 are coordinatively unsaturated, both will react with Lewis bases. This can be shown very clearly in a $^{31}P\{^1H\}$ NMR experiment where *n* equiv of L ($0 \le n \le 8$) are added to $[Au_9L_8]^{3+}$ (Figure 7). In Figure 7 it can be seen how $[Au_8L_7]^{2+}$ appears as an intermediate product, which ultimately is completely converted into $[Au_8L_8]^{2+}$ when 2 equiv or more of L are added. With increasing *n* the position of the $[AuL_2]^+$ shifts toward the position of free phosphine, due to fast exchange processes. The peak belonging to $[Au_8L_8]^{2+}$ does not shift upon addition of phosphine. Until now there has been no indication for any *fast* exchange processes (on the NMR time scale) of gold phosphine clusters with free phosphine in solution, which is a behavior well-known for Au(I) compounds.[25] *Slow* exchange processes have, however, been shown, in the substitution reaction of $Au_{11}L'_7(SCN)_3$ with L (L′ = $P(p\text{-}ClC_6H_4)_3$, L = PPh_3).[26]

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(20) P. L. Bellow, M. Manassero, and M. Sansoni, *J. Chem. Soc., Dalton Trans.*, 2423 (1973).

(21) J. W. A. van der Velden, J. J. Bour, F. A. Vollenbroek, P. T. Beurskens, and J. M. M. Smits, *J. Chem. Soc., Chem. Commun.*, 1162 (1980).

(22) J. W. A. van der Velden, F. A. Vollenbroek, J. J. Bour, P. T. Beurskens, J. M. M. Smits, and W. P. Bosman, *Recl. Trav. Chim. Pays-Bas*, **100**, 148 (1981).

(23) F. Demartin, M. Manassero, L. Naldini, R. Ruggeri, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 222 (1981).

(24) J. W. A. van der Velden, J. J. Bour, and J. J. Steggerda, submitted for publication in *Inorg. Chem.*

(25) E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, **92**, 4114 (1970).

The reverse reaction is observed when a methylene chloride solution of $[Au_8L_8]^{2+}$ is reacted with the phosphine acceptor $AuL(NO_3)$. Since $[Au_8L_8]^{2+}$ is also spherically screened by phosphine ligands again, a dissociative mechanism imposes itself:

$$[Au_8L_8]^{2+} \rightleftarrows [Au_8L_7]^{2+} + L \qquad (3)$$

When 2 equiv of $AuL(NO_3)$ is added to a solution of $[Au_8L_8]^{2+}$, the final products are $[Au_9L_8]^{3+}$ and $[AuL_2]^+$.

These interconversion reactions proceed according to Scheme: As can be seen, $[Au_8L_7]^{2+}$ resides at a central place. We therefore designed a route to synthesize and isolate this species. We succeeded in the preparation of $[Au_8L_7]^{2+}$ by reacting $[Au_8L_8]^{2+}$ with $[RhCl(C_8H_{14})_2]_2$, a well -known phosphine scavenger, in a mole ratio 4:1 in CH_2Cl_2, according to

$$[Au_8L_8]^{2+} + {}^1/_4[RhCl(C_8H_{14})_2]_2 \rightarrow [Au_8L_7]^{2+} + {}^1/_4[RhClL_2]_2 + C_8H_{14} \qquad (4)$$

$[Au_8L_7]^{2+}$ could be isolated in a reasonable yield (74%). From its X-ray structure analysis it has clearly been shown that this compound possesses a rather exposed central gold atom and should therefore be reactive toward Lewis bases. In order to synthesize mixed-metal clusters, we reacted $[Au_8L_7]^{2+}$ with $[Co(CO)_4]^-$ (mole ratio 1:2). From a number of as yet uncharacterized products, which were present in the reaction mixture, we succeeded in isolating a small amount of crystals of $Au_6L_4[Co(CO)_4]_2$.

Although a large number of mixed gold-transition metal compounds has been reported,[27] only a few mixed-metal clusters of gold and a transition metal are known at this moment: $Os_3(CO)_{10}(AuPPh_3)X$ (X = H[28] and halide[29]), $Os_3(CO)_{10}S_2(AuPPh_3)_2$,[29] and $V(CO)_5(AuPPh_3)_3$.[30] A promising and interesting area, which is currently under investigation, concerns the reations of the coordinatively unsaturated $[Au_8L_7]^{2+}$ with small molecules such as isocyanides and CO.

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Registry No. $[Au_9(PPh_3)_8](NO_3)_3$, 37336-35-9; $[Au_8(PPh_3)_8](NO_3)_2$, 81283-09-2; $[Au_8(PPh_3)_8](PF_6)_2$, 72271-20-6; $[Au_8(PPh_3)_7](NO_3)_2{\cdot}2CH_2Cl_2$, 81283-11-6; $Au_6(PPh_3)_4[Co(CO)_4]_2$, 79008-51-8; $Au(PPh_3)NO_3$, 14897-32-6; cobalt, 7440-48-4; gold, 7440-57-5.

Supplementary Material Available: Listings for both $[Au_8(PPh_3)_7](NO_3)_2{\cdot}2CH_2Cl_2$ and $Au_6(PPh_3)_4[Co(CO)_4]_2$ of structure factor tables and fractional coordinates of the carbon, nitrogen, oxygen, and chlorine atoms and a listing of fractional coordinates of the hydrogen atoms attached to the phenyl carbon atoms calculated for $[Au_8(PPh_3)_7](NO_3)_2{\cdot}2CH_2Cl_2$ (37 pages). Ordering information is given on any current masthead page.

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(26) F. A. Vollenbroek, J. P. van den Berg, J. W. A. van der Velden, and J. J. Bour, *Inorg. Chem.*, **19**, 2685 (1980).

(27) R. J. Puddephatt, "The Chemistry of Gold", Elsevier, Amsterdam, 1979, pp 157-178.

(28) L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 260 (1978).

(29) C. W. Bradford, W. van Bronswigk, R. J. H. Clark, and R. S. Nyholm, *J. Chem. Soc. A*, 2889 (1970).

(30) J. E. Ellis, *J. Am. Chem. Soc.*, **103**, 6106 (1981).

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Carbon-13 and Phosphorus-31 NMR Studies of Interactions of Organorhodium Complexes with Guanosine, Inosine, 6-Mercaptoguanosine, and 8-Mercaptoguanosine in Neutral and Basic Dimethyl-d_6 Sulfoxide Solutions

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The interactions of the carbonylbis(triphenylphosphine)rhodium(I) electrophile with inosine, guanosine, 6-mercaptoguanosine, and 8-mercaptoguanosine have been investigated in neutral and basic dimethyl-d_6 sulfoxide solutions with the use of ^{13}C and $^{31}P\{^1H\}$ NMR spectroscopy. The binding of $[(PPh_3)_2(CO)Rh]^+$ to O(6) of guanosine and inosine has been found to increase the acidity of N(1)-H. Complexation of the Rh(I) cation at S(6) of 6-mercaptoguanosine has also been found to promote deprotonation at N(1), while binding at S(8) of 8-mercaptoguanosine promotes deprotonation at N(7). Data are presented that indicate that the complexation of $[(PPh_3)_2(CO)Rh]^+$ with 8-mercaptoguanosine changes the preferred site of deprotonation for the thionucleoside, providing more evidence that interactions of transition metals with nucleic base derivatives can significantly alter the chemical behavior of those derivatives. It has been shown that carbon atoms near a site of deprotonation and a site of metal complexation can experience opposing effects under basic conditions, leading to an overall negligible shift in the resonances of those carbon atoms. Problems that can arise under these conditions are discussed.

Introduction

The report of the antitumor behavior of platinum(II) compounds[1] has led to a flurry of activity over the past decade in the area of metal interactions with nucleic acids.[2-4] The interaction of metal species at O(6) of guanosine (Guo) and its derivatives has taken on added significance since it was postulated that the antitumor behavior of some substances might be linked to their ability to interact at O(6) of the

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(1) Rosenberg, B.; van Camp, L.; Trosko, J. E.; Mansour, V. H. *Nature (London)* **1969**, *222*, 385.

(2) Marzilli, L. G. *Adv. Inorg. Biochem.* **1981**, *3*, 47.

(3) Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 225.

(4) Martin, R. B.; Mariam, Y. H. *Met. Ions Biol. Syst.* **1977**, *8*, 57.