Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Rhodium Complexes of 2-(Diphenylphosphino)pyridine. X-ray Crystal and Molecular Structure of $Rh_2[(C_6H_5)_2PC_5H_4N]_2(\mu\text{-}CO)Cl_2$ and Some Chemical Transformations of This Complex

JAMES P. FARR, MARILYN M. OLMSTEAD, CATHERINE H. HUNT, and ALAN L. BALCH*

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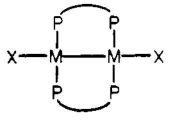
Addition of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ to 2-(diphenylphosphino)pyridine (Ph_2Ppy) yields planar $Rh(Ph_2Ppy)_2(CO)Cl$. Reaction of $Rh(Ph_2Ppy)_2(CO)Cl$ with $[Rh(CO)_2(\mu\text{-}Cl)]_2$ yields $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. Treatment of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ with sulfur dioxide produces $Rh_2(Ph_2Ppy)_2(\mu\text{-}SO_2)Cl_2$; this reaction may be reversed by adding carbon monoxide. The structure of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ has been determined by X-ray crystallography. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell of dimensions $a = 9.920$ (6) Å, $b = 12.509$ (6) Å, $c = 13.860$ (7) Å, $\alpha = 93.06$ (4)°, $\beta = 107.57$ (4)°, and $\gamma = 100.01$ (4)°. Full-matrix least-squares refinement yielded $R = 0.034$.

Introduction

Binuclear complexes using bis(diphenylphosphino)methane (dpm) to hold two metal atoms in close proximity have received considerable attention in recent years. This ligand has been found to bridge metal atoms with various coordination numbers in a number of different geometries. If we use the symbol $\overset{\sqcap}{\underset{\sqcup}{6\ 6}}$ to represent a binuclear complex with two six-coordinate metal ions and two bridging dpm ligands, then examples of each of the following types of binuclear, dpm-bridged complexes are known: $\overset{\sqcap}{7\ 7}$, $Re_2(dpm)(\mu\text{-}H)_2(CO)_6$;[1] $\overset{\sqcap}{\underset{\sqcup}{6\ 6}}$, $Rh_2(dpm)_2(CNR)_4I_2^{2+}$;[2] $\overset{\sqcap}{6\ 6}$, $Fe_2(dpm)(\mu\text{-}CO)(CO)_6$;[3] $\overset{\sqcap}{\underset{\sqcup}{6\ 5}}$, $Re_2(dpm)_2Cl_5$;[4] $\overset{\sqcap}{\underset{\sqcup}{5\ 5}}$, $Mo_2(dpm)_2(NCS)_4$;[5] $\overset{\sqcap}{\underset{\sqcup}{5\ 4}}$, $Pt_2(dpm)_3(CH_3)_3^+$;[5] and $\overset{\sqcap}{\underset{\sqcup}{4\ 4}}$, $Pd_2(dpm)_2(\mu\text{-}SO_2)Cl_2$.[6] Within these classes additional structural variation can occur. Complexes of the $\overset{\sqcap}{\underset{\sqcup}{4\ 4}}$ type have received particular attention. Here interconversion between three structural types, **1**, the side-by-side dimer, **2**, the molecular A-frame, and **3**, the face-to-face dimer, are known.[8] As a result of the proximity of the two metals in these complexes, a number of unique chemical reactions have been observed. These frequently involve metal-metal bond forming or bond breaking. They include the facile insertion of small molecules into the Pd-Pd bond of $Pd_2(dpm)_2Cl_2$,[7-9] oxidation of Rh(I) to Rh(II) compounds with the formation of a Rh-Rh bond,[2] and the addition of carbon monoxide to two Rh(I) centers to form a metal-metal bond.[10,11] Among the novel structures which result are compounds with bridging carbonyl,[8,12] isocyanide,[8,13] or methylene ligands[14] and long (ca. 3.2 Å) metal-metal separation and compounds with side-on bonded carbonyl[15] and isocyanide[16] ligands.



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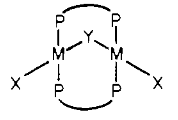

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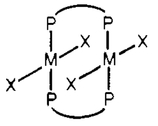

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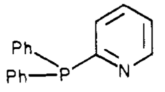
We have embarked on a program to construct and utilize other phosphine ligands to support binuclear metal complexes. Here we report on some rhodium chemistry involving 2-(diphenylphosphino)pyridine, **4**, Ph_2Ppy. This ligand should be capable of substituting for triphenylphosphine in any of the numerous complexes that the latter ligand forms, but Ph_2Ppy has a nitrogen atom positioned so that it can bind to a second metal. The phosphorus and nitrogen donors are oriented so that the ligand should function as a bridging ligand rather than as a chelating ligand. In the past this ligand has attracted relatively little attention.[17,18] However we have recently reported on the construction of binuclear metal complexes using this ligand.[19] Details of some of that work are reported here.



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Experimental Section

Preparation of Compounds. Ph_2Ppy was prepared by the method of Mann and Watson.[20]

$Rh(Ph_2Ppy)_2(CO)Cl$. A solution of 0.169 g (0.434 mmol) of chlororhodium dicarbonyl dimer in 15 mL of dichloromethane was added dropwise to a solution of 0.458 g (1.74 mmol) of Ph_2Ppy in 15 mL of dichloromethane. After filtration of the solution, ether was added dropwise to the filtrate. The yellow crystals which precipitated were collected by filtration and dried under vacuum; yield 0.56 g (88%). Anal. Calcd for $C_{35}H_{28}ClN_2OP_2Rh$: C, 60.67; H, 4.07; N, 4.04. Found: C, 60.37; H, 4.30; N, 4.47.

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$Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. Method 1. A solution of 0.475 g (1.8 mmol) of Ph_2Ppy in 15 mL of dichloromethane was added dropwise to a solution of 0.351 g (0.90 mmol) of chlororhodium dicarbonyl dimer in 15 mL of dichloromethane. The red-brown solution was filtered, and ether was added dropwise to the filtrate. The brown crystalline solid which formed was collected by filtration, washed with ether, and vacuum dried; yield 0.73 g (97%). Anal. Calcd for $C_{35}H_{28}Cl_2N_2OP_2Rh_2$: C, 50.57; H, 3.39. Found: C, 49.74; H, 3.48.

Method 2. A solution of 33.2 mg (0.085 mmol) of chlororhodium dicarbonyl dimer in 10 mL of dichloromethane was added dropwise to a solution of 117.5 mg (0.169 mmol) of $Rh(Ph_2Ppy)_2(CO)Cl$ in 10 mL dichloromethane. Red-brown crystals of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ formed when ethyl ether was added dropwise to the solution. The product was collected by filtration, washed with ethyl ether, and vacuum dried; yield 110 mg (78%).

$Rh_2(Ph_2Ppy)_2(\mu\text{-}SO_2)Cl_2$. Sulfur dioxide was bubbled through a solution of 0.082 g (0.099 mmol) of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ in 15 mL of dichloromethane for 15 min. Ethyl ether was added to this solution dropwise, and red-brown crystals were formed. These were collected by filtration. Purification was accomplished by recrystallization from dichloromethane–ether; yield 0.045 g (53%). Anal. Calcd for $C_{34}H_{28}Cl_2N_2O_2P_2RhS$: C, 47.08; H, 3.25; Cl, 8.17; N, 3.23. Found: C, 47.02; H, 3.64; Cl, 8.26; N, 3.32.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 180 infrared spectrometer. ^1H NMR and proton-decoupled ^{31}P NMR spectra were recorded on a Nicolet NT-200 Fourier Transform spectrometer at 200 and 81 MHz, respectively. An external, 85% phosphoric acid reference was used for ^{31}P NMR spectra and the high-frequency-positive convention, recommended by IUPAC, has been used in reporting chemical shifts.

Simulations of the entire ^{31}P spectra were performed with use of the noniterative simulation routine of the Nicolet software on a model 1180 Nicolet data system. This simulation routine is a modified version of LAOCOON III. The fit of the simulation was based on matching the individual peak positions and intensities of the observed and the calculated spectra.

X-ray Data Collection. Well-formed crystals were grown by slow diffusion of diethyl ether into a dichloromethane solution of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. A red-brown crystal of dimensions 0.035 × 0.02 × 0.0125 mm was attached to a thin-glass fiber with use of silicon grease and mounted on a Syntex $P2_1$ diffractometer in a nitrogen stream at 140 K. On the basis of the automatic indexing feature of the diffractometer software and axial photographs, the crystal lattice was triclinic with space group $P\bar{1}$. Ten centered reflections together with their Friedel pairs, in the range $30° < 2\theta < 40°$, yielded lattice constants of $a = 9.920$ (6) Å, $b = 12.509$ (6) Å, $c = 13.860$ (7) Å, $\alpha = 93.06$ (4)°, $\beta = 107.57$ (4)°, and $\gamma = 100.01$ (4)°. The density at room temperature was determined by flotation to be 1.66 g cm^{-3}. On the basis of $Z = 2$ and a volume at 140 K of 1604.4 $Å^3$, the calculated density is 1.72 g cm^{-3}.

Data collection was carried out by using graphite-monochromatized Mo Kα ($\lambda = 0.71069$ Å) radiation, a variable-speed (2–60° min^{-1}) ω scan of 1° range and 1° offset for stationary-background counts. Two standard reflections which were checked after every 118 reflections showed no decay. Data were collected to 2θ of 45°, giving 4204 unique reflections of which 3746 with $I > 3\sigma(I)$ were used in the final refinement. The usual Lorentz and polarization corrections were made, but no correction was made for absorption in view of the crystal size and absorption coefficient (12.5 cm^{-1}) for Mo Kα radiation.

Solution and Refinement of the Structure. The structure was solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares methods with use of procedures outlined previously, with corrections for anomalous dispersion applied to Rh, Cl, and P.[7] Solution of the structure proceeded smoothly with use of the space group $P\bar{1}$ and this choice of space group was assumed to be correct. Final refinement was carried out with anisotropic thermal parameters for Rh, Cl, and P and isotropic thermal parameters for the remaining nonhydrogen atoms. Hydrogen atoms were not included. The final discrepancy index, $R = (\sum||F_o| - |F_c||)/\sum|F_o|$, is 0.034, with 19 reflections/parameter. A difference Fourier map showed no features larger than those that could be assigned to hydrogen atoms.

Results

Synthetic Studies. Addition of $[Rh(CO)_2Cl]_2$ to Ph_2Ppy in dichloromethane solution produces yellow $Rh(Ph_2Ppy)_2(CO)Cl$ in nearly quantitative yield. In appearance as well as chemical and physical properties, this compound resembles the well-known $Rh(Ph_3P)_2(CO)Cl$. Spectroscopic parameters for $Rh(Ph_2Ppy)_2(CO)Cl$ are compared with those of $Rh(Ph_3P)_2(CO)Cl$ in parentheses in the following list: ν_{CO} 1962 cm^{-1}, Nujol; ν_{CO} 1982, dichloromethane solution (1968 cm^{-1}, dichloromethane);[20] ν_{Rh-Cl} 304 cm^{-1} (313);[21] $^{31}P\{^1H\}$ NMR δ 30.13 (29.1),[22] $J(Rh\text{-}P) = 127.8$ Hz (124 Hz);[21] λ_{max} 364 nm; ϵ 2680 M^{-1} cm^{-1} (364 nm, 3300).[23]

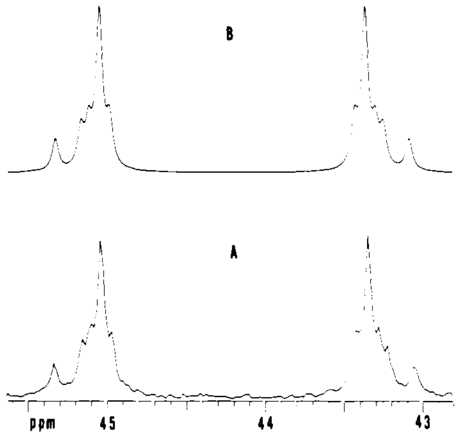
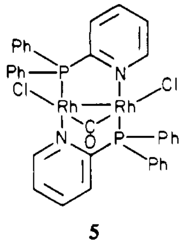


Figure 1. The $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ in dichloromethane solution: A, observed spectrum; B, simulated spectrum.

Treatment of $Rh(Ph_2Ppy)_2(CO)Cl$ with $[Rh(CO)_2Cl]_2$ in dichloromethane solution followed by precipitation with ether produces red-brown $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. This complex may also be prepared directly from $[Rh(CO)_2Cl]_2$ and the free ligand by adding the correct stoichiometric amount of the ligand to the rhodium complex. This reverse addition limits the formation of $Rh(Ph_2Ppy)_2(CO)Cl$. The red-brown dinuclear complex is soluble in dichloromethane, chloroform, and to a lesser extent benzene. It shows an infrared band at 1797 cm^{-1} in dichloromethane solution which is assigned to a bridged carbon monoxide. There are no infrared bands indicative of terminal carbon monoxide ligands. However infrared absorptions at 320 and 305 cm^{-1} indicate that terminal chloride ligands are present. The $^{31}P\{^1H\}$ NMR spectrum of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ is shown in Figure 1 along with its simulation. The simulation is based on an analysis of the spectrum as belonging to the AXX′A′ spin system (A = P, X = Rh) with δ 44.18, $^1J(P\text{-}Rh) = 144.0$ Hz, $^2J(P\text{-}Rh) = -7.39$ Hz, $^3J(P\text{-}P) = 16.0$ Hz, and $^1J(Rh\text{-}Rh) = 12.0$ Hz. These spectral features are consistent with the assignment of structure **5** to this compound. The values for the one-bond Rh–P coupling and the Rh–Rh coupling are consistent with previously obtained values in related molecules.[24–30] The isomeric structure



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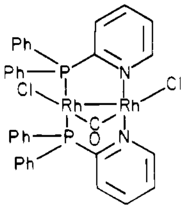

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Table I. Atomic Fractional Coordinates and Temperature Factors for $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh(1)	0.21479 (4)	0.08409 (3)	0.17639 (3)	1.04 (2)	0.89 (2)	1.11 (2)	0.29 (1)	0.44 (2)	0.15 (1)
Rh(2)	0.11466 (4)	0.25758 (3)	0.20935 (3)	1.11 (2)	0.79 (2)	1.12 (2)	0.25 (2)	0.44 (1)	0.11 (1)
Cl(1)	0.36336 (14)	−0.04632 (10)	0.20738 (10)	1.43 (5)	1.48 (5)	1.94 (6)	0.67 (4)	0.58 (4)	0.29 (4)
Cl(2)	0.10702 (15)	0.4190 (10)	0.30140 (10)	2.31 (6)	1.30 (5)	1.83 (6)	0.61 (4)	0.75 (5)	−0.15 (4)
P(1)	0.13223 (14)	0.04087 (10)	0.30318 (10)	1.04 (5)	1.04 (5)	1.20 (6)	0.26 (4)	0.34 (4)	0.23 (4)
P(2)	0.29369 (14)	0.33847 (11)	0.15782 (10)	1.27 (6)	1.04 (5)	1.19 (6)	0.17 (4)	0.37 (5)	0.16 (4)

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
N(1)	0.3100 (5)	0.1460 (3)	0.0680 (2)	1.3 (1)	C(17)	0.4895 (7)	0.1614 (5)	0.5469 (5)	2.4 (1)
N(2)	−0.0552 (5)	0.1746 (3)	0.2564 (3)	1.3 (1)	C(18)	0.3952 (6)	0.1072 (5)	0.4574 (4)	1.8 (1)
O(1)	−0.0468 (4)	0.1143 (3)	0.0217 (3)	2.0 (1)	C(19)	0.3388 (6)	0.2547 (4)	0.0621 (4)	1.3 (1)
C(1)	0.0482 (5)	0.1390 (4)	0.0983 (4)	1.1 (1)	C(20)	0.3982 (6)	0.2966 (5)	−0.0090 (5)	2.0 (1)
C(2)	−0.0421 (6)	0.0772 (4)	0.2934 (4)	1.2 (1)	C(21)	0.4286 (7)	0.2250 (5)	−0.0770 (5)	2.4 (1)
C(3)	−0.1526 (6)	0.0147 (4)	0.3188 (4)	1.5 (1)	C(22)	0.3988 (6)	0.1136 (5)	−0.0700 (4)	2.0 (1)
C(4)	−0.2787 (6)	0.0523 (5)	0.3090 (4)	1.8 (1)	C(23)	0.3404 (6)	0.0769 (4)	0.0016 (4)	1.5 (1)
C(5)	−0.2924 (6)	0.1527 (5)	0.2714 (4)	2.0 (1)	C(24)	0.4687 (6)	0.3848 (4)	0.2559 (4)	1.4 (1)
C(6)	−0.1772 (6)	0.2126 (4)	0.2475 (4)	1.7 (1)	C(25)	0.4797 (6)	0.3783 (5)	0.3586 (5)	2.0 (1)
C(7)	0.1055 (5)	−0.1014 (4)	0.3308 (4)	1.2 (1)	C(26)	0.6115 (7)	0.4176 (5)	0.4334 (5)	2.6 (1)
C(8)	0.0668 (6)	−0.1839 (5)	0.2507 (4)	1.8 (1)	C(27)	0.7313 (7)	0.4642 (5)	0.4080 (5)	2.5 (1)
C(9)	0.0495 (6)	−0.2924 (5)	0.2711 (5)	2.2 (1)	C(28)	0.7217 (7)	0.4698 (5)	0.3070 (5)	2.5 (1)
C(10)	0.0713 (6)	−0.3173 (5)	0.3709 (4)	1.8 (1)	C(29)	0.5909 (6)	0.4312 (5)	0.2302 (4)	2.0 (1)
C(11)	0.1095 (6)	−0.2357 (5)	0.4485 (4)	1.8 (1)	C(30)	0.2591 (6)	0.4606 (4)	0.0960 (4)	1.3 (1)
C(12)	0.1273 (6)	−0.1259 (4)	0.4295 (4)	1.5 (1)	C(31)	0.1777 (7)	0.4513 (5)	−0.0078 (5)	2.2 (1)
C(13)	0.2511 (6)	0.1170 (4)	0.4255 (4)	1.3 (1)	C(32)	0.1400 (7)	0.5433 (5)	−0.0510 (5)	2.4 (1)
C(14)	0.2026 (6)	0.1840 (5)	0.4842 (4)	1.8 (1)	C(33)	0.1785 (7)	0.6446 (5)	0.0071 (5)	2.4 (1)
C(15)	0.2971 (7)	0.2402 (5)	0.5769 (5)	2.4 (1)	C(34)	0.2555 (7)	0.6529 (5)	0.1110 (5)	2.3 (1)
C(16)	0.4397 (7)	0.2288 (5)	0.6079 (5)	2.3 (1)	C(35)	0.2952 (6)	0.5608 (5)	0.1550 (4)	1.7 (1)

6 would produce a pair of equally intense doublets in the spectrum due to one-bond and two-bond rhodium–phosphorus coupling.

Exposure of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ to sulfur dioxide at 1 atm at room temperature in dichloromethane solution results in the replacement of the carbonyl group by a sulfur dioxide molecule. The product, $Rh_2(Ph_2Ppy)_2(\mu\text{-}SO_2)Cl_2$, has been isolated as red-brown crystals. Infrared bands due to ν_{Rh-Cl} at 320 and 296 cm^{-1} and to ν_{S-O} at 1227 sh, 1214, and 1080 cm^{-1} are observed for this compound, but no carbonyl stretching vibrations are detectable. The sulfur–oxygen stretching vibrations fall near the range found for other examples of sulfur dioxide occupying a bridging location.[31] The $^{31}P\{^1H\}$ NMR spectrum is similar to that of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. Analysis of the ^{31}P NMR spectrum of $Rh_2(Ph_2Ppy)_2(\mu\text{-}SO_2)Cl_2$ as an AXX′A′ spin system yields the parameters δ 41.70, ^1J(Rh–P) = 138.4 Hz, ^2J(P–Rh) = −6.2 Hz, ^3J(P–P) = 18, and ^1J(Rh–Rh) = 11.7 Hz. Structure 7 is proposed for this compound.

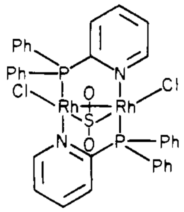

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Table II. Interatomic Distances (Å) for $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$

Rh(1)–Rh(2)	2.612 (1)	P(1)–C(8)	2.778 (6)
Rh(1)–P(1)	2.206 (1)	P(1)–C(12)	2.797 (6)
Rh(2)–P(2)	2.215 (1)	P(1)–C(13)	1.845 (5)
Rh(1)–N(1)	2.116 (5)	P(1)–C(14)	2.831 (6)
Rh(2)–N(2)	2.114 (5)	P(1)–C(18)	2.831 (6)
Rh(1)–Cl(1)	2.355 (1)	P(2)–N(1)	2.703 (5)
Rh(2)–Cl(2)	2.355 (1)	P(2)–C(20)	2.864 (6)
Rh(1)–C(1)	1.941 (5)	P(2)–C(24)	1.827 (6)
Rh(2)–C(1)	1.951 (5)	P(2)–C(25)	2.798 (6)
P(1)–N(2)	2.672 (5)	P(2)–C(29)	2.819 (7)
P(1)–C(2)	1.831 (6)	P(2)–C(30)	1.826 (6)
P(1)–C(3)	2.863 (6)	P(2)–C(31)	2.810 (6)
P(1)–C(7)	1.832 (5)	C(1)–O(1)	1.171 (5)

Table III. Interatomic Angles (Deg) for $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$

Rh(1)–C(1)–Rh(2)	84.3 (0.2)	Cl(2)–Rh(2)–N(2)	88.8 (0.1)
Rh(1)–C(1)–O(1)	138.5 (0.4)	Cl(1)–Rh(1)–C(1)	153.2 (0.2)
Rh(2)–C(1)–O(1)	137.2 (0.4)	Cl(2)–Rh(2)–C(1)	156.4 (0.2)
P(1)–Rh(1)–N(1)	172.0 (0.1)	P(1)–C(2)–N(2)	113.0 (0.4)
P(2)–Rh(2)–N(2)	177.8 (0.1)	P(1)–C(2)–C(3)	125.6 (0.3)
P(1)–Rh(1)–Rh(2)	78.8 (0.0)	P(2)–C(19)–N(1)	114.2 (0.4)
P(2)–Rh(2)–Rh(1)	82.1 (0.0)	P(2)–C(19)–C(20)	124.4 (0.4)
N(1)–Rh(1)–Rh(2)	96.1 (0.1)	C(2)–P(1)–Rh(1)	114.5 (0.2)
N(2)–Rh(2)–Rh(1)	95.7 (0.1)	C(7)–P(1)–Rh(1)	119.5 (0.2)
Cl(1)–Rh(1)–Rh(2)	158.7 (0.0)	C(13)–P(1)–Rh(1)	111.6 (0.2)
Cl(2)–Rh(2)–Rh(1)	155.8 (0.0)	C(19)–P(2)–Rh(2)	115.5 (0.2)
Cl(1)–Rh(1)–P(1)	91.9 (0.1)	C(24)–P(2)–Rh(2)	116.5 (0.2)
Cl(2)–Rh(2)–P(2)	93.3 (0.1)	C(30)–P(2)–Rh(2)	113.7 (0.2)
Cl(1)–Rh(1)–N(1)	90.6 (0.1)		

Addition of carbon monoxide to $Rh_2(Ph_2Ppy)_2(\mu\text{-}SO_2)Cl_2$ (**7**) transforms it back to $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ (**5**). Additional carbon monoxide has no effect upon $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. The interconversion of **5** and **7** has been monitored by infrared spectroscopy. No evidence for the formation of intermediates has been found.

X-ray Crystallographic Structure of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. In order to obtain accurate structural information for $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ and to characterize the geometry of Ph_2Ppy when it acts as a bridging ligand, we undertook an X-ray crystallographic study of this compound. $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ crystallizes with one molecule in the

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(25) The low value for J(Rh–Rh) is consistent with values measured for $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$, $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3(CH_2)$, and $(\eta^5\text{-}C_5H_5)_2Rh_2(NO)_2$[26] and with the absence of second-order effects in the ^{31}P NMR spectrum of $Rh_2(PR_3)_8$ (R = F,[27] OCH_3[28]) and in ^{13}C NMR spectrum of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$.[29] Larger Rh–Rh coupling constants (ca. 125 Hz) have been reported for dpm-bridged dirhodium compounds.[30] However the approximations[30] made in not including P–P coupling in the analysis of the spectra of these dpm-rhodium complexes appear to have created errors in estimating the Rh–Rh coupling.

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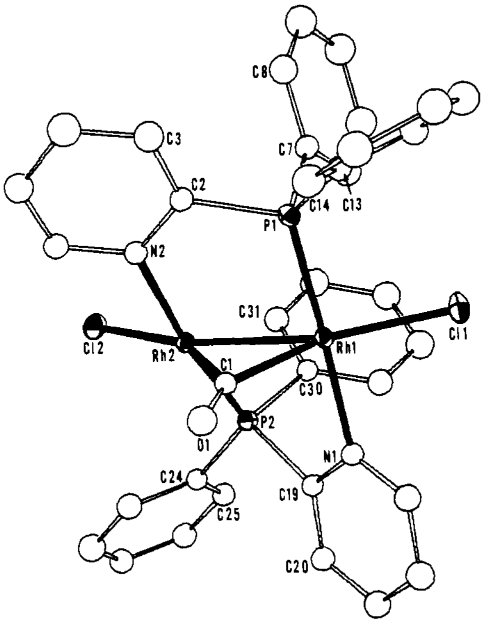


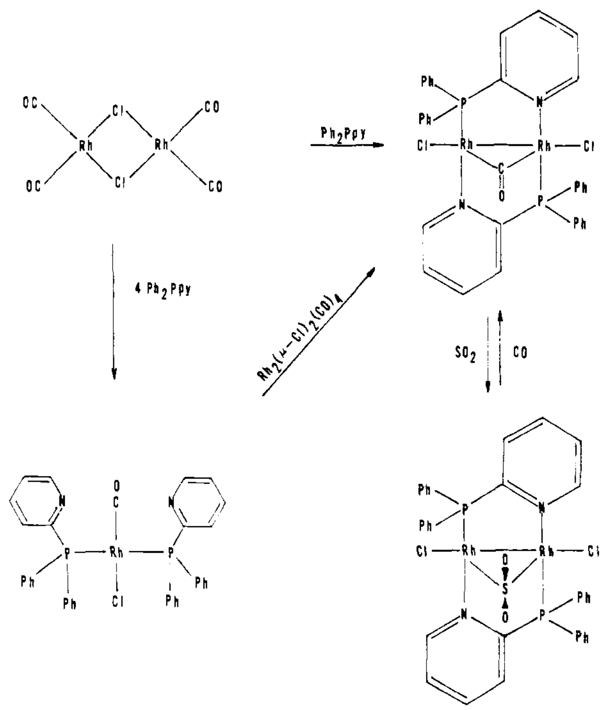
Figure 2. Perspective drawing of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ showing the numbering system. Only the lowest two numbers are given for carbon atoms in aromatic rings.

asymmetric unit and with no unusual intermolecular contacts. An ORTEP drawing of the entire molecule is presented in Figure 2. This figure also presents the numbering system used for the various atoms. Final atomic coordinates and temperature factors are given in Table I. Selected interatomic distances and angles are presented in Tables II and III, respectively. Although the molecule has no crystallographically imposed symmetry, it has approximate C_2 symmetry with the twofold axis running through the carbonyl ligand and bisecting the Rh-Rh bond. Because of the low symmetry, the molecule is chiral. In the crystal the molecules pack about the center of symmetry as a racemic mixture.

The overall geometry of the molecule is that of a molecular A-frame, but a highly distorted one. The two rhodium atoms, the carbon monoxide ligand, and the chloride ligands lie in plane. Unlike the situation with most A-frame molecules employing dpm as a bridging ligand, the bridging Ph_2Ppy ligands are not coordinated perpendicularly to that plane. While the trans PRhN units are nearly linear with PRhN angles of 177.8 (0.1) and 172.0 (0.1)° at the two rhodium centers, these PRhN units are skewed so that they are not parallel to one another nor are they perpendicular to the $Rh_2(CO)Cl_2$ plane. This is reflected in the N-Rh-Rh-P torsional angles. The values for these angles are $N_1Rh_1Rh_2P_2$ 25.1° and $N_2Rh_2Rh_1P_1$ 32.0°. Of the known molecular A-frames involving dpm as a bridging ligand, only $Rh_2(dpm)_2(\mu\text{-}S)(CO)_2$[32] shows a significant skewing in the manner shown by $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$.

Each rhodium atom is situated in an irregular, five-coordinate site and is bound to the terminal chloride ligand, a phosphorus atom of one bridging Ph_2Ppy ligand, a nitrogen atom of the other Ph_2Ppy ligand, the other rhodium atom, and the carbonyl carbon. The Rh-Rh separation of 2.612 (1) Å is short and indicative of the presence of a Rh-Rh bond. This distance is shorter than the Rh-Rh distance in other carbonyl-bridged dirhodium species including $Rh_2(dpm)_2(\mu\text{-}CO)(\mu\text{-}Cl)(CO)_2$ (2.838 (1) Å),[10,11] $Rh_2(dpm)_2(\mu\text{-}CO)Br_2$ (2.7566 (9)),[33] $Rh_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)(CO)_2$ (2.681 (2)),[34] $Rh_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_3$ (2.622 (3), 2.617 (3)),[35] $Rh_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_2(CO)$ (2.620 (2)),[36] and $Rh_4(\mu\text{-}CO)_3(CO)_9$ (2.734 (7), 2.716 (6), 2.796 (8)).[37] Only the acetate[38] or carbonate-bridged,[39] binuclear Rh(II) complexes have shorter Rh-Rh bond distances. The other rhodium-ligand bond distances are normal. The Rh-Cl distances compare well to the terminal Rh-Cl distances in $(Ph_3P)_3RhCl$[40] and $PhP[(CH_2)_3PPh_2]_2RhCl$.[41] The rhodium-carbonyl distances fall in the short end of the range found for bridging carbonyl ligands.[10,11,33-37] While the Rh-P distance is shorter than that found in many dpm-bridged rhodium A-frames,[10,11,32,33,42] this shortening is expected since the metal-phosphorus distance is effected by the trans ligand.[43] In the present case since the Rh-P bond is trans to a Rh-N bond, a shortening (relative to having a trans phosphine) is expected due to the change to a nitrogen donor which is a stronger σ donor and weaker π acceptor than is a phosphine. The Rh-N distance is comparable to the Rh-N distances found for rhodium pyridine complexes although these are all Rh(III) species.[43,44]

Chart I



Since this is the first structural study of Ph_2Ppy, and it defines the geometry of this ligand as a bridging group, structural parameters deserve particular attention. The Ppy portion of the molecule, as expected, is planar. Because this plane defines the direction of the pyridine lone pair, the rhodium atoms bound to nitrogen should lie in the Ppy plane. In fact both rhodium atoms are very slightly out of this plane; Rh(1) lies 0.051 Å from the plane of Ppy involving N(1) and P(2) while Rh(2) is 0.154 Å from the plane containing N(2) and P(1). Because there should be no restriction to the rotation about the P-C(py) bond, the phosphorus-bound rhodium atom

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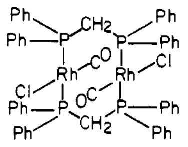
is not constrained to lie in the Ppy plane, and, in fact, large displacements from the plane are found. The distance from Rh(1) to the Ppy plane of N(2) and P(1) is 1.256 Å, and the analogous distance for Rh(2) is 0.943 Å. This twisting about the P–C bonds to place the phosphorus-bound rhodium atoms out of the Ppy planes is linked to the skewing of the A-frame. If the phosphorus-bound metals lay in the Ppy plane, then the A-frame would appear more regular with the trans Ppy donor sets lying near a single plane.

Discussion

The chemical transformations observed in this study are summarized in Chart I. The species found here may be compared with the rich array of dpm rhodium complexes previously reported. As yet $Rh(Ph_2Ppy)_2(CO)Cl$ has no counterpart in dpm-based rhodium chemistry. In fact monodentate dpm ligands have not been encountered in rhodium chemistry although they are known for other metals. Both dpm and Ph_2Ppy form binuclear species of the type $Rh_2(bidentate)_2(\mu\text{-}CO)Cl_2$ with similar structures. Each rhodium in these dinuclear molecules has 16 valence electrons (8 from the Rh(I), 2 from the terminal chloride, 4 from the bridging ligand [P or N donor centers], 1 from the bridging carbonyl, and 1 from the metal–metal bond). In this respect these molecules contain an unusual juxtaposition of features. Most carbonyl-bridged polynuclear metal complexes are electron precise (18-electron) species. dpm and Ph_2Ppy also are alike in forming bridged-sulfur-dioxide complexes of the type $Rh_2(bidentate)_2(\mu\text{-}SO_2)Cl_2$.[45] The electronic structure of the sulfur-dioxide-bridged and the carbon-monoxide-bridged complexes are expected to be similar. dpm forms three additional dinuclear species with rhodium(I): the face-to-face complex **8**,[46] the A-frame **9**,[42] and the carbonyl-bridged **10**.[10,11]



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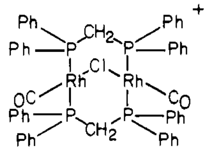

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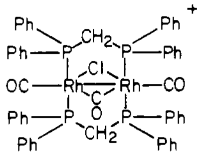

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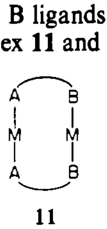
We have not been able as yet to form analogs of these using Ph_2Ppy. The inability of Ph_2Ppy to form counterparts of **8** and **9** may have its origin in the bite of this ligand (vida infra). Both **8** and **9** lack a metal–metal bond and have Rh–Rh separations of about 3.2 Å, much longer than the Rh–Rh distance found in $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$. Ph_2Ppy may not be able to accommodate such a long metal–metal separation.

The use of a bidentate ligand (symbolized by $\overset{\frown}{A\ B}$) with different donor sites to form binuclear metal complexes creates new areas of structural variation which are not possible with a symmetrical ligand like dpm. For binuclear complexes formed from two $\overset{\frown}{A\ B}$ ligands, two structural types exist: the head-to-head complex **11** and the head-to-tail complex **12**. If



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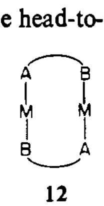

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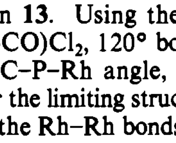
the two metals involved are different, then the head-to-head complex can exist in two variants depending on the placement of the two metal ions in the two different coordination sites.

In the example of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$, we are clearly dealing with a head-to-tail dimer. Interestingly, the formation of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ from $Rh(Ph_2Ppy)_2(CO)Cl$ and $Rh_2(\mu\text{-}Cl)_2(CO)_4$ requires that one of the Ph_2Ppy ligands reorients itself. Metal–phosphorus bond breaking (and reformation) has received relatively little attention in most studies of diphosphine-bridged binuclear complexes. It may be anticipated that the use of unsymmetrical ligands to form binuclear complexes will make such processes more apparent. Another structural embellishment present in complexes derived from the skeletons of **11** and **12** involves the formation of chiral A-frames. $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ and any other A-frame formed from the head-to-tail skeleton **12** is chiral. However A-frames formed from the head-to-head unit **8** are not inherently chiral. If the potential of A-frame molecules in catalysis is realized, the chirality of head-to-tail A-frames may offer a convenient entry into asymmetric syntheses.

Other structural features of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ which deserve comment are the nature and cause of the skewed geometry and the placement of the Ph_2Ppy ligands. We suspect that the skewing is related to the bite of the Ph_2Ppy ligand rather than to a tendency of the rhodium atoms to acquire the particular angular distribution of ligands found in this complex. In particular it should be noted that the isoelectronic dpm complex $Rh_2(dpm)_2(\mu\text{-}CO)Br_2$ has a more regular structure with the Rh–P bonds nearly perpendicular to the $Rh_2(CO)Br_2$ plane.[32] This latter complex also has a longer Rh–Rh separation (2.800 Å). While the nonbonded P–N separations in the Ph_2Ppy ligands of $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ are close to the Rh–Rh distance, the bite of the Ph_2Ppy ligand is not simply related to the P–N distance. In fact, for an isolated Ph_2PpyM_2 unit, the Rh–Rh separation is highly variable, as shown by the two extreme, planar structures **13** and **14**, while the P···N separation remains fixed. The key to



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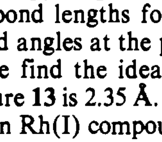

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the variation in M–M separation is the freedom of rotation about the P–C(py) bond. The closest approach of the two metals will occur when the entire $pyPM_2$ unit is planar and oriented as in **13**. Using the bond lengths found for $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$, 120° bond angles at the pyridine ring, and a 109° C–P–Rh angle, we find the idealized Rh–Rh separation for the limiting structure **13** is 2.35 Å. This is much shorter than the Rh–Rh bonds in Rh(I) compounds. So that a longer Rh–Rh bond can be accommodated, rotation about the P–C(py) bond may occur. This is actually the case in $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ for, as has been noted previously, the phosphorus-bound rhodium ion lies about 1 Å from the Ppy plane. Lengthening of the Rh–Rh distance by rotation about the P–C(py) bond is limited in this complex by the presence of the second Ph_2Ppy ligand. Clearly two Ph_2Ppy ligands cannot bind trans to one another and at the same time adopt an extreme orientation such as **14**. Consequently the ability of the $(Ph_2Ppy)_2M_2$ unit to adapt to a variety of M–M separations is limited. We suspect that this ligand will not be capable of spanning as wide a range of metal–metal separations as already observed with two trans dpm ligands. These can span M–M distances from 2.2 to 3.5 Å.[10] In particular it appears that Ph_2Ppy will have difficulty in spanning the long end of this range. In this context, note that the Rh–Rh separation in $Rh_2(Ph_2Ppy)_2(\mu\text{-}CO)Cl_2$ is 0.14 Å less than that found in $Rh_2(dpm)_2(\mu\text{-}CO)Br_2$.

Acknowledgment. We thank the National Science Foun-

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dation and the University of California, Davis, NMR Facility for support and the Johnson Matthey Corp. for a generous loan of rhodium salts.

Registry No. **5**, 75361-61-4; **7**, 76069-01-7; $Rh(Ph_2Ppy)_2(CO)Cl$, 75361-60-3; $[Rh(CO)_2(\mu\text{-}Cl)]_2$, 14523-22-9.

Supplementary Material Available: A listing of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department,
University of Houston, Houston, Texas 77004

Crystal Structure and Absolute Configuration of Tartrate Derivatives. 2. $[\Lambda(\delta\delta\delta)\text{-}Co(en)_3][(+)_{589}\text{-}(\boldsymbol{R},\boldsymbol{R})\text{-}tart^{2-}]Cl\cdot 5H_2O$

LINDA S. MAGILL, JAMES D. KORP, and IVAN BERNAL*

Received July 28, 1980

The structure and absolute configuration of the title compound were determined as part of a continuing project to structurally document the mechanism(s) of chiral resolution of simple resolving agents such as tartaric acid and its derivatives. The substance crystallizes in the triclinic space group $P1$ with cell constants $a = 8.136$ (5) Å, $b = 8.253$ (7) Å, $c = 8.517$ (6) Å, $\alpha = 102.32$ (6)°, $\beta = 101.32$ (6)°, $\gamma = 95.18$°, $V = 542.65$ Å^3, and d(calcd) ($Z = 1$) = 1.569 g cm^{-3}. When (R,R)-d-tartrate(2−) is used as the resolving agent, the absolute configuration of the $Co(en)_3{}^{3+}$ with which it is selectively crystallizes is $\Lambda(\delta\delta\delta)$. The main interactions observed between the cation, anions, and waters are as follows. (a) The cation has two "faces" perpendicular to the pseudo-threefold axis. One face consists of three axial N–H units bonded to the Cl^-, while the other has the opposite three axial N–H units hydrogen bonded to three oxygens of a given tartrate anion. (b) The tartrate dianion is involved in complicated hydrogen-bonding contacts with water and with two separate cationic units but never to another tartrate. (c) Every hydrogen of the five independent waters of crystallization is involved in an intermolecular bond with either tartrate or chloride anions or with another water. All five waters are mutually hydrogen bonded into a right-handed spiraling chain, linked through chloride ions. When one compares the nature of these interactions with those reported previously, it is clear that d-tartrate(2−) is not limited to a single mechanism of resolution for even simple tris(bidentate diamines). Instead, it is a flexible resolving agent capable of a variety of modes of interaction which can be quite different from one case to another.

Introduction

This study is our second contribution to a long-range project to structurally document the mechanism(s) of chiral resolution of simple resolving agents such as tartrate and its derivatives.[1] It is interesting to note that, while the structures and absolute configuration of four simple derivatives of $Co(en)_3{}^{3+}$ have been determined,[2] the structure and absolute configuration of $Co(en)_3{}^{3+}$ together with its resolving agent, tartrate, has not been studied in detail in its most commonly isolated form—the $[Co(en)_3](tart)Cl\cdot 5H_2O$ derivative found in ref 3. Furthermore, the recent study of Yoneda et al.[4] does not give coordinates for the atoms and lacks vital information concerning the hydrogen atoms, details of the hydrogen bonding, and the role of water in the lattice. As shown below, when one examines the differential thermal calorimetric behavior of $[Co(en)_3](tart)Cl\cdot 5H_2O$, one finds a very interesting phase transition associated with the loss of water, which is not readily interpretable based solely on Yoneda's work on the analogous bromide, in view of the absence of data on the structural behavior of the five waters.

Yoneda and associates[5,6] have made, however, interesting observations concerning stereoselectivity in ion pair formation for tartrate resolving agents, on the influence of tartaric acid and its derivatives on the mechanism of the Pfeiffer effect, and on discriminating action in these processes. We had already noted an interesting mode of interaction of dibenzoyltartrate with a bis(phosphine) dioxide being resolved into its diastereomers,[1] and we therefore decided to investigate the structure of the title compound as part of our series.

Table I. Summary of Data Collection and Processing Parameters

space group	$P1$, triclinic
cell consts	$a = 8.136$ (5) Å,
	$b = 8.253$ (7) Å,
	$c = 8.517$ (6) Å,
	$\alpha = 102.32$ (6)°
	$\beta = 101.32$ (6)°
	$\gamma = 95.18$ (6)°
	$V = 542.65$ Å^3, $Z = 1$
molecular formula	$C_{10}H_{38}O_{11}N_6CoCl$
mol wt	512.85
density	1.57 (calcd),
	1.58 (measd) g cm^{-3}
abs coeff	$\mu = 9.10$ cm^{-1}
data collection range	$4° \leqslant 2\theta \leqslant 65°$
scan width	$\Delta\theta = (1.00 + 0.35 \tan\theta)°$
max scan time	300 s
scan speed range	0.31–3.5° min^{-1}
total data collected	3825
data with $I > 3\sigma(I)$	3545
total variables	393
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.026
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o\rvert^2]^{1/2}$	0.022
weights	$w = \sigma(\lvert F\rvert)^{-2}$
approx orientation of data cryst	[110]

Experimental Section

1. X-ray Diffraction Measurements. The title compound was synthesized according to Angelici's method.[3] The resulting racemic mixture was resolved with use of barium d-tartrate, and orange crystals of optically active $[Co(en)_3](d\text{-}tart)Cl\cdot 5H_2O$ were grown by slow evaporation of the aqueous solution. A crystal of dimensions 0.62 × 0.47 × 0.47 mm was coated with Krylon and mounted on a goniometer head.

All measurements were done on a computer controlled Enraf-Nonius CAD-4 automatic diffractometer equipped with a graphite monochromator aligned to select Mo Kα radiation. The lattice parameters used in data collection were obtained from a least-squares fit of 25 automatically centered reflections. The final lattice constants and other pertinent crystal data are given in Table I. The space group was determined from the systematic absences to be either $P1$ or $P\bar{1}$,

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