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

Preparation of Heterobinuclear Rhodium/Palladium Complexes Using 2-(Diphenylphosphino)pyridine as a Connecting Ligand

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

The reaction between Rh(Ph$_2$Ppy)$_2$(CO)Cl and (1,5-cyclooctadiene)PdCl$_2$ or between Pd(Ph$_2$Ppy)$_2$Cl$_2$ and $^1/_2$ molar equiv of Rh$_2$(μ-Cl)$_2$(CO)$_4$ produces the head-to-tail complex RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ whose structure has been determined by X-ray crystallography. RhPd(Ph$_2$Ppy)$_2$(CO)Cl$_3$ crystallizes in the space group $Pc2_1b$ (*bca* setting of $Pca2_1$, No. 29) with cell dimensions (determined at 140 K) of a = 10.353 (5), b = 15.426 (7), and c = 21.219 (11) Å, Z = 4, and V = 3391 Å^3. The structure was refined to a conventional R value of 0.039 by using 2018 significant reflections. The complex exhibits a six-coordinate Rh atom (ligand atoms are N, P, 2 Cl, Pd, C) and a planar Pd atom (ligand atoms are N, P, Cl, Rh) linked by a Rh–Pd single bond. Evidence for a strong trans effect of the metal–metal bond is found in the long axial Rh–Cl and Pd–Cl bonds. A mechanism of formation of RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ is proposed on the basis of the ^{31}P{^{1}H} NMR spectra of the reacting species at low temperature. Head-to-head (phosphorus trans to phosphorus at rhodium) and head-to-tail (phosphorus trans to nitrogen at rhodium) isomers of [RhPd(μ-Ph$_2$Ppy)$_2$(CNCH$_3$)$_2$Cl$_2$]$^+$ have been prepared by the reaction of [(CH$_3$NC)$_2$Rh(Ph$_2$Ppy)$_2$]$^+$ with (PhCN)$_2$PdCl$_2$ or (1,5-cyclooctadiene)PdCl$_2$, respectively. The thermal interconversion of these isomers is examined. The head-to-tail isomers are thermodynamically more stable.

Introduction

2-(Diphenylphosphino)pyridine is a convenient building block for the construction of binuclear transition-metal complexes.[1-5] For many transition metals it preferentially binds through the phosphorus atom to give mononuclear complexes that are similar in physical properties to their well-known triphenylphosphine analogues. These mononuclear complexes are expected to readily capture a second metal ion by coordination to the pyridine nitrogen as shown in idealized form for a bis[2-(diphenylphosphino)pyridine] complex in eq 1. In


(1)
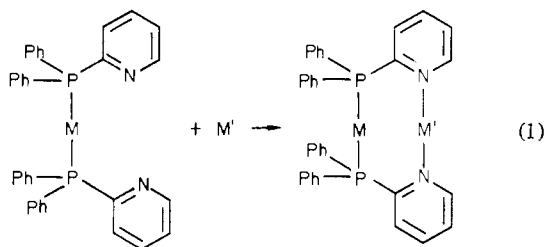
an early experiment designed to test this hypothesis, (1,5-cyclooctadiene)palladium(II) chloride was added to bis[2-(diphenylphosphino)pyridine)]rhodium(I) carbonyl chloride, and indeed a new binuclear complex **1** was formed as shown in eq 2.[1] We have subsequently extended this type of reaction

1

1,5-COD   (2)
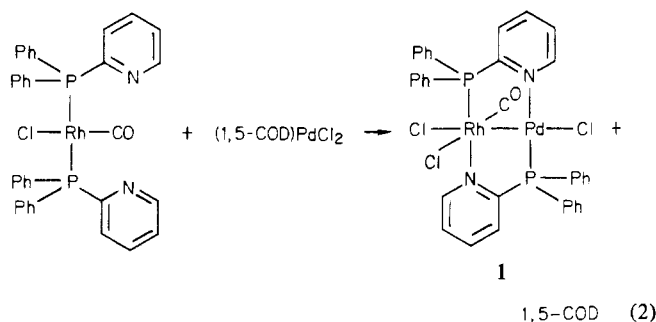
to allow for the formation of both homonuclear (Rh–Rh, Pd–Pd, Pt–Pt) and heteronuclear (Pd–Pt, Pd–Rh, Pd–Ru, Rh–Pt) metal–metal single bonds.[2-5]

The reaction (2) differs from the initially anticipated reaction (1) in two significant aspects. Not only has the rhodium compound captured the palladium atom by complexation, but it has undergone oxidative addition of a palladium–chlorine bond. Formally we may consider the product a complex of Rh(II) and Pd(I). Additionally the orientation of the 2-(diphenylphosphino)pyridine ligands has changed. The head-to-head (*HH*) arrangement **2**, anticipated to result because

2, *HH*(M)   **3,** *HT*   **4,** *HH*(M′)
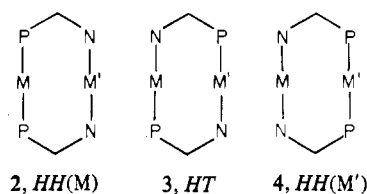
both phosphorus atoms were initially bonded to rhodium, is not found in the product. Rather a head-to-tail arrangement, **3**, of the bridging phosphines is present in the product. Note that, in addition to these two isomers, a third, **4**, in which the phosphorus atoms are bound to M′, is also possible for a heterobinuclear complex of this type.[6]

Here we report details of some of the routes by which **1** may be prepared, a structural analysis of **1** by X-ray crystallography, studies of intermediates involved in its formation, and the preparation of some analogous complexes containing isocyanide ligands.

Experimental Section

Preparation of Compounds. 2-(Diphenylphosphino)pyridine,[4] [(CH$_3$NC)$_4$Rh][PF$_6$],[7] [(CH$_3$NC)$_4$Rh][BPh$_4$],[7] (1,5-COD)PdCl$_2$,[8] and (PhCN)$_2$PdCl$_2$[9] were prepared by established procedures.

[(CH$_3$NC)$_2$Rh(Ph$_2$Ppy)$_2$][BPh$_4$]. 2-(Diphenylphosphino)pyridine (0.53 g, 2.01 mmol) was added to a slurry of 0.308 g (0.525 mmol) of [(CH$_3$NC)$_4$Rh][BPh$_4$] in 20 mL of acetone. The mixture was heated on a hotplate for 30 min and filtered. Ten milliliters of 1-propanol was added to the filtrate, and the solvent was removed by the use of a rotary evaporator until yellow crystals formed. The yellow crystals were collected by filtration and recrystallized by dissolving in 200 mL of hot methanol and reducing the volume to 40

(1) Farr, P. P.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 6654.
(2) Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 1182.
(3) Maisonnat, A.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta* **1981**, *53*, L217.
(4) Maisonnet, A.; Farr, J. P.; Olmstead, M. M.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 3961.
(5) Farr, J. P.; Olmstead, M. M.; Wood, F.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 792.

(6) In indicating *HH* or *HT* isomers in this fashion, we do not differentiate between cis and trans orientations of the bridging ligands at M and M′.
(7) Balch, A. L.; Miller, J. *J. Organomet. Chem.* **1971**, *32*, 263.
(8) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413.
(9) Kharasch, M. S.; Seylen, R. C.; Major, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

mL. At this point the solution was cooled and the yellow precipitate was collected by filtration and vacuum dried (yield 0.491 g, 90.6%). Anal. Calcd for $C_{62}H_{54}BN_4P_2Rh$: C, 72.24; H, 5.28; N, 5.44. Found: C, 73.37; H, 5.42; N, 5.40.

[(CH₃NC)₂Rh(Ph₂Ppy)₂][PF₆]. This complex was obtained from [(CH₃NC)₄Rh][PF₆] by the procedure described above with the exception that the mixture was heated on a hotplate for 3 h instead of 30 min. Anal. Calcd for $C_{38}H_{34}F_6N_4P_3Rh$: C, 53.29; H, 4.00; N, 6.54. Found: C, 53.39; H, 4.09; N, 6.60.

Pd(Ph₂Ppy)₂Cl₂·1.7CH₂Cl₂. A solution of 0.51 g (1.3 mmol) of bis(benzonitrile)palladium(II) chloride in 10 mL of dichloromethane was added dropwise to 0.74 g (2.8 mmol) of 2-(diphenyl-phosphino)pyridine in 10 mL of dichloromethane. After filtration, ethyl ether was added dropwise to precipitate a yellow solid, which was collected by filtration and vacuum dried; yield 0.92 g (99%). Anal. Calcd for $C_{35.7}H_{31.4}Cl_{5.4}N_2P_2Pd$: C, 50.58; H, 3.73; N, 3.31; Cl, 22.51. Found: C, 50.45; H, 3.87; N, 3.19; Cl, 22.71. The presence of dichloromethane was verified by ^1H NMR spectroscopy. The ^{31}P NMR spectrum of this material shows two resonances, suggesting that both cis and trans isomers are present.

[Pd(Ph₂Ppy)₂Cl][PF₆]. A solution of 0.038 g (0.22 mmol) of silver nitrate in 20 mL of hot methanol was added dropwise to a solution of 0.159 g (0.23 mmol) of Pd(Ph₂Ppy)₂Cl₂ in 30 mL of hot methanol. A white precipitate formed, which was removed by filtration. A solution of 0.038 g (0.22 mmol) of ammonium hexafluorophosphate in 10 mL of methanol was added to the filtrate. The solution was evaporated under vacuum until a tan precipitate formed. This was collected by filtration and vacuum dried. Anal. Calcd for $C_{34}H_{28}ClF_6N_2P_3Pd$: C, 50.21; H, 3.47; N, 3.44; Cl, 4.36. Found: C, 49.88; H, 3.41; N, 3.62; Cl, 4.27.

RhPd(μ-Ph₂Ppy)₂(CO)Cl₃ (*HT*). A. A solution of 0.064 g (0.22 mmol) of (1,5-cyclooctadiene)palladium(II) chloride in 10 mL of dichloromethane was added dropwise to a solution of 0.1 g (0.22 mmol) of Rh(Ph₂Ppy)₂(CO)Cl in 10 mL of dichloromethane. The color of the solution changed from yellow to red. Ethyl ether was added dropwise to precipitate a red crystalline solid, which was collected by filtration and vacuum dried; yield 0.138 g (72%). Anal. Calcd for $C_{35}H_{28}Cl_3N_2OP_2Pd_2Rh$: C, 48.31; H, 3.24; N, 3.22. Found: C, 48.33; H, 3.37; N, 3.14.

B. A solution of 0.031 g (0.08 mmol) of chlororhodium dicarbonyl dimer in 10 mL of dichloromethane was added dropwise to 0.114 g (0.16 mmol) of Pd(Ph₂Ppy)₂Cl₂ in 10 mL of dichloromethane. Ethyl ether was added dropwise to the red solution to precipitate a red crystalline solid, which was collected by filtration and vacuum dried. Spectroscopic properties (IR; ^1H and ^{31}P NMR) indicate that the product is identical with that formed in preparation A.

[RhPd(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂][PF₆] (*HT*). A solution of 0.043 g (0.015 mmol) of (1,5-cyclooctadiene)palladium(II) chloride in 10 mL of dichloromethane was added dropwise to a solution of 0.129 g (0.015 mmol) of [Rh(Ph₂Ppy)₂(CNCH₃)₂][PF₆] in 10 mL of dichloromethane. Five milliliters of 1-propanol was added to the solution, and the volume was reduced by the use of a rotary evaporator until a red solid formed. The solid was collected, washed with methanol, and recrystallized from dichloromethane and 1-propanol (yield 0.088 g, 57%). Anal. Calcd for $C_{38}H_{34}Cl_2F_6N_4P_3PdRh$: C, 44.15; H, 3.13; N, 5.42; Cl, 6.85. Found: C, 44.33; H, 3.38; N, 5.14; Cl, 7.32.

[RhPd(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂][BPh₄] (*HT*). An acetone solution of 0.104 g (0.177 mmol) of [Rh(CNCH₃)₄][BPh₄] and 0.125 g (0.178 mmol) of Pd(Ph₂Ppy)₂Cl₂ was heated on a hotplate for 2 h. The volume was then reduced to 20 mL, filtered, and cooled to 0 °C to obtain red crystals, which were collected by filtration and vacuum dried (yield 0.15 g, 70%). Anal. Calcd for $C_{62}H_{54}BCl_2N_4P_2PdRh$: C, 61.64; H, 4.51; N, 4.64; Cl, 5.87. Found: C, 60.75; H, 4.70; N, 4.49; Cl, 6.02.

[RhPd(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂][BPh₄] (*HH*). A solution of 0.087 g (0.23 mmol) of bis(benzonitrile)palladium(II) chloride in 5 mL of dichloromethane was added dropwise to a solution of 0.20 g (0.20 mmol) of [Rh(Ph₂Ppy)₂(CNCH₃)₂][BPh₄] in 5 mL of dichloromethane. The color changed from yellow to dark red. Ethyl ether was added dropwise to induce precipitation of an orange solid. Purification was achieved by recrystallization from acetone/1-propanol (yield 0.13 g, 54%). Anal. Calcd for $C_{62}H_{54}BCl_2N_4P_2PdRh$: C, 61.64; H, 4.51; N, 4.64; Cl, 5.87. Found: C, 61.87; H, 4.69; N, 4.59; Cl, 5.69.

Physical Measurements. ^1H (5-mm tubes, 200 MHz) and $^{31}P\{^1H\}$ (12-mm tubes, 81 MHz) NMR spectra were recorded on a Nicolet NT-200 Fourier transform spectrometer. An external 85% phosphoric acid reference was used for ^{31}P NMR spectra, and the high-frequency-positive convention, recommended by IUPAC, is used in reporting chemical shifts. Infrared spectra were recorded from Nujol mulls or dichloromethane solutions on a Perkin-Elmer 180 infrared spectrometer. Electrical conductivities were determined by use of an Industrial Instruments conductivity bridge with 10^{-3} M solutions. Elemental analyses were performed at the Berkeley Microanalytical Laboratory, University of California, Berkeley.

X-ray Data Collection. Well-formed crystals were grown by slow diffusion of diethyl ether into a dichloromethane solution of RhPd-(μ-Ph₂Ppy)₂(CO)Cl₃. A triangularly shaped red crystal of dimensions 0.25 × 0.25 × 0.23 mm and 0.08 mm thick was attached at its base to a glass fiber and mounted on a Syntex P2₁ diffractometer with the long axis parallel to φ. The temperature of the crystal was maintained at 140 K with a modified LT-1 low-temperature apparatus. From the automatic indexing feature of the diffractometer software and axial photographs, the crystal lattice was found to be orthorhombic P. The conditions for observed reflections were as follows: *hk*0, *k* = 2*n*; 0*kl*, *l* = 2*n* (00*l*, *l* = 2*n*; 0*k*0, *k* = 2*n*); *h*00 and *h*0*l*, no conditions. The two possible space groups were the *acb* setting of *Pbcm*, No. 57 (centrosymmetric), and the *bca* setting, *Pc2₁b*, of *Pca2₁*, No. 29 (noncentrosymmetric). Eight centered reflections, including Friedel pairs, in the range 22° < 2θ < 38° yielded lattice constants of *a* = 10.353 (5), *b* = 15.426 (7), and *c* = 21.219 (11) Å. The density at room temperature was determined by flotation to be 1.66 g cm⁻³. On the basis of *Z* = 4 and a volume at 140 K of 3391 Å³, the calculated density was 1.70 g cm⁻³.

Data collection was carried out by using graphite-monochromatized Mo Kα (λ = 0.710 69 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 2314 unique reflections of which 2018 with *I* > 3σ(*I*) were used in the final refinement. The usual Lorentz and polarization corrections were made. No correction was made for absorption in view of the crystal size, absorption coefficient (μ(Mo Kα) = 12.5 cm⁻¹), and minimum and maximum transmission factors of 0.67–0.85.

Solution and Refinement of the Structure. The positions of the palladium and rhodium atoms were determined by solution of the Patterson map with the noncentrosymmetric space group, *Pc2₁b*, assumed to be correct. The centrosymmetric space group would have generated double the number of atoms in the unit cell, contrary to the density measurement. The *y* coordinate of the rhodium atom was arbitrarily set at 0.25. The remaining atoms were easily located from successive Fourier maps, further confirming the choice of space group. The handedness of the crystal was determined by application of the program ABSCON.[10] For the 301 reflections with a high significance (*D* = [(*F*c − *F*cm)/σ(*F*o)]² > 1.0), *R* = 0.037 for the original hand and *R*m = 0.039 for its mirror image.

Final refinement was carried out with anisotropic thermal parameters for Rh, Pd, Cl, and P and isotropic thermal parameters for the remaining non-hydrogen atoms. Hydrogen atoms were not included. Corrections for anomalous dispersion were applied to Rh, Pd, Cl, and P.[11a] Neutral-atom scattering factors were those of Cromer and Waber.[11b] A final *R* value of 0.039 was obtained, with nine reflections per parameter. A difference Fourier map showed no features larger than those that could be assigned to hydrogen atoms.

Results and Discussion

Synthetic Studies. Addition of (1,5-COD)PdCl₂ in dichloromethane to a dichloromethane solution of *trans*-Rh-(CO)(Cl)(Ph₂Ppy)₂[2] in 1:1 stoichiometry produces a red solution from which a red crystalline solid, RhPd(μ-Ph₂Ppy)₂-(CO)Cl₃ (**1**), can be isolated in high yields by the addition of ethyl ether. Compound **1** is an air-stable solid, which is soluble in dichloromethane, chloroform, and acetone but has poor solubility in alkanes and alcohols. In solution it behaves as an air-stable nonelectrolyte. Physical data that serve to characterize **1** and other new compounds are collected in Table I. Compound **1** shows a strong carbon monoxide stretching

(10) Hope, H.; De La Camp, U. *Acta Crystallogr., Sect. A* **1972**, *A28*, 201.
(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 149–150; (b) pp 99–101.

**Table I.** Physical Properties of 2-(Diphenylphosphino)pyridine Complexes

compd	^{31}P NMR^a δ	^1J(Rh-P), Hz	^{1}H NMR^a δ	ν(C≡N) or ν(CO),^{b} cm^{-1}	Λ$_M$,^{c} cm² mol^{-1} Ω^{-1}
Pd(Ph₃P)₂Cl₂	23.6 s				
Pd(Ph₂Ppy)₂Cl₂	22.9 s, 28.5 s				5
[Pd(Ph₂Ppy)₂Cl][PF₆]	42.7, -42.3				154
Rh(Ph₂Ppy)₂(CO)Cl	30.1	127.8		1982	3
Rh(Ph₃P)₂(CO)Cl	29.1	124		1968^g	
Rh(Ph₂Ppy)₂(CO)Br	29.1	125.9		1965^g	4
[(CH₃NC)₂Rh(Ph₂Ppy)₂][PF₆]	28.3^e	130.5^e	2.48	2179	116
[(CH₃NC)₂Rh(Ph₃P)₂][PF₆]	26.5^f	137.7^f	2.43	2177	98
[(CH₃NC)₂Rh(Ph₂Ppy)₂][BPh₄]	28.3^e	128.5^e	2.08	2179	79
[(CH₃NC)₂Rh(Ph₃P)₂][BPh₄]	26.5	128.8	2.09	2176	
RhPd(μ-Ph₂Ppy)₂(CO)Cl₃ (HT)	21.9, 16.2	112.7 (2.3)^h		2053	2
RhPd(μ-Ph₂Ppy)₂(CO)Br₃ (HT)	19.6, 14.3	112.0 (2.9)^i		2052	
[RhPd(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂][PF₆] (HT)	26.9, 17.5	108.9 (1.6)^j	2.67	2215, 2224 sh	123
[RhPd(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂][BPh₄] (HH)	7.9	94.2	2.00	2218	87
[RhPd(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂][BPh₄] (HT)	27.6	109.3^k	2.44	2214	93

^{a} In chloroform-d. ^{b} In dichloromethane solution. ^{c} In acetone solution. ^{d} In dichloromethane-d_2. ^{e} Taken at -40 °C. ^{f} Taken at -60 °C. ^{g} In Nujol mull. ^{h} J(P-P) = 17.4 Hz. ^{i} J(P-P) = 17.3 Hz. ^{j} J(P-P) = 17.7 Hz. ^{k} J(P-P) = 17.1 Hz.

frequency at 2040 cm^{-1}. This indicates that the carbon monoxide ligand occupies a terminal site. There are no other absorptions in the region between 2250 and 1700 cm^{-1}. The shift of the carbon monoxide stretching frequency from 1982 cm^{-1} in Rh(CO)(Cl)(Ph₂Ppy)₂ to 2040 cm^{-1} in 1 indicates that the rhodium center has been oxidized during the reaction. The ^{1}H NMR of 1 provides little structural information. The ^{31}P{^{1}H} NMR spectrum of 1 in chloroform is shown in Figure 1. The ^{31}P{^{1}H} NMR spectrum consists of two sets of four equally intense lines arising from chemically inequivalent phosphorus atoms. One of the phosphorus atoms is bonded directly to the rhodium atom and gives rise to the set of lines centered at δ 21.89 with a rhodium–phosphorus coupling constant of 112.7 Hz. This is smaller than the Rh–P coupling constant found in Rh(Ph₂Ppy)₂(CO)Cl ($^1J_{Rh–P}$ = 127.8 Hz)² and is consistent with an oxidized rhodium center in compound 1.¹² The other phosphorus atom is bonded to palladium. It produces the set of lines centered at δ 16.15 and shows a two-bond Rh–P coupling of 2.3 Hz. Both groups of lines show a three-bond phosphorus–phosphorus coupling of 17.4 Hz, which falls in the range normally found for such couplings.²⁻⁵

RhPd(μ-Ph₂Ppy)₂(CO)Cl₃ may also be prepared in good yield from the reaction between Pd(Ph₂Ppy)₂Cl₂ and Rh₂(μ-Cl)₂(CO)₄.

A series of cationic, binuclear metal complexes have been synthesized starting from the monomeric rhodium species [Rh(CNMe)₂(Ph₂Ppy)₂][PF₆] (**5a**) and [Rh(CNMe)₂-

5a, X⁻ = PF₆⁻
b, X⁻ = BPh₄⁻

6a, X⁻ = PF₆⁻
b, X⁻ = BPh₄⁻
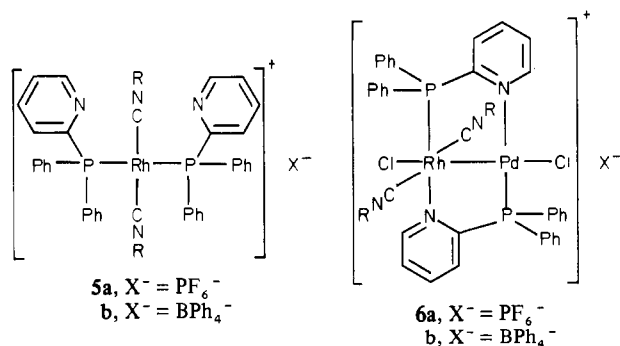
(Ph₂Ppy)₂][BPh₄]³ (**5b**). These salts are easily synthesized from [Rh(CNMe)₄][X] (X = PF₆⁻, BPh₄⁻) and 2-(diphenylphosphino)pyridine in acetone. They are air-stable, yellow, crystalline solids, which are very soluble in chloroform, dichloromethane, acetone, and methanol. Conductivity
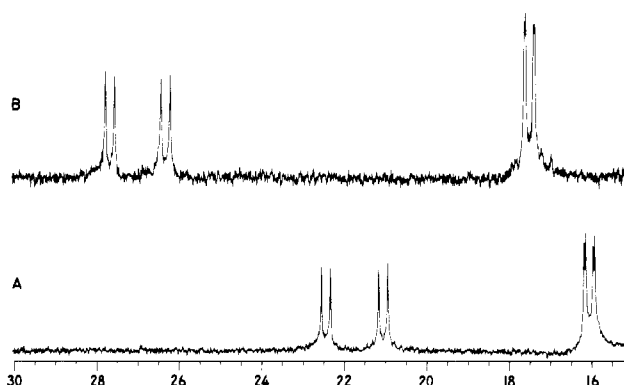
(12) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*, 101–123.

Figure 1. ^{31}P{^{1}H} NMR spectra of (A) RhPd(μ-Ph₂Ppy)₂(CO)Cl₃ (HT) and (B) [RhPd(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂][PF₆] (HT) in CDCl₃ solution at 25 °C.

measurements on acetone solutions of **5a** and **5b** show that they are 1:1 electrolytes. The infrared and ^{1}H and ^{31}P NMR spectra of **5a** and **5b** are similar to their triphenylphosphine analogues. The room-temperature ^{31}P{^{1}H} NMR spectra show a broad singlet at 28 ppm in chloroform-d_1. This singlet separates into a sharp doublet at -40 °C with a Rh–P coupling constant of 130.5 Hz for **5a**. The ^{31}P{^{1}H} NMR spectra of the triphenylphosphine analogues of **5a** and **5b** show similar temperature dependences. It appears that the temperature dependencies of these spectra are caused by rapid interionic exchange of the phosphine ligands. For these planar, 16-electron complexes, this may be caused by the presence of trace amounts of free ligands. Addition of methyl isocyanide to solutions of **5a** or **5b** at -40 °C causes a collapse of the doublet, resulting in a broad singlet.

Addition of (1,5-cyclooctadiene)palladium(II) chloride to a dichloromethane solution of [(CH₃NC)₂Rh(Ph₂Ppy)₂][PF₆] changes the color of the solution from yellow to dark red. A red, crystalline solid, [RhPd(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂][PF₆] (HT) (**6**), is obtained by the addition of 1-propanol or ether. The compound is an air-stable, 1:1 electrolyte, which is soluble in chloroform, acetone, and methanol. The infrared spectrum of **6** indicates that only terminal isocyanide ligands are present. The shift of the isocyanide stretching frequency from 2179 cm^{-1} in [(CH₃NC)₂Rh(Ph₂Ppy)₂]⁺ to 2215 cm^{-1} in [RhPd-(μ-Ph₂Ppy)₂(CNCH₃)₂Cl₂]⁺ indicates that the rhodium atom has been oxidized in this reaction. The ^{31}P NMR spectrum of **6** is extremely similar to that of RhPd(μ-Ph₂Ppy)₂(CO)Cl₃ as seen in Figure 1. Of particular significance is the reduction of ^1J(Rh–P) that is noted in the conversion of [(CH₃NC)₂Rh(Ph₂Ppy)₂]⁺ (^1J(Rh–P) = 127.7 Hz) to

[RhPd(μ-Ph$_2$Ppy)$_2$(CNCH$_3$)$_2$Cl$_2$]$^+$ (^1J(Rh–P) = 108.9 Hz). This reduction of ^1J(Rh–P) is indicative of oxidation of the rhodium atom. A preliminary X-ray crystallographic study of **6a** indicates that it does, in fact, have the structure indicated.[13]

The tetraphenylborate salt **6b** has been obtained by heating a stoichiometric mixture of Pd(Ph$_2$Ppy)$_2$Cl$_2$ and [(CH$_3$NC)$_4$Rh][BPh$_4$] in boiling acetone solution for 2 h. The spectroscopic properties of **6b** are similar to those of **6a** and indicate that a common cation is present in both salts.

A head-to-head isomer, **7**, has also been isolated. The ad-

7
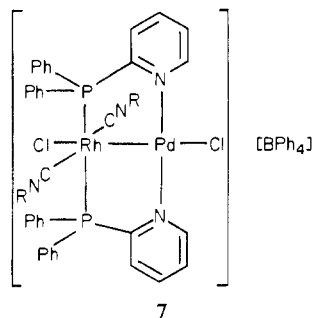
dition of equimolar quantities of (PhCN)$_2$PdCl$_2$ and [(CH$_3$NC)$_2$Rh(Ph$_2$Ppy)$_2$][BPh$_4$] produces a red solution from which orange crystals of [RhPd(μ-Ph$_2$Ppy)$_2$(CNCH$_3$)$_2$Cl$_2$]-[BPh$_4$] (*HH*(Rh)) (**7**) have been isolated. The ^{1}H NMR spectrum and the infrared spectrum of this material are similar to those of its isomer, **6b**. However the ^{31}P{^{1}H} NMR spectrum is a simple doublet with ^1J(Rh–P) of 94.2 Hz. Thus, the phosphine ligands are equivalent and are both bonded to rhodium. The smaller value of ^1J(Rh–P) (relative to [(CH$_3$NC)$_2$Rh(Ph$_2$Ppy)$_2$]$^+$) and the corresponding larger value of ν(CN) in **7** indicates that oxidative addition has occurred at the rhodium atom. The observation of a single isocyanide stretching frequency in solution indicates that these two terminal ligands occupy equivalent sites trans to one another.

In order to better understand the reaction of [(CH$_3$NC)$_2$Rh(Ph$_2$Ppy)$_2$]$^+$ with palladium complexes, these reactions have been directly monitored by ^{31}P{^{1}H} NMR on the freshly reacted solution. The products depend on the leaving groups initially bound to palladium but are essentially independent of the anion (BPh$_4^-$ or PF$_6^-$) that accompanies the rhodium cation. Thus the reaction between [(CH$_3$NC)$_2$Rh(Ph$_2$Ppy)$_2$][BPh$_4$] and (1,5-COD)PdCl$_2$ yields predominantly the *HT* species **6b**. Some Pd$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$[3] is present as well as small quantities of *HH* isomer **7**. Several other species are present in minor concentration, and these remain unidentified. The reaction between [(CH$_3$NC)$_2$Rh-(Ph$_2$Ppy)$_2$][BPh$_4$] and (PhCN)$_2$PdCl$_2$ yields a mixture containing 47% of RhPd(μ-Ph$_2$Ppy)$_2$(CNCH$_3$)$_2$Cl$_2$]$^{2+}$ (*HH*) (**7**) and 53% of the *HT* isomer, **6**. Since the *HH* isomer **7** can be thermally converted into the *HT* isomer **5**, the relative amounts formed from mononuclear procursors appear to be kinetically controlled. With a good leaving group on palladium, as is the case with (PhCN)$_2$PdCl$_2$,[14] the reaction produces a significant quantity of the thermodynamically less stable *HH* isomer **7**. However, with a chelated diolefin, which is more difficult to displace from palladium, the reaction proceeds to produce the thermodynamically favored *HT* isomer **6**.

Successive treatment of Pd(Ph$_2$Ppy)$_2$Cl$_2$ with silver nitrate and ammonium hexafluorophosphate yields [Pd-(Ph$_2$Ppy)$_2$Cl][PF$_6$]. The ^{31}P NMR spectrum indicates that
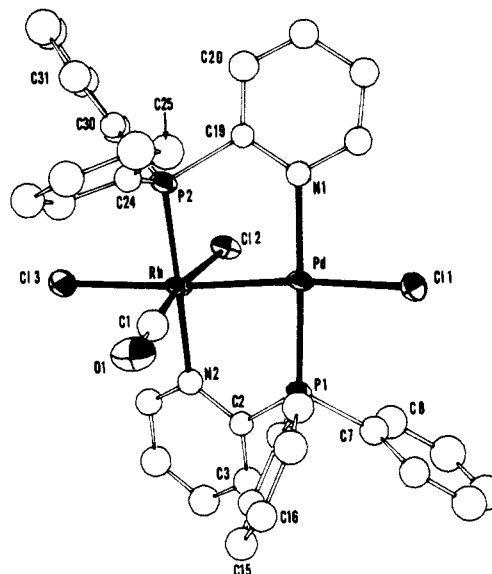
Figure 2. Perspective drawing of RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ (*HT*) (**1**).

the cation contains two nonequivalent phosphine ligands with cis orientation. Thus the cation must have structure **8** with

8
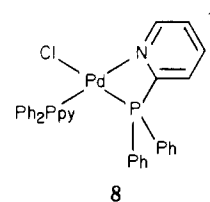
one chelating and one monodentate 2-(diphenylphosphino)-pyridine. An X-ray crystal structure of the analogous platinum-containing cation has been determined.[5]

Molecular Structure of RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$. The detailed geometry of RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ has been established by an X-ray crystal structure determination. This complex crystallizes with one molecule within the asymmetric unit. A perspective view of the molecule, which has no symmetry, is shown in Figure 2. Atomic coordinates are given in Table II, and selected bond distances and angles are presented in Tables III and IV. The structure contains a six-coordinate rhodium atom that is directly bonded to a four-coordinate, planar palladium atom. The Rh–Pd distance (2.594 Å) is consistent with the presence of a metal–metal single bond. The bridging ligands are arranged in the head-to-tail fashion.

Most of the bond lengths fall within the usual ranges found for analogous groups. However, the Rh–Cl(3) distance (2.499 Å) is unusually long. For comparison it is 0.100 Å longer than the Rh–Cl(2) distance. The unusual length of the Rh–Cl(3) bond can be attributed to the high trans effect of the metal–metal (Rh–Pd) bond. Similarly the Pd–Cl distance is at the long end of the range of known Pd–Cl bond lengths. Palladium chlorine distances depend strongly on the trans ligand and fall into the following ranges depending on the trans ligand: Cl, 2.24–2.30; N, 2.30–2.33; olefin, 2.31–2.34; S, 2.31–2.35; P, 2.35–2.37; σ-C, 2.38–2.45 Å.[15] The range of distances is similar for Pt–Cl and Rh–Cl bonds.[16] Some cases of long

(13) Olmstead, M. M.; Farr, J. P.; Balch, A. L., unpublished work.
(14) In dichloromethane solution there is appreciable dissociation of benzonitrile from (PhCN)$_2$PdCl$_2$. Kubota, M.; Denechand, B. A.; McKinney, P. M.; Needham, T. E.; Spessard, G. O. *J. Catal.* **1970**, *18*, 119.

(15) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432.
(16) Manojlovic-Muir, Lj.; Muir, K. W. *Inorg. Chim. Acta* **1974**, *10*, 47.
(17) Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* **1979**, *32*, 193.
(18) Manojlovic-Muir, Lj.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1979**, *179*, 479.

Table II. Atomic Fractional Coordinates and Temperature Factors for RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0.1446 (1)	0.1606 (1)	0.13074 (4)	2.44 (4)	10.00 (3)	2.03 (4)	0.14 (4)	0.01 (3)	−0.05 (4)
Rh	0.2578 (1)	0.2500 (1)	0.04313 (4)	2.67 (4)	0.94 (4)	1.69 (4)	0.09 (4)	−0.14 (3)	−0.10 (4)
Cl(1)	0.0492 (3)	0.0903 (2)	0.2198 (2)	3.74 (16)	1.98 (14)	2.88 (14)	−0.01 (12)	0.81 (13)	0.51 (12)
Cl(2)	0.0669 (3)	0.2141 (2)	−0.0153 (2)	3.41 (16)	1.74 (13)	2.84 (14)	0.00 (12)	−0.42 (12)	−0.39 (12)
Cl(3)	0.3818 (4)	0.3248 (2)	−0.0420 (2)	4.38 (18)	1.98 (14)	3.08 (15)	−0.19 (13)	0.99 (14)	0.22 (12)
P(1)	0.1093 (3)	0.2868 (2)	0.1781 (1)	2.36 (14)	1.09 (12)	2.07 (13)	0.01 (11)	−0.04 (11)	−0.15 (11)
P(2)	0.3579 (3)	0.1273 (2)	0.0144 (2)	2.86 (15)	1.14 (12)	2.09 (14)	0.07 (11)	0.05 (12)	−0.02 (10)
O(1)	0.4667 (11)	0.2985 (8)	0.1330 (5)	3.5 (5)	5.1 (6)	5.3 (6)	0.4 (5)	−1.1 (5)	−2.0 (5)

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
N(1)	0.1758 (10)	0.0418 (7)	0.0823 (5)	2.0 (2)	C(18)	0.2956 (12)	0.2497 (11)	0.2664 (6)	2.9 (3)
N(2)	0.1613 (10)	0.3694 (7)	0.0676 (5)	2.3 (2)	C(19)	0.2626 (12)	0.0312 (8)	0.0354 (6)	1.8 (2)
C(1)	0.3851 (14)	0.2769 (10)	0.0988 (7)	3.1 (3)	C(20)	0.2816 (14)	−0.0474 (10)	0.0053 (7)	3.0 (3)
C(2)	0.1005 (12)	0.3806 (9)	0.1260 (6)	2.0 (2)	C(21)	0.2030 (14)	−0.1163 (10)	0.0201 (7)	2.9 (3)
C(3)	0.0379 (14)	0.4565 (10)	0.1406 (7)	3.0 (3)	C(22)	0.1055 (14)	−0.1053 (9)	0.0671 (6)	2.8 (3)
C(4)	0.0355 (15)	0.5259 (10)	0.0986 (7)	3.5 (3)	C(23)	0.0990 (13)	−0.0259 (9)	0.0965 (6)	2.5 (2)
C(5)	0.0951 (15)	0.5150 (11)	0.0418 (7)	3.5 (3)	C(24)	0.5169 (12)	0.1132 (9)	0.0522 (6)	2.3 (2)
C(6)	0.1600 (13)	0.4348 (10)	0.0278 (6)	2.5 (3)	C(25)	0.5386 (15)	0.0482 (11)	0.0955 (7)	3.5 (3)
C(7)	−0.0399 (13)	0.2986 (9)	0.2217 (6)	2.8 (3)	C(26)	0.6620 (16)	0.0415 (12)	0.1265 (7)	4.0 (3)
C(8)	−0.1522 (16)	0.3044 (11)	0.1904 (7)	3.9 (3)	C(27)	0.7555 (14)	0.1016 (11)	0.1108 (7)	3.4 (3)
C(9)	−0.2727 (17)	0.3155 (12)	0.2251 (8)	4.6 (4)	C(28)	0.7355 (12)	0.1629 (11)	0.0637 (7)	3.3 (3)
C(10)	−0.2631 (16)	0.3186 (12)	0.2911 (8)	4.2 (3)	C(29)	0.6148 (13)	0.1729 (11)	0.0351 (7)	3.4 (3)
C(11)	−0.1479 (16)	0.3141 (11)	0.3217 (7)	3.9 (3)	C(30)	0.3906 (12)	0.1053 (9)	−0.0681 (6)	2.2 (2)
C(12)	−0.0369 (14)	0.3029 (10)	0.2895 (6)	3.0 (3)	C(31)	0.5010 (15)	0.0604 (10)	−0.0853 (7)	3.3 (3)
C(13)	0.2318 (12)	0.3141 (9)	0.2354 (6)	2.4 (3)	C(32)	0.5192 (17)	0.0317 (12)	−0.1488 (8)	4.3 (3)
C(14)	0.2552 (10)	0.4021 (9)	0.2514 (7)	2.3 (2)	C(33)	0.4301 (17)	0.0526 (13)	−0.1925 (8)	4.5 (3)
C(15)	0.3412 (14)	0.4221 (10)	0.2998 (7)	3.0 (3)	C(34)	0.3216 (15)	0.1024 (11)	−0.1769 (7)	3.6 (3)
C(16)	0.4011 (13)	0.3551 (9)	0.3317 (6)	2.6 (3)	C(35)	0.3002 (14)	0.1286 (9)	−0.1135 (6)	3.0 (3)
C(17)	0.3807 (4)	0.2697 (10)	0.3164 (7)	3.2 (3)					

Table III. Interatomic Distances (Å) for RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$

Rh-Pd	2.594 (1)	Pd-N(1)	2.13 (1)
Rh-C(1)	1.82 (1)	Pd-P(1)	2.220 (4)
Rh-Cl(2)	2.399 (3)	P(1)-C(2)	1.823 (4)
Rh-Cl(3)	2.499 (4)	P(2)-C(19)	1.835 (4)
Rh-N(2)	2.16 (1)	C(1)-O(1)	1.16 (2)
Rh-P(2)	2.243 (3)	P(2)···N(1)	2.716
Pd-Cl(1)	2.393 (4)	P(1)···N(2)	2.689

Table IV. Interatomic Angles (deg) for RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$

Rh-Pd-Cl(1)	173.5 (1)	N(2)-Rh-Cl(2)	86.5 (3)
Rh-Pd-N(1)	92.4 (3)	N(2)-Rh-Cl(3)	91.0 (3)
Rh-Pd-P(1)	86.2 (1)	N(2)-Rh-Pd	94.1 (3)
Rh-C(1)-O(1)	176 (1)	C(1)-Rh-Cl(2)	93.1 (3)
Rh-N(2)-C(2)	121.7 (6)	C(1)-Rh-Pd	89.1 (5)
Pd-N(1)-C(19)	124.2 (5)	Cl(2)-Rh-Pd	82.8 (1)
Rh-P(2)-C(19)	111.5 (4)	Cl(3)-Rh-Cl(2)	99.0 (1)
Pd-P(1)-C(2)	115.4 (3)	Cl(3)-Rh-C(1)	89.5 (5)
P(2)-Rh-N(2)	178.1 (3)	Cl(3)-Rh-Pd	174.7 (1)
P(2)-Rh-Cl(1)	92.0 (5)	P(1)-Pd-Cl(1)	88.4 (1)
P(2)-Rh-Cl(2)	92.6 (1)	P(1)-Pd-N(1)	177.9 (3)
P(2)-Rh-Cl(3)	87.5 (1)	N(1)-Pd-Cl(1)	93.1 (3)
P(2)-Rh-Pd	87.4 (1)	P(1)-C(2)-N(2)	115.0 (1)
N(2)-Rh-C(1)	89.1 (6)	P(2)-C(19)-N(1)	116.0 (1)

M–Cl bonds, where the M–Cl unit is trans to the metal–metal single bond, are collected in Table V. It is apparent that the metal–metal single bond produces a high structural trans effect.[22-26]

The bond angles between the cis ligands are nearly 90° for both palladium and rhodium. The largest deviation in this regard is the Cl(2)–Rh–Cl(3) angle, which is 99.0°. The carbonyl group is linearly coordinated, and the bond angles

(19) Manojlovic-Muir, Lj.; Muir, K. W.; Solomun, T. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1237.

(20) Modinos, A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 1516.

(21) Cowie, M.; Dwight, S. K. *J. Organomet. Chem.* **1981**, *214*, 233.

(22) Further evidence of the strong trans effect of metal–metal bonds comes from examining cases where a particular type of ligand occupies two different sites in a binuclear complex. If one of those sites is trans to a metal–metal bond, it is that ligand which displays the longer metal–ligand bond. For example, in Pd$_2$(CNCH$_3$)$_6^{2+}$ the mean Pd–C distance is 2.049 (6) Å for the two isocyanide ligands that are trans to the Pd–Pd bond while it is 1.963 (5) Å for the four equatorial isocyanide ligands (trans C–Pd–C units).[23] In [Pt$_2$(μ-dpm)$_2$H(dpm)]$^+$ the Pt–P unit that is trans to the Pt–Pt bond is 2.347 (4) Å long while the range of the other four Pt–P bonds (all of which are trans to another phosphorus atom) is 2.248 (3)–2.289 (4) Å.[24] In Pt$_2$(μ-OC$_6$H$_4$P(Ph)CH$_2$-CH$_2$PPh$_2$)$_2$, the Pt–P bond trans to the Pt–Pt bond is 2.272 Å long while the other type of Pt–P bond, which is trans to the Pt–C(aryl) bond, is 2.240 Å long.[25] However, this trend is not observed, nor expected, in cases where very strong π bonding of the ligands involved occurs. Thus in Mn$_2$(CO)$_{10}$ and Re$_2$(CO)$_{10}$ the M–C(axial) distances are 1.811 (3) and 1.929 (7) Å, respectively, while the average M–C(equatorial) distances are 1.856 (7) and 1.987 (15) Å.[26]

(23) Doonan, D. J.; Balch, A. L.; Goldberg, S. Z.; Eisenberg, R.; Miller, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 1961.

(24) Manojlovic-Muir, Lj.; Muir, K. W. *J. Organomet. Chem.* **1981**, *219*, 129.

(25) Arnold, D. P.; Bennett, M. A.; Bilton, M. S.; Robertson, G. B. *J. Chem. Soc., Chem. Commun.* **1982**, 115.

(26) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

Table V. Some Long M–Cl Distances Where the M–Cl Group Is Trans to a Metal–Metal Single Bond

compd	M–Cl dist, Å	trans unit	ref
RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ (*HT*)	2.393 (4)	Cl–Pd–Rh	this work
	[2.399 (3)	Cl–Rh–CO]	
	2.499 (3)	Cl–Rh–Pd	
RuPd(μ-Ph$_2$Ppy)$_2$(CO)$_2$Cl$_2$ (*HT*)	2.426 (2)	Cl–Pd–Ru	4
	2.477 (2)	Cl–Ru–Pd	
Pd$_2$(μ-dpm)$_2$Cl(SnCl$_3$)^a	2.396 (4)	Cl–Pd–Pd	17
Pt$_2$(μ-dpm)$_2$(CO)Cl^a	2.384 (5)	Cl–Pt–Pt	18
Pt$_2$(μ-dpm)$_2$Cl$_2$	2.408 (5),	Cl–Pt–Pt	19
	2.401 (5)		
Pt$_2$(CO)$_2$Cl$_4^{2-}$	2.426 (9),	Cl–Pt–Pt	20
	2.382 (10)		
	[2.327 (7),	Cl–Pt–CO]	
	2.327 (7)		
Rh$_2$(μ-dpm)$_2$(μ-C$_2$S$_4$)(CO)Cl$_2^a$	2.527 (2)	Cl–Rh–Rh	21
	[2.455 (5)	Cl–Rh–C]	

^{a} dpm is Ph$_2$PCH$_2$PPh$_2$.

within the bridging ligands all are normal.

^{31}P NMR Studies of the Formation of the Binuclear Rh/Pd Compounds.

In order to detect possible intermediates formed during the synthesis of RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$, the precursor complexes have been mixed at low temperature, and the course of the reaction has been monitored by ^{31}P NMR

Figure 3. $^{31}P\{^{1}H\}$ NMR spectra obtained from a dichloromethane solution containing equimolar quantities of *trans*-Rh(Ph$_2$Ppy)$_2$(CO)Cl and (PhCN)$_2$PdCl$_2$ prepared at −55 °C and then allowed to warm successively to the temperatures indicated. The following resonances have been identified by comparison with authentic samples: A, Rh(Ph$_2$Ppy)$_2$(CO)Cl; C, RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ (*HT*) (1); D, Rh$_2$(μ-Ph$_2$Ppy)$_2$(μ-CO)Cl$_2$ (*HT*); E, Pd$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$. Possible origins of other peaks are discussed in the text.

spectroscopy. Two different reactions have been examined. These are the reaction between Rh(Ph$_2$Ppy)$_2$(CO)Cl and (PhCN)$_2$PdCl$_2$ and the reaction between Pd(Ph$_2$Ppy)$_2$Cl$_2$ and Rh$_2$(μ-Cl)$_2$(CO)$_4$. Each takes a different course.

Figure 3 shows the effect of mixing equimolar quantities of Rh(Ph$_2$Ppy)$_2$(CO)Cl and (PhCN)$_2$PdCl$_2$ at −55 °C and allowing the mixture to warm to room temperature. At −55 °C (trace I) resonance A of unreacted Rh(Ph$_2$Ppy)$_2$(CO)Cl dominates the spectrum, but a set of four lines (labeled B) in the region 6–10 ppm appears. When the mixture is warmed to −40 (trace II) and to −20 °C (trace III), the B peaks grow in intensity and a new set of peaks, labeled C, also appear. Peaks C are identified as belonging to RhPd(μ-Ph$_2$Ppy)$_2$-(CO)Cl$_3$ by comparison with the isolated complex. At −20 °C a multiplet labeled D is also detectable. This feature is identified as resulting from Rh$_2$(μ-Ph$_2$Ppy)$_2$(μ-CO)Cl$_2$ by comparison with an authentic sample.[2] When the mixture is further warmed to 0 °C, the resonances due to Rh-(Ph$_2$Ppy)$_2$(CO)Cl decrease in intensity while those of peaks B, C, and D as well as other new peaks E and F have grown. Peak F is due to Pd$_2$(Ph$_2$Ppy)$_2$Cl$_2$ while E remains unidentified. The species responsible for peak B is thermally unstable. Warming to 60 °C results in the conversion of resonance B into that for RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ (*HT*) (1).

During warming, the group of peaks labeled B has undergone coalescence from four equally intense lines to two narrow lines. These changes in the features of the B resonances are fully reversible on lowering the temperature. At 20 °C the apparent ^{1}J(Rh–P) is 97.5 Hz. The low-temperature spectrum could result from the presence of two species, each with its phosphine ligands bound to rhodium or to a single species with two chemically distinct, rhodium-bound phosphorus atoms. The low-temperature behavior has been examined in several solvents including dichloromethane, dimethylformamide, and toluene. In each case, four resonances appear with equal intensity at ca. −55 °C. Since there is no solvent effect on the intensities of these lines, we believe that only a single species is responsible for the four resonances. Had two different molecules been present, we suspect that changing that solvent would have produced changes in the relative amounts of the two species and hence changes in the resonance
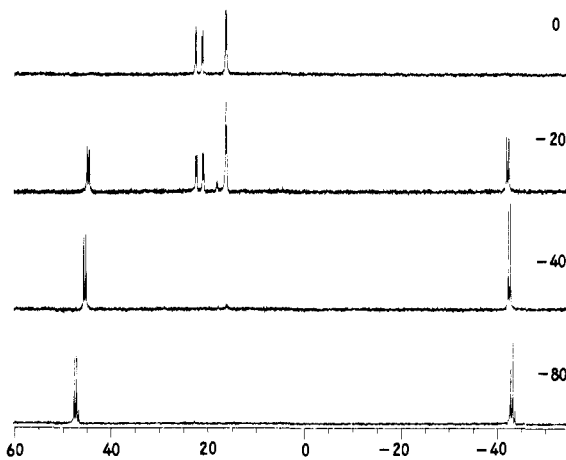
Figure 4. $^{31}P\{^{1}H\}$ NMR spectra obtained from a mixture of (Ph$_2$Ppy)$_2$PdCl$_2$ and $^{1}/_2$ molar equiv of Rh$_2$(μ-Cl)$_2$(CO)$_4$ in dichloromethane solution. The sample was prepared at −80 °C and then successively warmed to the temperatures indicated.

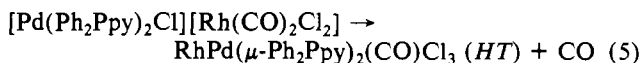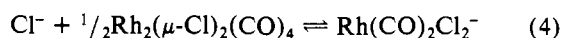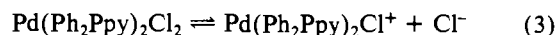intensities. From the available data, we believe that one species containing two nonequivalent phosphine ligands with δ_1 7.7, ^{1}J(Rh–P) = 95 Hz, and δ_2 8.1, ^{1}J(Rh–P) = 96.1 Hz, is present. This species is fluxional. On warming, the environments of the two phosphine ligands are rapidly exchanged. The small values of ^{1}J(Rh–P) suggest that the rhodium center in this species is oxidized. The available data suggest that the species responsible for resonance B is a *HH* isomer of RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ with structure **9** being the most reasonable.
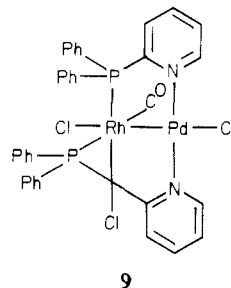
9

As required, the two phosphine ligands are in equivalent positions. Since they are cis to one another, ^{2}J(P–P) is expected to be small (<50 Hz). In fact it is less than the natural line width (7 Hz) and is not observed. To account for the fluxional behavior of **9**, interchange of the position of the chloride and carbonyl ligands would have to occur.

The results of following the reaction between Pd-(Ph$_2$Ppy)$_2$Cl$_2$ and $^{1}/_2$ molar equiv of Rh$_2$(μ-Cl)$_2$(CO)$_4$ are shown in Figure 4. At −80 °C all of the Pd(Ph$_2$Ppy)$_2$Cl$_2$ has reacted. The principal phosphorus-containing species present is [Pd(Ph$_2$Ppy)$_2$Cl]$^{+}$ (**8**) which has been independently synthesized. Its ^{31}P NMR spectrum consists of a doublet at 42.7 ppm due to the terminal phosphine and a doublet at −42.3 ppm due to the chelating phosphine. A small pair of peaks to high field of each doublet has not been identified. Warming the sample results in the smooth conversion of this intermediate into RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ (*HT*), so that at room temperature only the latter is found. Thus the course of the reaction proceeds in steps as shown in eq 3–5. A similar

$$Pd(Ph_2Ppy)_2Cl_2 \rightleftharpoons Pd(Ph_2Ppy)_2Cl^+ + Cl^- \quad (3)$$

$$Cl^- + {}^{1}/_2Rh_2(\mu\text{-}Cl)_2(CO)_4 \rightleftharpoons Rh(CO)_2Cl_2^- \quad (4)$$

$$[Pd(Ph_2Ppy)_2Cl][Rh(CO)_2Cl_2] \rightarrow$$
$$RhPd(\mu\text{-}Ph_2Ppy)_2(CO)Cl_3 \ (HT) + CO \quad (5)$$

course has been established for the reaction between *cis*-Pt-(Ph$_2$Ppy)$_2$Cl$_2$ and Rh$_2$(μ-Cl)$_2$(CO)$_4$, and the intermediate,
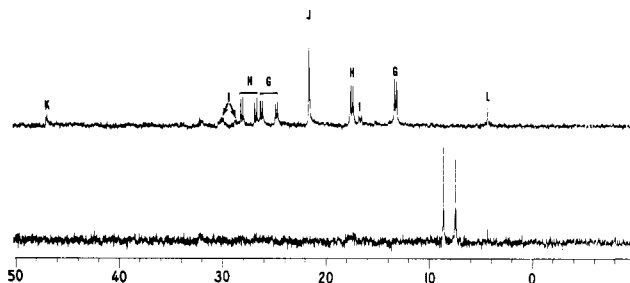
Figure 5. $^{31}P\{^1H\}$ NMR spectrum of [RhPd(μ-Ph$_2$Ppy)$_2$-(CNCH$_3$)$_2$Cl$_2$][BPh$_4$] (*HH*(Rh)) at the bottom and the products obtained by heating this compound in boiling acetonitrile solution for 12 h at the top. After the mixture was heated, the solvent was removed by vacuum evaporation and the sample dissolved in CDCl$_3$ to record the spectrum.

[Pt(Ph$_2$Ppy)$_2$Cl][Rh(CO)$_2$Cl$_2$], has been isolated and characterized by an X-ray crystal structure.[5]

Thermolysis of [RhPd(μ-Ph$_2$Ppy)$_2$(CNCH$_3$)$_2$Cl$_2$]$^+$ (*HH*(Rh)). The thermal interconversion of the *HH*(Rh), **7**, and *HT*, **6**, isomers of [RhPd(μ-Ph$_2$Ppy)$_2$(CNCH$_3$)$_2$Cl$_2$]$^+$ has been examined. The *HT* isomer **6** is thermally inert. Heating complex **6** for 24 h in boiling acetonitrile results is no change in the ^{31}P NMR spectrum of the sample. However the *HH*-(Rh), **7**, isomer is thermally reactive. The products produced by heating a sample of [RhPd(μ-Ph$_2$Ppy)$_2$(CNCH$_3$)$_2$Cl$_2$]-[BPh$_4$] (*HH*(Rh)) in boiling acetonitrile for 12 h can be partially identified from the ^{31}P NMR spectrum shown in Figure 5. During the reaction, the starting complex is completely consumed. The *HT* isomer **6** (peaks labeled H) is formed in appreciable yield as are several other products including Pd$_2$(μ-Ph$_2$Ppy)$_2$Cl$_2$[3] (peak labeled L). The peaks labeled G and I appear to be due to other *HT* isomers since they contain the same basic spectral pattern as that of **5**. The spectral parameters for G are δ_1 12.98, δ_2 25.23, ^1J(Rh–P) = 118.4 Hz, and ^3J(P–P) = 16.5 Hz, and the corresponding values for I are δ_1 16.38, δ_2 29.1, ^1J(Rh–P) = 105.9 Hz, and ^3J(P–P) = 17.6 Hz. There are five structures, **10–14**, that are compatible with the available data for the species responsible
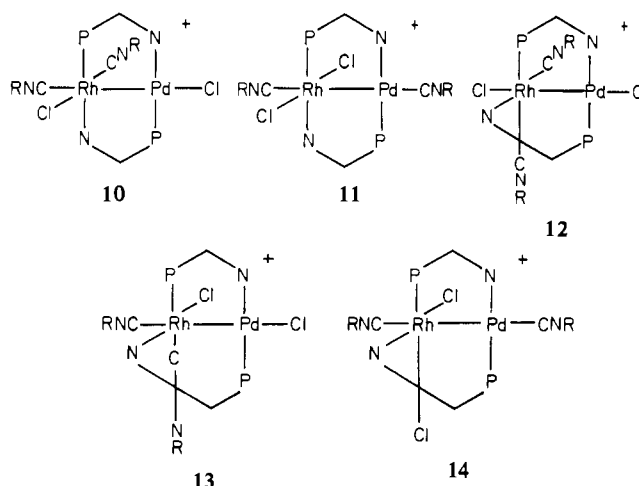
for the resonances G and I. Less is known about the singlets labeled J and K. These are not associated with any known palladium complexes of 2-(diphenylphosphino)pyridine. The possibility exists that one is a *HH*(Pd) isomer, but until the species responsible for this spectrum are separated, identification remains incomplete.

Registry No. 1, 75361-88-5; **5a**, 84695-82-9; **5b**, 84695-81-8; **6a**, 84695-86-3; **6b**, 84773-44-4; **7**, 84695-88-5; **8**, 84695-84-1; *trans*-Pd(Ph$_2$Ppy)$_2$Cl$_2$, 38255-46-8; *cis*-Pd(Ph$_2$Ppy)$_2$Cl$_2$, 84773-43-3; [(CH$_3$N)$_4$Rh][BPh$_4$], 34742-53-5; (PhCN)$_2$PdCl$_2$, 14220-64-5; (1,5-COD)PdCl$_2$, 12107-56-1; *trans*-Rh(CO)(Cl)(Ph$_2$Ppy)$_2$, 75361-60-3; Rh$_2$(μ-Cl)$_2$(CO)$_4$, 14523-22-9; Pd(Ph$_3$P)$_2$Cl$_2$, 13965-03-2; Rh(Ph$_3$P)$_2$(CO)Cl, 13938-94-8; Rh(Ph$_3$Ppy)$_2$(CO)Br, 84695-89-6; [(CH$_3$NC)$_2$Rh(Ph$_3$P)$_2$][PF$_6$], 61160-81-4; [(CH$_3$NC)$_2$Rh-(Ph$_3$P)$_2$][BPh$_4$], 84695-90-9; RhPd(μ-Ph$_2$Ppy)$_2$(CO)Br$_3$, 84695-91-0; Pd, 7440-05-3; Rh, 7440-16-6.

Supplementary Material Available: Table of structure factors for RhPd(μ-Ph$_2$Ppy)$_2$(CO)Cl$_3$ (12 pages). Ordering information is given on any current masthead page.

Contribution from the William Ramsay and Ralph Forster Laboratories, University College, London WC1, England

Kinetics of the Reversible Displacement of Chloride by Amines under the Trans Effect of Phosphines, Phosphites, and Arsines

ROY GOSLING and MARTIN L. TOBE*

The rate and equilibrium constants are reported for the reaction [Pt(L)Cl$_3$]$^-$ + am → *trans*-[Pt(L)(am)Cl$_2$] + Cl$^-$ (L = PMe$_3$, PEt$_3$, P-*n*-Bu$_3$, PPh$_3$, P(OMe)$_3$, AsEt$_3$; am is one of a series of amines and heterocyclic bases covering a wide range of basicity) in methanol at 30.0 °C, μ = 0.50. The behavior patterns are discussed and compared with those of complexes where L is a sulfur donor ligand. The lability is strongly dependent upon the nature of the donor atom (P, As, or S) but far less sensitive to the nature of the substituents.

Introduction

As part of our study of the trans effects of ligands with second- and third-row donor atoms we have examined the kinetics and equilibria of the reactions associated with the reversible processes

$$[Pt(L)Cl_3]^- + am \rightarrow trans\text{-}[Pt(L)(am)Cl_2] + Cl^-$$

where L = Me$_2$SO,[1] Me$_2$S,[2] and Et$_2$S[3] and am is one of a series

of amines and heterocyclic bases covering a wide range of basicity. Kinetically, these donors exert a moderately strong trans effect when compared to that of chloride and the nitrogen donors even though this is not accompanied by a similarly

(1) Romeo, R.; Tobe, M. L. *Inorg. Chem.* **1974**, *13*, 1991.
(2) Kennedy, B. P.; Gosling, R.; Tobe, M. L. *Inorg. Chem.* **1977**, *16*, 1744.
(3) Gosling, R.; Tobe, M. L. *Inorg. Chim. Acta* **1980**, *42*, 223.