

Thermogravimetric analyses of $[\text{Cr}(\text{THF})_3\text{X}_3]$ and $\text{K}[\text{Cr}(\text{THF})_2(\text{NCS})_4]^{15}$ in dry argon showed weight losses corresponding to the loss of the THF.

$[\text{Cr}(\text{THF})_3\text{Cl}_3]$ and $[\text{Cr}(\text{THF})_3\text{I}_3]$ lose three molecules of THF in one step over the temperature ranges 150–200 and 80–130 °C, respectively. In the case of $[\text{Cr}(\text{THF})_3\text{Br}_3]$, one molecule of THF is lost at 90–120 °C and two molecules of THF are lost at 160–200 °C. For $\text{K}[\text{Cr}(\text{THF})_2(\text{NCS})_4]$ the weight loss occurs in two ill-defined steps at ca. 150 and 350 °C.

We have used the THF adducts here as starting materials for the synthesis of chromium(III) complexes of a wide range of neutral ligands, details of which will be reported elsewhere. As examples of their use may be cited the preparations of $[\text{Cr}(\sigma\text{-C}_6\text{H}_4(\text{AsMe}_2)_2(\text{NCS})_4)]^{-9}$ from $\text{K}[\text{Cr}(\text{THF})_2(\text{NCS})_4]$, of $[n\text{-Bu}_4\text{N}][\text{Cr}(\text{L-L})\text{X}_4]$ (L-L = $\sigma\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$, *cis*- $\text{Ph}_2\text{AsCH}=\text{CHAsPh}_2$) from $[\text{Cr}(\text{THF})_2\text{X}_4]^{-16}$ of $[\text{Cr}(\text{L-L-L})\text{X}_3]$ (L-L-L = $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$, $\text{CH}_3\text{C}(\text{CH}_2\text{AsMe}_2)_3$) from $[\text{Cr}(\text{THF})_3\text{X}_3]^{17}$ and of $[\text{Cr}(\text{L-L-L})_2](\text{BF}_4)_3$ from $[\text{Cr}(\text{THF})_6]^{3+}$.

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Registry No. $[\text{Cr}(\text{THF})_3\text{Cl}_3]$, 10170-68-0; $[\text{Cr}(\text{THF})_3\text{Br}_3]$, 86286-48-8; $[\text{Cr}(\text{THF})_3\text{I}_3]$, 86217-22-3; $[n\text{-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{Cl}_4]$, 86217-24-5; $[n\text{-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{Br}_4]$, 86217-26-7; $[n\text{-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{I}_4]$, 86217-28-9; $\text{K}[\text{Cr}(\text{THF})_2(\text{NCS})_4]$, 86217-29-0; $[\text{Cr}(\text{THF})_6](\text{BF}_4)_3$, 86217-31-4.

(15) Moisture sensitivity prevented a similar study of $[n\text{-Bu}_4\text{N}][\text{Cr}(\text{THF})_2\text{X}_4]$ (X = halide). $[\text{Cr}(\text{THF})_3\text{I}_3]$ continued to lose weight on further heating, indicating loss of I_2 .

(16) Hale, A. L.; Levason, W.; McCullough, F. P., Jr. *Inorg. Chem.* **1982**, *21*, 3570.

(17) Hale, A. L., unpublished work.

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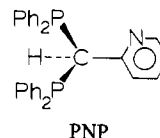
Synthesis and X-ray Structural Characterization of a Rhodium(I) Complex of a Pyridyldiphosphine (PNP) Tridentate Ligand

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There has been much recent interest in the use of cationic rhodium(I) complexes that contain chelating diphosphine ligands for catalytic hydrogenation¹⁻⁴ and decarbonylation⁵⁻⁷ reactions. Results from our laboratory on the catalytic decarbonylation of aldehydes using $[\text{Rh}(\text{diphosphine})_2]^+$ complexes strongly implicate a mechanism that involves an initial Rh–P bond rupture that leads to a catalytically active three-coordinate complex.^{7,8} In order to test this possibility, a study that makes use of complexes of chelating phosphorus–nitrogen (PN) donor ligands was initiated. With such ligands the N donor end is known to be labile.⁹ As part of this general investigation a PNP ligand was synthesized.

Metallo compounds of this potentially tridentate ligand should serve as reasonable models for catalytic decarbonylation



intermediates, and they are of interest in their own right because bridged binuclear complexes of the well-known face-to-face and A-frame type are likely.¹⁰⁻¹⁸ The ligand also offers a choice of P–P or P–N bidentate or PNP tridentate coordination with four- and/or five-membered chelate rings. In this paper we report the reaction of PNP with a solution of $[(\text{nbd})\text{RhCl}]_2$ (nbd = norbornadiene) and AgBF_4 and the complete characterization of the resulting new complex $[\text{Rh}(\text{nbd})(\text{PNP})]\text{BF}_4$ (**1**). In addition, some preliminary results on the novel reaction chemistry of **1**, which yields bridged binuclear compounds, is discussed.

Experimental Section

Physical Measurements. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 120.5 MHz and at 25 °C on a Nicolet NT-300 spectrometer. The chemical shifts are reported in ppm relative to the external standard 85% H_3PO_4 with positive shifts downfield. IR spectra were recorded on a Beckman Model 4250 grating spectrometer using KBr disks.

Preparation of Compounds. $[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{CHC}_5\text{H}_4\text{N}$ (PNP) was prepared by the reaction of 1 mol of 2-picolone anion with 2 mol of chlorodiphenylphosphine. All manipulations were carried out under a purified atmosphere on a N_2 by using standard Schlenk techniques. The red 2-picolone anion is formed by the slow addition of *n*-butyllithium (31.5 mL of 2 M hexane solution; 0.063 mol) to a stirred solution of 2-picolone (6.2 mL, 0.063 mol) and tetramethylethylenediamine (12 mL, 0.080 mol) in 10 mL of dry thf at –78 °C. The suspension of 2-picolone anion is slowly added via a cannula tube to chlorodiphenylphosphine (22.6 mL, 0.126 mol) at 0 °C and with constant stirring. After the solution is stirred for 1 h, its volume is reduced by vacuum distillation, and upon addition of 10 mL of ethanol and 5 mL of distilled water a white globular precipitate forms. This mixture is heated to reflux to dissolve the solid, and after rapid filtration white crystals separate on cooling. The crystals are collected by filtration and washed respectively with hexane and distilled water until

- (1) Chan, A. S. C.; Pluth, J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952.
- (2) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.
- (3) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. In "Homogeneous Catalysis—II"; Forster, D., Roth, J. E., Eds.; American Chemical Society: Washington, DC, 1974; Adv. Chem. Ser. No. 132, p 274.
- (4) James, B. R.; Mahajan, D. *Can. J. Chem.* **1979**, *57*, 180.
- (5) Doughty, D. H.; Anderson, M. P.; Casalnuovo, A. L.; McGuiggan, M. F.; Tso, C. C.; Wang, H. H.; Pignolet, L. H. In "Catalytic Aspects of Metal Phosphine Complexes"; Alyea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, DC, 1982; Adv. Chem. Ser. No. 196, p 65.
- (6) Doughty, D. H.; Pignolet, L. H. *J. Am. Chem. Soc.* **1978**, *100*, 7083.
- (7) Doughty, D. H.; Pignolet, L. H. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, in press.
- (8) Anderson, M. P.; Pignolet, L. H., results to be submitted for publication.
- (9) Knebel, W. J.; Angelici, R. *J. Inorg. Chem.* **1974**, *13*, 632.
- (10) Balch, A. L. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, in press.
- (11) Balch, A. L. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, p 167.
- (12) Puddephatt, R. J. In "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, p 187.
- (13) Balch, A. L. In "Catalytic Aspects of Metal Phosphine Complexes"; Alyea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, DC, 1982; Adv. Chem. Ser. No. 196, p 243.
- (14) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733.
- (15) Cowie, M.; Dickson, R. S. *Inorg. Chem.* **1981**, *20*, 2682.
- (16) Mague, J. T.; Sanger, A. R. *Inorg. Chem.* **1979**, *18*, 2060.
- (17) Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543.
- (18) Maisonne, A.; Farr, J. P.; Olmstead, M. M.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 3961.

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Table I. Summary of Crystal Data and Intensity Collection

| Crystal Parameters | |
|-----------------------------------|--|
| cryst syst | monoclinic |
| space group | $P2_1/m$ (No. 11) |
| cell parameters | |
| a , Å | 9.639 (2) |
| b , Å | 15.334 (3) |
| c , Å | 11.333 (3) |
| β , deg | 98.89 (2) |
| V , Å ³ | 1655 (1) |
| Z | 2 |
| calcd density, g cm ⁻³ | 1.492 |
| temp, °C | 22 |
| abs coeff, cm ⁻¹ | 6.5 |
| formula | C ₃₇ H ₃₃ B ₁ F ₄ N ₁ P ₂ Rh |
| fw | 743.3 |
| cryst dimens, mm ³ | 0.2 × 0.3 × 0.15 |
| Measurement of Intensity Data | |
| diffractometer | CAD 4 |
| radiation | Mo K α ($\lambda = 0.71069$ Å); graphite monochromatized |
| scan range, 2θ , deg | 0–50 |
| unique reflns measd (quadrant) | 3031 (+ h , + k , $\pm l$) |
| obsd reflns ^a | 2428 [$F_o^2 \geq 1.0\sigma(F_o^2)$] |
| refinement | full-matrix least squares |
| no. of parameters | 233 |
| R^b | 0.052 |
| R_w^b | 0.066 |
| GOF ^b | 1.87 |
| p^a | 0.03 |

^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_o is given by $F_o = (I/Lp)^{1/2}$, where $Lp =$ product of Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = 1/2 [\sigma(I)/F_o]$. ^b The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]^2$. The unweighted and weighted residuals are defined as $R = (\sum |F_o| - |F_c|) / \sum |F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)^2) / (\sum w |F_o|^2)]^{1/2}$. The error in an observation of unit weight (GOF) is $[\sum w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

no chloride ion is detected in the wash and finally with cold ethanol. The white crystalline product is vacuum dried and stored under a purified atmosphere of N₂: yield 7.1 g (48% based on phosphine); mp 138–142 °C dec; ³¹P NMR (CH₂Cl₂) δ -4.5 (s); IR ν (py CN) 1580 cm⁻¹; MS m/e (M⁺) 461. Anal. Calcd for C₃₀H₂₅NP₂: C, 78.08; H, 5.46; N, 3.04. Found: C, 78.20; H, 5.61; N, 2.98. A similar procedure for the preparation of this ligand has been reported.¹⁹

[Rh(nbd)(PNP)]BF₄ (**1**) was obtained as yellow crystals by reaction of PNP ligand (0.409 g, 0.886 mmol) dissolved in 25 mL of toluene with the filtrate of the reaction of [(nbd)RhCl]₂²⁰ (0.200 g, 0.868 mmol) with AgBF₄ (0.177 g, 0.909 mmol) in acetone. Large yellow crystals were obtained by recrystallization of the solid product from CH₂Cl₂-diethyl ether solution: yield 70%; ³¹P NMR (CH₂Cl₂) δ 32.2 (d, $J_{Rh-P} = 96.5$ Hz); IR ν (py CN) 1600 cm⁻¹. Anal. Calcd for C₃₇H₃₃BF₄NP₂Rh: C, 59.79; H, 4.48; N, 1.88; P, 8.33. Found: C, 59.91; H, 4.64; N, 1.89; P, 8.43.

Collection and Reduction of X-ray Data. A summary of crystal and intensity collection data is presented in Table I. A crystal of [Rh(PNP)(nbd)]BF₄ was secured to the end of a glass fiber with 5-min epoxy resin. The crystal was found to belong to the monoclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs.²¹ Background counts were measured at both ends

Table II. Positional and Thermal Parameters and Their Esd's for [Rh(nbd)(PNP)]BF₄

| atom | x | y | z | B_{iso} , Å ² |
|------|--------------|-------------|-------------|----------------------------|
| Rh | 0.10267 (6) | 0.2500 (0) | 0.00243 (4) | 3.048 |
| P | 0.1177 (1) | 0.15857 (8) | 0.1766 (1) | 2.656 |
| F1 | 0.4035 (6) | 0.2500 (0) | 0.7103 (4) | 5.861 |
| F2A | 0.5096 (10) | 0.2500 (0) | 0.5542 (8) | 9.886 |
| F3A | 0.3106 (8) | 0.3238 (4) | 0.5481 (6) | 10.450 |
| F2B | 0.224 (2) | 0.250 (0) | 0.558 (2) | 9.9 (6) ^b |
| F3B | 0.408 (2) | 0.184 (1) | 0.531 (1) | 9.9 (4) ^b |
| N | 0.3223 (6) | 0.2500 (0) | 0.0745 (5) | 2.879 |
| C1 | 0.2205 (7) | 0.2500 (0) | 0.2538 (5) | 2.683 |
| C2 | 0.3528 (7) | 0.2500 (0) | 0.1959 (6) | 3.094 |
| C3 | 0.4888 (7) | 0.2500 (0) | 0.2550 (6) | 3.378 |
| C4 | 0.5977 (9) | 0.2500 (0) | 0.1905 (8) | 5.017 |
| C5 | 0.5691 (8) | 0.2500 (0) | 0.0657 (7) | 4.402 |
| C6 | 0.4338 (7) | 0.2500 (0) | 0.0134 (6) | 3.386 |
| C7 | -0.0912 (11) | 0.2500 (0) | -0.2973 (7) | 6.262 |
| C8 | -0.0292 (8) | 0.1776 (5) | -0.2094 (6) | 6.725 |
| C9 | 0.1189 (7) | 0.2957 (4) | -0.1751 (5) | 4.926 |
| C10 | -0.0929 (6) | 0.2956 (4) | -0.0993 (5) | 5.272 |
| C1A | 0.2384 (5) | 0.0661 (3) | 0.1926 (4) | 2.988 |
| C2A | 0.2824 (5) | 0.0329 (3) | 0.0910 (4) | 3.503 |
| C3A | 0.3743 (6) | -0.0383 (4) | 0.0994 (5) | 4.455 |
| C4A | 0.4211 (6) | -0.0743 (4) | 0.2086 (6) | 4.905 |
| C5A | 0.3809 (6) | -0.0409 (4) | 0.3102 (5) | 5.101 |
| C6A | 0.2892 (6) | 0.0293 (4) | 0.3019 (4) | 4.199 |
| C1B | -0.0189 (5) | 0.1242 (3) | 0.2607 (4) | 2.990 |
| C2B | -0.1277 (6) | 0.0780 (4) | 0.1963 (4) | 4.323 |
| C3B | -0.2308 (6) | 0.0409 (5) | 0.2525 (5) | 5.451 |
| C4B | -0.2277 (6) | 0.0524 (5) | 0.3725 (6) | 6.187 |
| C5B | -0.1216 (7) | 0.0977 (5) | 0.4358 (5) | 6.885 |
| C6B | -0.0140 (6) | 0.1339 (4) | 0.3818 (4) | 5.062 |
| B | 0.375 (1) | 0.2500 (0) | 0.5898 (9) | 5.431 |

^a Anisotropic thermal parameters are reported as supplementary material. ^b Refined with isotropic thermal parameters and correspond to the minor disordered fluorine atoms (multiplicities used for atoms F2A, F3A, F2B, and F3B are respectively 0.33, 0.66, 0.17, and 0.34).

of the scan range with the use of an ω - 2θ scan, equal, at each side, to one-fourth of the scan range of this peak. In this manner, the total duration of background measurements is equal to half of the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure, and no decay with time was noted. The data were corrected for Lorentz, polarization, and background effects but not for the effects of absorption ($\mu = 6.5$ cm⁻¹).

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom techniques. The Rh atom was located by Patterson synthesis. Full-matrix least-squares refinement and difference-Fourier calculations were used to locate all remaining non-hydrogen atoms. The atomic scattering factors were taken from the usual tabulation,²² and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers²³ values of $\Delta f'$ and $\Delta f''$. A table of observed and calculated structure factor amplitudes is available.²⁴ In the final least-squares cycle the largest parameter shift was 0.16 times its esd. The final difference-Fourier map did not reveal significant residual electron density (largest peak is 1 e Å⁻³ located 0.8 Å from the Rh atom). Hydrogen atom positions were calculated (C-H distance set at 0.95 Å) and included in structure factor calculations but were not refined. In the BF₄ group three of the four fluorine positions showed a rotational disorder. A satisfactory model was found (see Table II). The final positional and thermal parameters of the refined atoms appear in Table II and as supplementary material.²⁴ The labeling scheme for the cation is presented

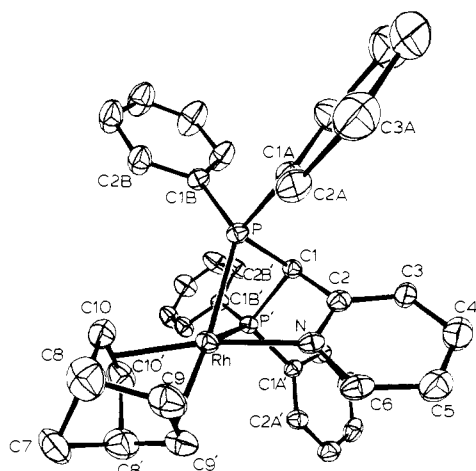
- (21) All calculations were carried out on PDP 8A and 11/34 computers with use of the Enraf-Nonius CAD 4-SPD programs. This crystallographic computing package is described by: (a) Frenz, B. A. In "Computing in Crystallography"; Schenck, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds., Delft University Press: Delft, Holland, 1978; pp 64–71. (b) "CAD 4 and SDP User's Manual"; Enraf-Nonius: Delft, Holland, 1978.
- (22) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromer, D. T. *Ibid.*, Table 2.3.1.
- (23) Cromer, D. T.; Ibers, J. A. In ref 21.
- (24) See paragraph at end of paper regarding supplementary material.

(19) Dahlhoff, W. V.; Dick, T. R.; Ford, G. H.; Kelly, W. S. J.; Nelson, S. M. *J. Chem. Soc. A* 1971, 3495.

(20) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* 1957, 4735.

Table III. Selected Distances and Angles in [Rh(nbd)(PNP)]BF₄

| Distances (Esd), Å | | | | | |
|--------------------|-----------|----------|-----------|-------------|-----------|
| Rh-P | 2.407 (1) | N-C2 | 1.362 (8) | C8-C9 | 1.478 (9) |
| Rh-N | 2.148 (5) | N-C6 | 1.365 (8) | C7-C8 | 1.548 (9) |
| Rh-C9 | 2.159 (5) | C2-C3 | 1.376 (9) | C8-C10 | 1.530 (9) |
| Rh-C10 | 2.168 (5) | C3-C4 | 1.37 (1) | B-F1 | 1.35 (1) |
| P-C1A | 1.826 (5) | C4-C5 | 1.40 (1) | B-F2A | 1.41 (1) |
| P-C1B | 1.819 (4) | C5-C6 | 1.35 (1) | B-F3A | 1.34 (1) |
| P-C1 | 1.855 (4) | C9-C9' | 1.40 (1) | | |
| C1-C2 | 1.522 (9) | C10-C10' | 1.40 (1) | | |
| Angles (Esd), deg | | | | | |
| P-Rh-P' | 71.25 (6) | N-Rh-C9 | 98.4 (2) | C9-C8-C10 | 101.8 (4) |
| P-Rh-N | 75.9 (1) | N-Rh-C10 | 158.0 (1) | C7-C8-C10 | 99.7 (5) |
| P-Rh-C9 | 124.8 (1) | Rh-N-C2 | 115.5 (3) | C7-C8-C9 | 103.4 (5) |
| P-Rh-C10 | 124.1 (1) | Rh-N-C6 | 127.9 (4) | C8-C7-C8' | 91.6 (5) |
| P'-Rh-C9 | 161.7 (1) | P-C1-P' | 98.1 (3) | C8-C9-C9' | 106.1 (3) |
| P'-Rh-C10 | 100.7 (1) | P-C1-C2 | 102.7 (3) | C8-C10-C10' | 105.6 (3) |
| Rh-P-C1A | 119.4 (1) | C1-C2-N | 111.8 (5) | Rh-C9-C8 | 97.4 (3) |
| Rh-P-C1B | 129.9 (1) | C1-C2-C3 | 126.1 (5) | Rh-C10-C8 | 95.4 (3) |
| Rh-P-C1 | 84.7 (1) | C2-C3-C4 | 119.5 (6) | C4-C5-C6 | 118.1 (6) |
| C1A-P-C1B | 103.0 (2) | C3-C4-C5 | 119.5 (6) | C5-C6-N | 124.2 (6) |
| C1A-P-C1 | 104.8 (2) | C3-N-C6 | 116.6 (6) | F1-B-F2A | 104 (1) |
| C1B-P-C1 | 110.4 (2) | | | F1-B-F3A | 111 (1) |
| | | | | F2A-B-F3A | 107 (1) |

Figure 1. ORTEP drawing of the cation [Rh(nbd)(PNP)]⁺ showing the atom-labeling scheme.

in Figure 1. A table of observed and calculated structure factor amplitudes is included as supplementary material.²⁴

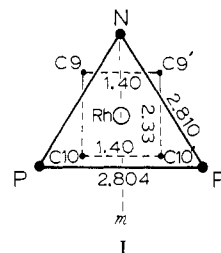
Results and Discussion

The PNP ligand [(C₆H₅)₂P]₂CHC₅H₄N was synthesized and its reaction chemistry with [Rh(nbd)(CH₃COCH₃)_x]BF₄ examined. The resulting complex [Rh(nbd)(PNP)]BF₄ (**1**) was prepared in good yield. ¹H NMR data show that the nbd group is coordinated to the Rh, and a single doublet in the ³¹P NMR spectrum indicates that both phosphorus atoms are coordinated to Rh and are equivalent. The ν(py CN) stretching frequency in the IR spectrum generally provides direct evidence regarding coordination of the pyridyl nitrogen. In free PNP the stretch comes at 1580 cm⁻¹, and upon coordination the frequency is increased to 1600 cm⁻¹ or higher.²⁵ The value of 1600 cm⁻¹ observed in **1** suggest that the pyridyl nitrogen is bound and therefore the ligand is tridentate. Since this complex is the precursor to several novel binuclear compounds (vide infra) and because of its intrinsic importance as a catalyst or catalyst precursor, a single-crystal X-ray analysis was carried out. There have been no previous X-ray structures reported for any PNP complexes.

X-ray Structure. Relevant crystallographic data are given in Table I, and positional and thermal parameters are reported

in Table II and as supplementary material.²⁴ Figure 1 shows an ORTEP drawing of the molecular structure of the cation, including an atom-labeling scheme.

The structure of **1** consists of discrete cations and anions. There are no unusually short interionic distances. Selected distances and angles are presented in Table III. A crystallographic mirror plane bisects the cation and the anion. For the cation this plane contains the following atoms: Rh, C1, C2, C3, C4, C5, C6, C7, and N. The primed atoms in Figure 1 are related to their unprimed counterparts by this mirror plane. The coordination core of **1** contains one nitrogen and two phosphorus atoms from the tridentate PNP ligand and four carbon atoms from the diolefin nbd. The Rh atom lies in the plane of the pyridine ring as required by the *m* symmetry. The coordination geometry is best described within the framework of coordination number 7 as a 4:3 piano stool. The rectangular plane formed by the four diolefin carbon atoms C9, C9', C10, and C10' is approximately parallel to the trigonal plane formed by P, P', and N (dihedral angle between these planes is 6.7°), and the distances from these planes to the Rh atom are 1.68 and 1.65 Å, respectively. Drawing I shows a projected view of these atoms that best illustrate this geometry.



The Rh-P distance (2.407 (1) Å) is somewhat long compared with those reported for rhodium-dppm complexes (2.30–2.38 Å).²⁶ The Rh-N distance (2.148 (5) Å) is also slightly long compared with those reported for rhodium-pyridine complexes^{27,28} and for Rh₂[Ph₂PC₅H₄N]₂(μ-CO)Cl₂.²⁹

(26) Pignolet, L. H.; Doughty, D. H.; Nowicki, S. C.; Casalnuovo, A. L. *Inorg. Chem.* **1980**, *19*, 2172.

(27) Mason, R.; Towl, A. D. C. *J. Chem. Soc. A* **1970**, 1601.

(28) Hoare, R. J.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2138.

(29) Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 1182.

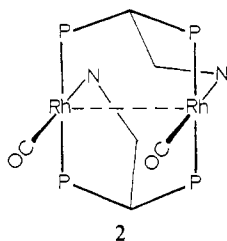
(30) Anderson, M. P.; Pignolet, L. H. *Inorg. Chem.* **1981**, *20*, 4101.

(25) This trend has been observed in numerous complexes that have been characterized in our laboratory and has been noted by others.¹⁹

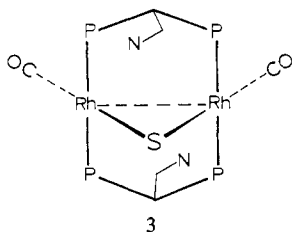
Since this is the first structure determination for a PNP complex, it is not possible to compare these distances with those of other tridentate PNP compounds. It is likely that ring strain is the cause of these long Rh-ligand distances. Indeed, it has been predicted that PNP-type ligands cannot achieve tridentate coordination to a single metal center.¹⁹ The internal angles within the Rh-PNP chelate rings are all small compared with their expected unstrained values. Thus, the Rh-N-C2, N-C2-C1, and C2-C1-P angles are 115.5 (3), 111.8 (5), and 102.7 (3)°, respectively. The Rh-P-C1 angle (84.7 (1)°) is also significantly decreased relative to a normal Rh-dppm value [93.5 (2)° found in [Rh(dppm)₂CO]BF₄²⁶] while the P-C1-P' angle (98.1 (3)°) is increased compared with a normal Rh-dppm value (94.3 (3)°).²⁶ These differences result from the increased folding in the four-membered RhP₂C-dppm type chelate ring about the P-P' vector in the direction of the pyridyl group. This ring folding is obviously caused by the coordination of the pyridyl group. The dihedral angle between the P-Rh-P' and the P-C1-P' planes is 49° and is well outside of the range observed in dppm complexes (0-29.8°).²⁶ The distances between rhodium and the double-bond centers of nbd are 2.04 and 2.05 Å and are within the range 2.00-2.14 Å found in heavy-metal diolefin complexes.^{30,31} The distances and angles within the nbd ligand are normal.

The chelate "bite" angles for the PNP ligand are smaller than those generally observed for four- to five-membered chelate rings. The values for the P-Rh-P' and P-Rh-N angles are 71.25 (6) and 75.9 (1)°, respectively. The N atom is approximately trans to the midpoint of the C10-C10' double bond (N-Rh-midpoint = 168°) while the P atoms are approximately trans to C9 and C9' (P-Rh-C9' = 162°).

Reactivity of [Rh(nbd)(PNP)]BF₄. Complex **1** readily reacts in acetone solution at 25 °C with 1 atm of CO, giving a purple binuclear compound of formula [Rh(PNP)(CO)]₂(BF₄)₂ (**2**). The formulation of this complex is based on IR [$\nu(\text{CO})$ 2002 cm⁻¹, $\nu(\text{py CN})$ 1602 cm⁻¹], ³¹P{¹H} NMR [δ_1 (d of d of d, intensity 1) 62.0, $J_{\text{P-P(trans)}}$ = 293.5 Hz, $J_{\text{Rh-P}}$ = 117.9 Hz, $J_{\text{P-P}}$ = 54.1 Hz; δ_2 (d of d of d, intensity 1) 40.2, $J_{\text{P-P(trans)}}$ = 293.0 Hz, $J_{\text{Rh-P}}$ = 134.3 Hz, $J_{\text{P-P}}$ = 54.0 Hz], and a single-crystal X-ray diffraction analysis.³² The structure of this complex is illustrated in **2** and is consistent with the above spectroscopic



data. This face-to-face dimer has a Rh...Rh separation of 3.054 (1) Å.³² This complex is novel in that it is the first example of a face-to-face dimer with two tridentate bridging ligands. Reaction of **2** with sulfide ion in methanol solution gives an orange-red complex **3** which is formulated as Rh₂-



(31) Kaiser, S. W.; Saillant, R. B.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* **1976**, *15*, 2681.

(32) The details of this X-ray analysis will be published elsewhere.

(μ -S)(CO)₂(PNP)₂. The proposed structure of **3** is that of a sulfide-bridged A-frame where the N atoms of the PNP ligands are unbound. This structure is based on Ir [$\nu(\text{py CN})$ 1582 cm⁻¹, $\nu(\text{CO})$ 1935 cm⁻¹] and ³¹P{¹H} NMR [δ (CDCl₃ solution) 30.7 (PNP, symmetric multiplet with two principal lines separated by ~139 Hz)]. The $\nu(\text{py CN})$ stretching frequency is very similar to that of the free PNP ligand, and the ³¹P NMR spectrum is typical of dppm-bridged A-frames of rhodium.³³ Crystals suitable for a single-crystal X-ray analysis have not yet been obtained for **3**.

Although the study of the reactivity and catalytic properties of these novel PNP complexes is in its preliminary stages, the above results illustrate a rich chemistry. Complex **1** also reacts with 1 atm of H₂, giving what appears to be a tetrahydrido binuclear complex. Preliminary results also show that **1** is an excellent aldehyde decarbonylation catalyst. The details of these studies will be presented in a future publication.

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Registry No. **1**, 86436-86-4; **2**, 86455-87-0; **3**, 86436-87-5; [(nbd)RhCl]₂, 12257-42-0; PNP, 60398-55-2; chlorodiphenylphosphine, 1079-66-9; 2-picoline, 109-06-8.

Supplementary Material Available: ORTEP stereoview of [Rh(nbd)(PNP)]⁺ and tables of general temperature factor expressions, calculated hydrogen atom positional parameters, and calculated and observed structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

(33) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1982**, *21*, 2119.

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Bis(bipyrazine)ruthenium(II) Complexes: Characterization, Spectroscopy, and Electrochemistry

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Recently we have reported the synthesis of an important new photocatalyst, the ruthenium(II) tris(bipyrazine) cation.¹ The chemical, physical, and photophysical properties of this cation have been discussed.^{2,3} Moreover, it has been shown to form a series of protonated species in acid media, including a hexaprotonated species in concentrated sulfuric acid.⁴

We believe that (bipyrazine)ruthenium(II) complexes may have an important role to play in the development of future photocatalysts and, to this end, report the synthesis and characterizations of bis(bipyrazine)ruthenium(II) complexes, *cis*-Ru(bpz)₂X₂ where X is Cl⁻, Br⁻, I⁻, SCN⁻, NO₂⁻, H₂O, OH⁻, CO₃²⁻, and oxalate. The complexes are characterized

(1) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7128.

(2) Crutchley, R. J.; Lever, A. B. P. *Inorg. Chem.* **1982**, *21*, 2276.

(3) Balk, R. W.; Stufkens, D. J.; Crutchley, R. J.; Lever, A. B. P. *Inorg. Chim. Acta* **1981**, *64*, L49.

(4) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170.