

Table I. Apparent Oxygen Binding Constants for CoSALEN-py in Zeolite Na-Y

temp, K	K_{O_2} , Torr ⁻¹	$P_{1/2}$, Torr	$P_{1/2}$ (CoSALEN), ^a Torr
233	0.53	1.9	0.04
253	0.056	17.7	0.36
273	0.012	80.1	2.21
293	0.0033	305.5	10.5

^aData for free CoSALEN in pyridine solvent calculated from thermodynamic data in ref 18.

absorption isotherm may be constructed as in Figure 4. From such data, Hill plots¹⁵ may be constructed, Figure 5, which in turn give the apparent oxygen binding constants listed in Table I. The Hill plots show slopes of 0.56 ± 0.02 , indicating a negative cooperativity between the Co binding sites.¹⁰ This translates as meaning that as oxygen is bound by the first cobalt sites, subsequent binding by further sites is inhibited. This is the reverse of the behavior displayed by hemoglobin.¹⁰ The explanation of such an observation is not clear but may simply be a manifestation of the oxygen adsorption behavior of the zeolite itself, which tends to "pump" oxygen so as to have a higher effective oxygen concentration inside the pores than the externally applied oxygen pressure would imply.¹⁴ This effect is more pronounced at lower oxygen pressures and so from the cobalt complex's point of view, the perceived oxygen pressure is not varying linearly with the applied oxygen pressure, with the deviation being such as to skew the Hill plot to a slope of less than 1. This behavior of the zeolite in raising the effective concentration of a reagent (oxygen) at an active site (cobalt) is very reminiscent of the function of the protein in creating an active site in an enzyme. In this way the zeolite may be considered an inorganic protein as we and others have previously suggested.^{16,17}

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Finally a van't Hoff plot of this data gives an excellent straight line ($R = 0.997$) from which $\Delta H = -11.4 \pm 0.5$ kcal/mol and $\Delta S = -51 \pm 2$ eu are deduced (standard state of 1 Torr). For comparison the equivalent complex in solution has $\Delta H = -12.4$ kcal/mol and $\Delta S = -47$ eu,¹⁸ implying that inside the zeolite the lower binding constants (see Table I) result from a reduced exothermicity. This effect is consistent with the oxygen being bound inside the zeolite cavity at a restrictive binding site where the sterics of interaction of bound oxygen with the zeolite walls will be important.

In conclusion, it has been shown that a molecular "ship in a bottle" complex can be made so that it carries oxygen as a cargo and that such a material is much more stable toward irreversible oxidation than the equivalent solution-phase species. Unusual effects on the magnetic properties and oxygen binding behavior of the complex as a result of the zeolite environment are manifest, and the striking analogies between zeolite-encapsulated active sites and natural enzyme systems are reinforced. We have identified a number of other oxygen carrier systems inside zeolites with properties similar to those reported above, and these will be reported in a full publication in the near future together with a detailed analysis of the oxygen adsorption kinetics and thermodynamics.

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Heterobimetallic Complexes of Rhodium with Platinum, Silver, and Gold Containing Bridging 2-[Bis(diphenylphosphino)methyl]pyridine (PNP) Ligands

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Several new heterobimetallic compounds that contain bridging PNP ligands have been synthesized. The reactions of $[\text{Rh}(\text{PNP})_2]\text{BF}_4$ with $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ and $\text{Ag}(\text{PPh}_3)(\text{NO}_3)$ led to the formation of $[\text{RhPt}(\mu\text{-PPh}_2)(\mu\text{-PNP})(\text{PN})(\text{PPh}_3)](\text{BF}_4)_2$ (1) and $[\text{RhAg}(\mu\text{-PNP})_2](\text{BF}_4)(\text{NO}_3)$ (2), respectively. The reactions of $[\text{RhAu}(\mu\text{-PNP})_2](\text{BF}_4)(\text{NO}_3)$ with CO and HCl gas and with aqueous HBr gave $[\text{RhAu}(\mu\text{-PNP})_2(\text{CO})_2](\text{BF}_4)(\text{NO}_3)$ (3) and $[\text{RhAu}(\mu\text{-PNP})_2\text{X}]\text{BF}_4$ with X = Cl (4) and Br (5), respectively. Compound 1 was characterized by single-crystal X-ray diffraction [$P2_1/c$, $a = 15.921$ (9) Å, $b = 16.128$ (3) Å, $c = 33.326$ (9) Å, $\beta = 101.44$ (2)°, $Z = 4$, $\rho = 1.439$ g cm⁻³, $R = 0.063$] and was found to have bridging diphenylphosphido and PNP ligands and a PN [2-[(diphenylphosphino)methyl]pyridine] ligand chelated to the Rh. The Rh-Pt distance [2.708 (1) Å] is consistent with a metal-metal bond. The PN and PPh₂ ligands resulted from cleavage of a phosphorus-carbon bond of a PNP ligand. The other compounds 2-5 were characterized in solution by ³¹P and ¹H NMR spectroscopy and by IR spectroscopy. They all have bis(μ-PNP) structures.

Introduction

Heterobimetallic complexes in which two metals are held in close proximity by bridging P-P or P-N ligands have received considerable attention in recent years.¹⁻³⁴ Interest in such

mixed-metal compounds stems from their potential use in catalysis and organometallic-based synthetic chemistry. These compounds

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can serve as models for more complex polymetallic systems and can possibly be used for the preparation of supported polymetallic, heterogeneous catalysts. Heterobimetallic complexes are also of interest in their own right because of their potential to promote unique patterns of substrate activation through cooperative or separate interactions.

Bifunctional ligands such as 2-(diphenylphosphino)pyridine, Ph₂Ppy, and (diphenylarsino)(diphenylphosphino)methane, dapm, have proved to be particularly useful in constructing heterobimetallic species.^{1-5,22,23} Mixed-metal complexes have also been synthesized by using the bidentate diphosphine bis(diphenylphosphino)methane, dppm,^{7-16,18-21} as well as the phosphido (PR₂) group.²⁴⁻³⁴ Strong phosphido bridges have been found to maintain the integrity of the binuclear framework during chemical transformations.

The bifunctional ligand 2-[bis(diphenylphosphino)methyl]pyridine, PNP, has been shown to be useful in the synthesis of bimetallic complexes of unusual stereochemistry.^{35,36} For example,

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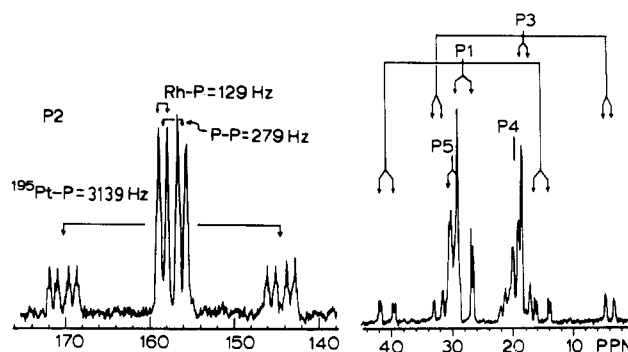
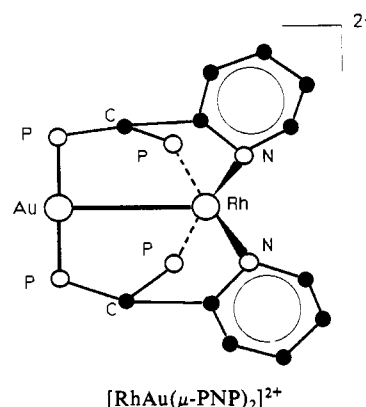


Figure 1. ³¹P{¹H} NMR spectrum of [RhPt(PPh₂)(PNP)(PN)(PPh₃)]²⁺ (cation of 1) showing the assignments. No other resonances were observed, and the spectrum was recorded at -90 °C with CH₂Cl₂ as solvent. The intensities of the two spectral regions are not on the same scale.

[Rh₂(CO)(μ-PNP)₂]²⁺ and [RhAu(μ-PNP)₂]²⁺ have recently been characterized by single-crystal X-ray crystallography and have the structure where the phosphorus atoms are arranged cis on one metal and trans on the other, as shown in the following drawing.



Reported here are the synthesis and characterization of two new PNP-bridged heterobimetallic complexes, [RhPt(μ-PPh₂)(μ-PNP)(PN)(PPh₃)](BF₄)₂ (1) and [RhAg(μ-PNP)₂](BF₄)(NO₃) (2), where PN = 2-[(diphenylphosphino)methyl]pyridine, and some new reaction chemistry of [RhAu(μ-PNP)₂](BF₄)(NO₃), which led to the characterization of the new heterobimetallic Rh-Au complexes [RhAu(μ-PNP)₂(CO)₂](BF₄)(NO₃) (3) and [RhAu(μ-PNP)₂(X)]BF₄ (X = Cl (4) and Br (5)). X-ray structural characterization of 1 showed that the coordination geometry about rhodium was distorted octahedral and that around platinum was four-coordinate and slightly distorted from planar. This is the first Rh-Pt phosphine complex that contains both diphosphine and phosphido bridges to be characterized by single-crystal X-ray diffraction. Spectroscopic characterization of 2 showed it to be very similar to the Rh-Au complex [RhAu(μ-PNP)₂]²⁺.

Experimental Section

Physical Measurements. ¹H and ³¹P{¹H} NMR spectra were recorded at 300 and 121.5 MHz, respectively, with the use of a Nicolet NT-300 spectrometer. ¹H chemical shifts are reported in ppm with positive shifts downfield. Ambient-temperature ³¹P chemical shifts are reported in ppm relative to the external 85% H₃PO₄, with positive shifts downfield. Low-temperature ³¹P NMR spectra are reported in ppm relative to the internal standard trimethyl phosphate (TMP). IR spectra were recorded on a Beckman Model 4250 grating spectrometer. Conductivity measurements were taken on a YSI Model 31 conductivity bridge using 10⁻³ M solutions.

Preparation of Compounds. All manipulations were carried out under a purified N₂ atmosphere by using standard Schlenk techniques. Solvents were dried and distilled prior to use. [RhAu(PNP)₂](BF₄)(NO₃)³⁵

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Pt(PPh₃)₂(C₂H₄),³⁷ [Rh(PNP)₂](BF₄)₂³⁵ and Ag(PPh₃)NO₃³⁸ were prepared according to literature methods.

[RhPt(PPh₃)(PNP)(PN)(PPh₃)](BF₄)₂ (1). A methylene chloride solution of Pt(PPh₃)₂(C₂H₄) (189.7 mg, 0.254 mmol) was added to a stirring methylene chloride solution of [Rh(PNP)₂](BF₄)₂ (282.0 mg, 0.254 mmol). The reaction solution changed from yellow to orange after the addition of Pt(PPh₃)₂(C₂H₄). After several hours of stirring, diethyl ether was added to precipitate a light orange product. The product was collected by filtration, washed with diethyl ether, and dried in vacuo. An orange crystalline product was obtained by slow solvent diffusion from methylene chloride and diethyl ether; yield 96% based on BF₄⁻. ¹H NMR (acetone-*d*₆): δ 9.45–5.84 (multiplet), 4.46 (d, *J*_{H-H} = 11.7 Hz), 4.41 (d, *J*_{H-H} = 11.7 Hz). ³¹P{¹H} NMR (–90 °C, CH₂Cl₂ (Figure 1; see text for assignment)): δ 157.2 (d of d of multiplets, *J*_{Pt-P} = 3139 Hz, *J*_{P-P} = 279 Hz, *J*_{Rh-P} = 129 Hz, Int = 1), 29.4 (d of symmetric multiplets separated by ca. 130 Hz, Int = 1), 27.62 (d of d of d, *J*_{Pt-P} = 3115 Hz, *J*_{P-P} = 279 Hz, *J*_{P-P} = 38 Hz, *J*_{P-P} = 13 Hz, Int = 1), 19.24 (complex multiplet, Int = 1), 17.55 (d of d, *J*_{Pt-P} = 3457 Hz, *J*_{P-P} = 170 Hz, *J*_{P-P} = 13 Hz, Int = 1). IR (KBr disk): ν(py CN) = 1596 cm⁻¹; absorptions due to BF₄⁻ (1080 cm⁻¹ br). Anal. Calcd for C₇₈H₆₆B₂F₈N₂O₃PtRh: C, 56.51; H, 4.01; N, 1.69; P, 9.34. Found: C, 56.44; H, 4.13; N, 1.78; P, 9.51.

[RhAg(PNP)₂](BF₄)NO₃ (2). A methylene chloride solution of Ag-(PPh₃)NO₃ (158.0 mg, 0.366 mmol) was added to a stirring solution of [Rh(PNP)₂](BF₄)₂ (202.0 mg, 0.182 mmol) in methylene chloride. The yellow solution immediately darkened upon addition of Ag(PPh₃)NO₃. The reaction was stirred in the dark for several hours. Precipitation with diethyl ether gave a yellow product, which was collected by filtration and washed with diethyl ether; yield 81%. The product can be obtained as yellow-orange microcrystals by slow solvent diffusion using a methylene chloride/diethyl ether solvent system. ³¹P{¹H} NMR (CH₂Cl₂): δ 53.84 (d of d of d, *J*_{Rh-P} = 143 Hz, *J*_{P-P} = 50 and 37 Hz, Int = 1), 25.66 (d of overlapping d of d), *J*_{109Ag-31P} = 543 Hz, *J*_{107Ag-31P} = 468 Hz, *J*_{P-P} = 50 and 37 Hz, Int = 1). IR: ν(py CN) = 1598 cm⁻¹; absorptions due to BF₄⁻ (1090 cm⁻¹, br) and NO₃⁻ (1310 cm⁻¹ br sh). Anal. Calcd for C₆₀H₅₀BF₄N₃O₃P₄RhAg: C, 56.19; H, 3.93; N, 3.28. Found: C, 56.01; H, 4.18; N, 3.35.

[RhAu(PNP)₂(CO)₂](BF₄)NO₃ (3) was prepared by the reaction of [RhAu(PNP)₂](BF₄)(NO₃) (73.0 mg, 0.0532 mmol) with carbon monoxide in methylene chloride solution. Carbon monoxide was allowed to bubble through the reaction solution for several hours during which time the initial orange solution darkened to a red-orange. The product was precipitated with diethyl ether, collected by filtration, and washed with diethyl ether. Red crystals were obtained by solvent diffusion from methylene chloride and diethyl ether; yield 67%. ³¹P{¹H} NMR (CH₂Cl₂): δ 51.99 (d of 5-line multiplets separated by ca. 140 Hz, Int = 1), 49.93 (5-line multiplet, Int = 1). IR (CH₂Cl₂ solution): ν(CO) = 2015, 1998 cm⁻¹; ν(py CN) = 1601, 1581 cm⁻¹; absorptions due to BF₄⁻ (1090 cm⁻¹ br) and NO₃⁻ (1335 cm⁻¹ br sh). Anal. Calcd for C₆₂H₅₀BF₄N₃O₃P₄RhAu: C, 52.16; H, 3.53; N, 2.94. Found: C, 52.50; H, 3.83; N, 2.89.

[RhAu(PNP)₂Cl](BF₄) (4). HCl (g) was bubbled through a methylene chloride solution containing [RhAu(PNP)₂](BF₄)(NO₃) (109.0 mg, 0.0795 mmol). The orange reaction solution immediately turned yellow upon exposure to the gas. The solution was purged immediately with N₂. The product was precipitated with diethyl ether, collected by filtration, and washed with diethyl ether. Yellow-orange crystals were obtained by solvent diffusion from methylene chloride and heptane; yield 66%. ³¹P{¹H} NMR (CH₂Cl₂): δ 68.89 (d of symmetric 6-line multiplets separated by ca. 171 Hz, Int = 1), 42.82 (symmetric 6-line multiplet, Int = 1). IR (CsI disk): ν(py CN) = 1608 cm⁻¹; absorption due to BF₄⁻ (1084 cm⁻¹ br). Anal. Calcd for C₆₀H₅₀BClF₄N₂P₄RhAu: C, 53.57; H, 3.75; N, 2.08; Cl, 2.64. Found: C, 53.68; H, 3.77; N, 2.13; Cl, 2.84.

[RhAu(PNP)₂Br](BF₄) (5). A 1.5-equiv amount of hydrobromic acid (48%) was added by microsyringe to a stirring methylene chloride solution of [RhAu(PNP)₂](BF₄)(NO₃) (90.0 mg, 0.0686 mmol). After approximately 10 min of stirring, the initial orange reaction solution had become yellow-orange. Precipitation with diethyl ether gave an orange product, which was collected by filtration and washed with diethyl ether. Light orange crystals were obtained by solvent diffusion using methylene chloride and heptane; yield 62%. ³¹P{¹H} NMR (CH₂Cl₂): δ 68.34 (d of symmetric 6-line multiplets separated by ca. 170 Hz, Int = 1), 43.33 (symmetric 6-line multiplet, Int = 1). IR (CsI disk): ν(py CN) = 1605 cm⁻¹; absorption due to BF₄⁻ (1085 cm⁻¹ br). Anal. Calcd for C₆₀H₅₀BBR_{3.5}F₄N₂P₄RhAu ([RhAu(PNP)₂Br](BF₄)·2.5HBr): C, 45.26; H, 3.32; N, 1.76; Br, 17.57. Found: C, 45.18; H, 3.49; N, 1.95; Br, 17.33.³⁹

Table I. Summary of Crystal Data and Intensity Collection for 1

Crystal Parameters	
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
cell params	
<i>a</i> , Å	15.921 (9)
<i>b</i> , Å	16.128 (3)
<i>c</i> , Å	33.326 (9)
β, deg	101.44 (2)
<i>V</i> , Å ³	8387 (9)
<i>Z</i>	4
calcd density, g cm ⁻³	1.439
temp, °C	25
abs coeff, cm ⁻¹	20.9
max, min, avg transmission factors	1.00, 0.88, 0.94
formula	C ₈₃ H ₇₈ B ₂ Cl ₂ F ₈ N ₂ O ₃ PtRh
fw	1816.94
cryst dims, mm ³	0.25 × 0.20 × 0.18
Measurement of Intensity Data	
diffractometer	CAD 4
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromatized
scan type; range (2θ), deg	ω scan; 0–44
no. of unique reflns measd (quadrant)	6307 (+ <i>h</i> , + <i>k</i> , ± <i>l</i>)
obsd reflns ^a	5500 [<i>F</i> ₀ ² ≥ 3σ(<i>F</i> ₀ ²)]
refinement by full-matrix least squares	
no. of params	507
<i>R</i> ^b	0.063
<i>R</i> _w ^b	0.077
GOF ^b	2.20
<i>p</i> ^a	0.04

^a The intensity data were processed as described in: *CAD4 and SDP User's Manual*; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = [K/(NPI)](C - 2B)$, where $K = 20.1166 \times$ attenuator factor, $NPI =$ ratio of fastest possible scan rate to scan rate for the measurement, $C =$ total count, and $B =$ total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = [K/(NPI)]^2[C + 4B + (pI)^2]$ where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_0 is given by $F_0 = (I/Lp)^{1/2}$, where $Lp =$ Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_0)$ by $\sigma(F_0) = 1/2[\sigma(I)/I]F_0$. ^b The function minimized was $\sum w(|F_{ol}| - |F_{cl}|)^2$, where $w = 1/[\sigma(F_0)]^2$. The unweighted and weighted residuals are defined as $R = (\sum ||F_{ol}| - |F_{cl}||) / \sum |F_{ol}|$ and $R_w = [(\sum w(|F_{ol}| - |F_{cl}|)^2) / (\sum w|F_{ol}|^2)]^{1/2}$. The error in an observation of unit weight (GOF) is $[\sum w(|F_{ol}| - |F_{cl}|)^2 / (NO - NV)]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

X-ray Structure Determination

Collection and Reduction of X-ray Data. A summary of crystal and intensity collection data for 1 is presented in Table I. Crystals of [RhPt(μ-PPh₃)(μ-PNP)(PN)(PPh₃)](BF₄)₂ were found to lose solvent upon removal from CH₂Cl₂–(C₂H₅)₂O solution. This solvent loss was rapid and caused single crystals to fracture. Therefore, the crystal used for data collection was mounted inside a 0.2-mm capillary that was half-filled with solvent. The crystal was subsequently found to contain one CH₂Cl₂ and one (C₂H₅)₂O solvate molecule in the asymmetric unit. The crystal was found to belong to the monoclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs and by a Delaunay reduction calculation.⁴⁰ The space group *P*2₁/*c* (No. 14) was chosen on the basis of systematic absences observed during data collection and was verified by successful solution and refinement (vide infra). The unit cell dimensions were determined by least-squares refinement of the angular settings of 25 peaks centered on

(39) Samples of 5 were contaminated with HBr. Analyses of this type have been observed previously by James and Mahajan.⁶²

(40) All calculations were carried out on PDP 8A and 11/34 computers with use of the Enraf-Nonius CAD 4-SDP-PLUS programs. This crystallographic computing package is described by: Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H.; Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. Frenz, B. A. In *Structure Determination Package and SDP-PLUS User's Guide*; B. A. Frenz & Associates, Inc.: College Station, TX, 1982.

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Table III. Distances and Angles in the Coordination Core of [PtRh(μ -PPh₂)(μ -PNP)(PN)(PPh₃)](BF₄)₂

Distances, Å			
Rh-Pt	2.708 (1)	Pt-P1	2.324 (3)
Rh-P2	2.276 (3)	Pt-P2	2.287 (3)
Rh-P4	2.381 (3)	Pt-P3	2.315 (3)
Rh-P5	2.282 (3)	P2-C1C	1.78 (1)
Rh-N1	2.19 (1)	P2-C1D	1.82 (1)
Rh-N2	2.12 (1)	P1-C16	1.93 (1)
P1-C1A	1.86 (1)	P5-C16	1.84 (1)
P1-C1B	1.84 (1)	P4-C26	1.82 (1)
P3-C1E	1.83 (1)	P4-C1H	1.79 (1)
P3-C1F	1.77 (1)	P4-C1I	1.80 (1)
P3-C1G	1.84 (1)	P5-C1J	1.82 (1)
		P5-C1K	1.80 (1)
Angles, deg			
Pt-Rh-P2	53.8 (1)	Rh-Pt-P1	89.7 (1)
Rh-Pt-P2	53.4 (1)	Rh-Pt-P3	158.5 (1)
Pt-P2-Rh	73.8 (1)	P2-Rh-P4	110.4 (1)
Pt-Rh-P4	163.4 (1)	P2-Rh-P5	102.5 (1)
Pt-Rh-P5	84.2 (1)	P2-Rh-N1	151.4 (3)
Pt-Rh-N1	98.7 (2)	P2-Rh-N2	86.6 (3)
Pt-Rh-N2	93.7 (3)	P4-Rh-P5	105.9 (1)
		P4-Rh-N1	96.1 (3)
P5-Rh-N1	79.4 (3)	P4-Rh-N2	79.4 (3)
P5-Rh-N2	166.7 (3)	Rh-P4-C26	99.0 (4)
N1-Rh-N2	88.0 (4)	Rh-P5-C16	96.5 (4)
Rh-N1-C11	122.2 (8)	Pt-P1-C16	107.0 (4)
Rh-N1-C15	117.8 (8)	Pt-P1-C1A	124.4 (4)
Rh-N2-C21	119.4 (8)	Pt-P1-C1B	116.1 (4)
Rh-N2-C25	121.1 (8)	Pt-P3-C1E	116.5 (4)
Rh-P2-C1C	123.2 (5)	Pt-P3-C1F	118.3 (5)
Rh-P2-C1D	118.0 (4)	Pt-P3-C1G	109.5 (4)
Pt-P2-C1C	117.0 (4)	Rh-P4-C1H	116.0 (4)
Pt-P2-C1D	126.3 (4)	Rh-P4-C1I	127.8 (4)
P1-C16-C15	106.6 (8)	Rh-P5-C1J	130.7 (4)
P5-C16-C15	108.0 (8)	Rh-P5-C1K	115.2 (4)
P4-C26-C25	107.9 (9)	P1-C16-P5	108.7 (6)

which symmetrically bridges the two metal atoms. The Pt-Rh-P2 angle is constrained and small (53.8 (1)°) while the P2-Rh-P4 and P2-Rh-P5 angles are opened to 110.4 (1) and 102.5 (1)°, respectively.

Around platinum the PPh₃ group is positioned ca. trans to the rhodium atom (Rh-Pt-P3 = 158.5 (1)°). The Rh-Pt-P1 angle is 89.7 (1)°, close to the idealized value of 90°. The significant distortion from square planar is caused by the bridging PPh₂ group, the Rh-Pt-P2 angle (53.4 (1)°) and the P1-Pt-P2 angle (137.3 (1)°) deviating significantly from their idealized values of 90 and 180°. As a result, the P2-Pt-P3 and P1-Pt-P3 angles are opened to 111.3 (1) and 109.5 (1)°, respectively.

The Rh-P distances that are trans to nitrogen atoms (average 2.279 (3) Å) are somewhat larger than similar Rh-P distances in [RhAu(μ -PNP)₂](BF₄)(NO₃) (average 2.217 (6) Å)³⁵ and in [Rh₂(CO)(μ -PNP)₂](BPh₄)₂ (average 2.233 (4) Å).³⁶ The Rh-N bond distances in **1** (average 2.16 (1) Å) are similar to values found in [RhAu(PNP)₂](BF₄)(NO₃) (average 2.17 (2) Å)³⁵ and in [Rh₂(CO)(μ -PNP)₂](BPh₄)₂ (average 2.15 (1) Å).³⁶ The Rh-P distance of the phosphorus atom trans to platinum (2.381 (3) Å) is elongated as a result of being ca. trans to a metal-metal bond (vide infra). The Pt-P distances (average 2.309 (3) Å) are normal and similar to values found in mixed Rh-Pt, W-Pt, and Mo-Pt phosphine dimers.^{4,8,22}

The Rh-Pt distance in **1** is 2.708 (1) Å and is indicative of the presence of a Rh-Pt bond. This distance compares well with those in the complexes *trans*-Rh(CO)Cl₂(μ -Ph₂AsCH₂PPh₂)₂-*trans*-PtCl (2.692 (1) Å) and *trans*-Rh(CO)I₂(μ -Ph₂AsCH₂PPh₂)₂-*trans*-PtI (2.737 (3) Å), which possess Rh-Pt bonds.²² In comparison, the metal-metal separations in *trans*-Rh(CO)Cl(μ -Ph₂AsCH₂PPh₂)₂-*cis*-PtCl₂³ and [ClPt(μ - σ - π -C=CMe)(μ -dppm)₂Rh(CO)](PF₆),¹¹ in which metal-metal bonds are absent, are 3.043 (1) and 3.066 (2) Å, respectively. In the bis(diphenylphosphido)-bridged dirhodium complex (Et₃P)₂Rh(μ -PPh₂)₂Rh(cod), which contains a Rh-Rh bond, the metal-metal

separation is 2.752 (1) Å.⁴⁷ The ³¹P NMR chemical shifts of the phosphido resonances also give direct evidence regarding the presence or absence of a metal-metal bond.^{47,48} A large downfield shift is characteristic of the three-membered ring created by a phosphido group that bridges a strong metal-metal bond. In compounds that do not contain M-M bonds in solution, the phosphido ligands have been found to display resonances that are significantly shifted upfield from that of the standard (85% H₃PO₄). The μ -PPh₂ resonance in **1** was observed at δ 157.2, in a region similar to that for the complex (Et₃P)₂Rh(μ -PPh₂)₂Rh(cod) (δ 217.0), in which a Rh-Rh bond is present, and thus is indicative of a strong Rh-Pt bond.

The ³¹P{¹H} NMR spectrum observed for **1** in CH₂Cl₂ solution (shown in Figure 1) is consistent with its solid-state structure. The resonance at δ 157.2 can be assigned to P2, the bridging phosphido group, and showed coupling to both ¹⁹⁵Pt (33.7% abundant, $J_{\text{Pt-P2}} = 3139$ Hz) and ¹⁰³Rh (100% abundant, $J_{\text{Rh-P2}} = 129$ Hz), as well as a large trans P-P coupling to P1 ($J_{\text{P2-P1}} = 279$ Hz). The resonance centered at δ 27.62 can be assigned to P1 and showed Pt-P spin-spin coupling ($J_{\text{Pt-P1}} = 3115$ Hz) and P-P coupling to trans P2 ($J_{\text{P1-P2}} = 279$ Hz), to cis P3 ($J_{\text{P1-P3}} = 13$ Hz), and to P5 ($J_{\text{P1-P5}} = 38$ Hz). The resonance centered at δ 17.55 can be assigned to P3 and showed Pt-P coupling ($J_{\text{Pt-P3}} = 3457$ Hz) and P-P coupling to cis P1 ($J_{\text{P3-P1}} = 13$ Hz) and to P4, which is trans across the cis Pt-Rh bond ($J_{\text{P3-P4}} = 170$ Hz). The three bond P-Rh-Pt-P coupling constant seems large but is in the range (160–180 Hz) generally observed for this approximately linear stereochemistry.^{49,50} The resonance centered at δ 29.4 is assigned to P5 with $J_{\text{Rh-P5}} \approx 130$ Hz and $J_{\text{P5-P1}} \approx 30$ Hz and the resonance centered at δ 19.24 ppm (multiplet) can be assigned to P4. These latter two resonances are partially obscured by the other aforementioned phosphorus signals so that coupling was not well resolved and accurate measurement of individual coupling constants was not possible. The multiplet pattern due to P4 is suggestive that $J_{\text{Rh-P4}}$ and $J_{\text{P4-P3}}$ are of similar magnitude.

The PPh₂ and PN groups in **1** presumably arise from P-C bond activation and cleavage in one of the PNP ligands of the [Rh-(PNP)₂](BF₄) starting reagent. The PNP ligand has previously been found to be susceptible to phosphorus-carbon bond cleavage at elevated temperatures.^{45,51} The complex [Rh(PN)(CO)Cl], for example, has been synthesized as the thermal decomposition product of the PNP ligand in the reaction of [Rh(CO)₂Cl]₂⁻ with PNP ligand in refluxing 2-methoxyethanol/toluene solution.⁴⁵ In addition, Pt(PPh₃)₂(C₂H₄) has been found to have a propensity for transition-metal-mediated P-C bond cleavage.⁵² Glockling and co-workers found that passing N₂ through an *o*-xylene solution of Pt(PPh₃)₂(C₂H₄) at 25 °C for 24 h resulted in the formation of [Pt(PPh₂)(C₆H₄PPh₂)₂], a bis(diphenylphosphido)-bridged complex.^{52,53} The reaction was suggested to proceed through an ortho-metalated hydride intermediate. The reaction of Pt(PPh₃)₂(C₂H₄) with 5,6-dimethyl-2,1,3-benzothiadiazole was found by Vrieze et al. to result in the formation of the phosphido-bridged complex [Pt₂S(N(6- μ -N-4,5-Me₂C₆H₂))(μ -PPh₂)(PPh₃)Ph].^{52,54} The byproduct formed in the synthesis of **1**, which was isolated from the reaction filtrate (a methylene chloride and diethyl ether mixture) as an orange crystalline product, is presumably a neutral Rh-phosphine complex. The ³¹P NMR of this complex consisted of two symmetric multiplets centered at δ -2.2 and -21.4. The identity of this compound has not been determined. Preliminary reactions have shown **1** to be unreactive toward H₂ (1 atm) and CO.

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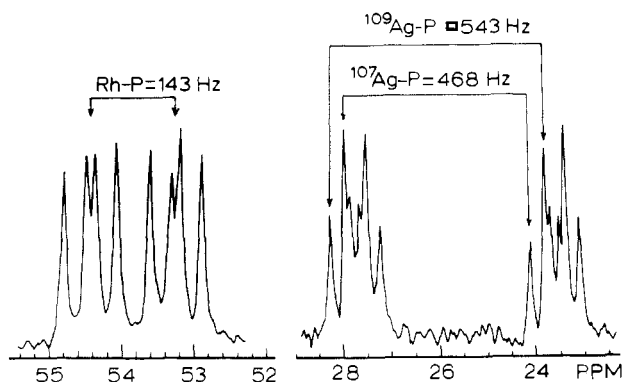
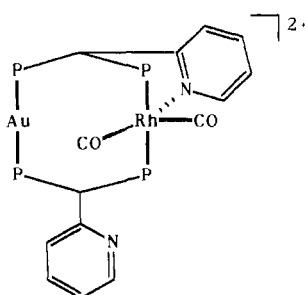


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{RhAg}(\text{PNP})_2]^{2+}$ (cation of **2**) recorded at ambient temperature with CH_2Cl_2 as solvent. No other resonances were observed in the spectrum.

$[\text{RhAg}(\mu\text{-PNP})_2](\text{BF}_4)(\text{NO}_3)$ (2**).** The reaction of $[\text{Rh}(\text{PNP})_2]\text{BF}_4$ with 2 equiv of $\text{Ag}(\text{PPh}_3)\text{NO}_3$ in CH_2Cl_2 solution resulted in the formation of the heterobimetallic complex $[\text{RhAg}(\text{PNP})_2](\text{BF}_4)(\text{NO}_3)$ (**2**). **2** was characterized by IR and ^{31}P NMR spectroscopy. The byproduct of the reaction was $\text{Ag}(\text{PPh}_3)_2\text{NO}_3$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** (CH_2Cl_2) consisted of two multiplets of equal intensity (Figure 3). The downfield resonance (δ 53.84) is assigned to the two equivalent phosphorus atoms on the Rh center and is similar to that observed for $[\text{RhAu}(\mu\text{-PNP})_2](\text{BF}_4)(\text{NO}_3)$.³⁵ The coupling constants are $J_{\text{Rh-P}} = 143$ Hz, $J_{\text{P-P}} = 50$ and 37 Hz and can be compared with values of 162, 38, and 28 Hz, respectively, for $[\text{RhAu}(\mu\text{-PNP})_2](\text{BF}_4)(\text{NO}_3)$.³⁵ The upfield resonance at δ 25.66 is complicated and is a result of overlapping doublets of four-line multiplets (d of d, $J_{\text{P-P}} = 50$ and 37 Hz) that arise from $^{109}\text{Ag}\text{-}^{31}\text{P}$ and $^{107}\text{Ag}\text{-}^{31}\text{P}$ spin-spin couplings of 543 and 468 Hz, respectively. The magnitude of the Ag-P coupling constants is consistent with those that have been observed previously for linear AgL_2^+ complexes where L is a phosphine ligand.⁵⁵ The ratio $J^{109\text{Ag}\text{-}^{31}\text{P}}/J^{107\text{Ag}\text{-}^{31}\text{P}}$ is 1.16 and is close to the gyromagnetic ratio, $\mu^{109\text{Ag}}/\mu^{107\text{Ag}}$, of 1.15. The IR spectrum showed a $\nu(\text{py CN})$ frequency of 1598 cm^{-1} , which is consistent with bound pyridyl nitrogen atoms. The structure of **2** is therefore analogous to that of $[\text{RhAu}(\mu\text{-PNP})_2](\text{BF}_4)(\text{NO}_3)$ ³⁵ with a trans,cis bis(diphosphine)-bridged stereochemistry. The phosphorus atoms are arranged cis around the rhodium and trans around the silver atom. The coordination geometry about the silver is T-shaped (AgP_2Rh) and that about the rhodium atom is square pyramidal ($\text{RhP}_2\text{N}_2\text{Ag}$) with the Ag atom occupying the axial position.

$[\text{RhAu}(\mu\text{-PNP})_2(\text{CO})_2](\text{BF}_4)(\text{NO}_3)$ (3**).** The reaction of $[\text{RhAu}(\text{PNP})_2](\text{BF}_4)(\text{NO}_3)$ ³⁵ with carbon monoxide at 1 atm and 25 °C resulted in the irreversible formation of **3** in good yield.⁵⁶

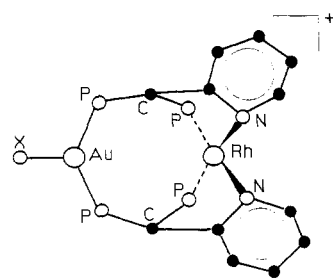


dication of **3**

Complex **3** has a deep red color and has been characterized with use of IR and ^{31}P NMR spectroscopy. The IR spectrum (CH_2Cl_2

solution) of **3** showed two terminal metal carbonyl stretches of equal intensity, $\nu(\text{CO}) = 2015$ and 1998 cm^{-1} , and two pyridyl C-N stretches, $\nu(\text{py CN}) = 1601$ and 1581 cm^{-1} . The py CN stretching frequency generally provides direct evidence regarding coordination of the pyridyl nitrogen atom. Free PNP has a pyridyl C-N stretch at 1580 cm^{-1} , and upon coordination the frequency is increased to ca. 1600 cm^{-1} or higher.^{35,36,44-46} The values observed for **3** indicated that one pyridyl nitrogen is coordinated and one is free or dangling. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** (CH_2Cl_2) consisted of two complex sets of multiplets of equal intensity centered at δ 51.99 and 49.93. The downfield resonance was a doublet of multiplets due to the presence of Rh-P spin-spin coupling ($J_{\text{Rh-P}} = 140$ Hz). Very similar ^{31}P NMR spectra have been observed previously for AA'BB' spin systems that contain four coplanar phosphorus atoms,^{57,58} for example in $\text{Pd}_2(\text{dppm})_2(\mu\text{-HC}_2\text{[CO}_2\text{H]Cl}_2)$.⁵⁷ These data are consistent with a heterobimetallic dimer that contains two bridging PNP ligands, two terminal CO ligands, and one coordinated and one dangling pyridyl nitrogen, as depicted in the drawing of **3**. However, the absence of large trans P-P couplings of the order of 300 Hz suggests that the molecule may be fluxional with the pyridyl groups rapidly exchanging places.

$[\text{RhAu}(\mu\text{-PNP})_2\text{X}](\text{BF}_4)$ (4** (X = Cl), **5** (X = Br)).** The reaction of $[\text{RhAu}(\text{PNP})_2](\text{BF}_4)(\text{NO}_3)$ with HX, where X = Cl or Br, resulted in the formation of $[\text{RhAu}(\text{PNP})_2\text{Cl}](\text{BF}_4)$ (**4**) and $[\text{RhAu}(\text{PNP})_2\text{Br}](\text{BF}_4)$ (**5**) in good yield. Both complexes have been characterized with use of IR and ^1H and ^{31}P NMR spectroscopy. The IR spectra (CsI disk) of **4** and **5** each showed one pyridyl C-N stretch at $\nu(\text{py CN}) = 1608$ and 1605 cm^{-1} , respectively, consistent with coordinated nitrogen atoms. No M-X stretches were observed due to lack of intensity. ^1H NMR spectra of **4** and **5** (CD_2Cl_2) indicated that no metal hydrides were present. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CH_2Cl_2) of **4** consisted of a doublet of symmetric multiplets (δ 68.89, $J_{\text{Rh-P}} = 171$ Hz) and a symmetric multiplet (δ 42.82) of equal intensity. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CH_2Cl_2) of **5** was very similar to that observed for **4** and consisted of two sets of complex multiplets of equal intensity at δ 68.34 ($J_{\text{Rh-P}} = 170$ Hz) and 43.33. Very similar ^{31}P NMR spectra have been observed previously for heterobimetallic compounds containing cis,trans phosphine-bridged stereochemistries^{10,12,13,16} and are very similar to the ^{31}P NMR spectrum observed for $[\text{RhAu}(\text{PNP})_2](\text{BF}_4)(\text{NO}_3)$.³⁵ These data are consistent with complexes that contain a similar PNP-bridged stereochemistry with the geometry about Rh being square planar (RhP_2N_2) with cis phosphorus and cis pyridyl nitrogen atoms and trigonal about Au (AuP_2X), where X = Cl or Br, as depicted in the drawing. The assignment of



cation of **4** (X = Cl), **5** (X = Br)

the halogen ligand bonded to Au is consistent with the fact that the ^{31}P NMR resonance due to the phosphorus atoms on Au is shifted greatly upfield from that of the starting $[\text{RhAu}(\text{PNP})_2](\text{BF}_4)(\text{NO}_3)$ complex ($\Delta\delta \approx 17$ ppm). Trigonal Au stereochemistries are not without precedence. The complex $[\text{Au}_2\text{Cl}_2(\mu\text{-dppm})_2]$ has been characterized by Schmidbaur⁵⁹ through X-ray analysis and was found to contain distorted trigonal-planar gold centers. Trigonal $\text{Au}(\text{PPh}_3)_2\text{Cl}$ and $\text{Au}(\text{PPh}_3)_3^+$ compounds

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(56) ^{31}P NMR spectra of reaction solutions of $[\text{RhAu}(\text{PNP})_2(\text{CO})_2](\text{BF}_4)(\text{NO}_3)$ (**3**) after 12 h of purging with N_2 showed only the presence of **3**; no $[\text{RhAu}(\text{PNP})_2]^{2+}$ was present.

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have also been well characterized.^{60,61} Conductivity measurements support the formulation of complexes **4** and **5** as 1:1 electrolytes ($\Delta_M(\mathbf{4}) = 57 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, $\Delta_M(\mathbf{5}) = 47 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). Molar conductivity values similar to these have been observed previously for other 1:1 electrolytes of this type.⁶²

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Supplementary Material Available: An ORTEP drawing of **1** and tables of positional parameters for phenyl group carbon atoms, general temperature factor expressions, calculated positional parameters for the hydrogen atoms, distances and angles within the ligands and solvate molecules, torsional angles, and least-squares planes for **1** (15 pages); a listing of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

Contribution from the Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Mono(aryl)cobalt(II) Compounds Stabilized by Bis Ortho Chelation

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The reaction of $\text{Li}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]_2$ with $\text{Co}^{\text{II}}\text{X}_2\text{L}_2$ (L = py, PPh_3 , X = Cl, Br, I; L = PEt_3 , X = Cl) yields the air-sensitive compounds $\text{Co}^{\text{II}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]\text{X}(\text{L})$. From elemental analyses and UV and ESR spectral data it was concluded that the complexes are five-coordinate and have a square-pyramidal structure with an apical ligand L.

Introduction

The relative scarcity of organometallic compounds among the transition metals having σ metal-carbon bonds is generally recognized as a combined result of thermodynamic and kinetic instability of such complexes.¹ Reductive elimination or β -hydrogen elimination of organic groups often occurs at already low temperatures, whereas empty low-lying orbitals and the polarity of the M-C bond favor an easy chemical attack. Some of these problems have been overcome in derivatives containing an alkyl group lacking β -hydrogens or having bulky substituents. It was also found that internal coordination may have a considerable stabilizing effect.²

Previously we used the terdentate anionic ligand $[o,o'-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]$ to prepare a series of stable compounds in which the ligand is bonded via at least a M-C interaction. Compounds with the same set of ligands but as monodentates are not known and probably not stable. The metals involved so far are of d^5 (Fe(III)), d^6 (Rh(III), Pt(IV)), d^7 (Ni(III)), d^8 (Ni(II), Pd(II), Pt(II), Rh(I), Ir(I)), and d^{10} (Cu(I), Hg(II), Tl(III), Sn(IV)) electronic configurations.^{3-5,7,18}

The recently reported paramagnetic congeners $\text{Ni}^{\text{III}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]\text{X}_2$ with X = Cl, Br, I^4 and $\text{Fe}^{\text{III}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]\text{Cl}_2^5$ were found to have square-pyramidal arrangements. ESR studies on the Ni(III) complexes have been a valuable tool in elucidating their electronic structure. The results were consistent with a low-spin d^7 state of Ni(III) in which the unpaired electron is located in the axial d_{z^2} orbital. As Co(II) is isoelectronic with Ni(III), the related $\text{Co}^{\text{II}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]$ compounds may well have similar structural features and in this way are of dual interest in understanding the bonding in these compounds.

Therefore, a series of paramagnetic cobalt complexes having the general formula $\text{Co}^{\text{II}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]\text{X}(\text{L})$, where X = Cl, Br, I and L = pyridine, PPh_3 , PEt_3 , were synthesized and spectroscopically characterized.

Experimental Section

All manipulations were performed under an atmosphere of nitrogen (99.999% pure; purchased from Hoekloos) with use of Schlenk techniques. Solvents were carefully dried and distilled prior to use. Cobalt

salts of the type CoX_2L_2 were prepared according to literature procedures.^{6,10} Elemental analyses were carried out at the Institute for Applied Chemistry TNO, Zeist, The Netherlands. ESR spectra were run on a Bruker ER200D-MR X-band spectrometer. UV spectra were recorded on a Cary 14 spectrophotometer.

Synthesis of $\text{Co}^{\text{II}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]\text{Cl}(\text{py})$. A solution of $\text{Li}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]_2$ in diethyl ether (10 mL) was prepared from $o,o'-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\text{Br}$ (1.45 g, 5.4 mmol) and Li.⁷ The solvent was removed in vacuo. The aryllithium compound was extracted with benzene (20 mL). This extract was added at room temperature to a blue suspension of $\text{CoCl}_2(\text{py})_2$ (1.11 g, 3.9 mmol) in benzene (30 mL). This resulted in the formation of an intensely orange solution within a few minutes. The mixture was stirred for another 2 h and filtered. The solvent was removed in vacuo. The orange-brown solid residue was washed with pentane (4×10 mL); yield 1.00 g (2.75 mmol, 70%). The complexes $\text{Co}^{\text{II}}[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]\text{X}(\text{L})$ were prepared in an analogous manner from the CoX_2L_2 complexes and $\text{Li}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-o,o'}]_2$. Yields are given in parentheses: L = py, X = Br (14%), I (70%); L = PPh_3 , X = Cl (27%), Br (55%), I (70%); L = PEt_3 , X = Cl (50%).

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