While the structures of the conducting, partially oxidized materials[11] derived from Ga(Pc)Cl are not known, the intermolecular contact in the pristine material is probably closely related to those in the doped materials and rationalizes the high conductivity observed.

Finally, in view of the similarity of the Pc and TPP macrocyclic ligands and the biological importance of the latter,[35] it is useful to compare the displacement above the macrocyclic ring for structures known in group 3. The most closely related structures (with displacements) to Al(Pc)Cl (0.410 (6) Å) and Ga(Pc)Cl (0.439 (1) Å) are those for In(TPP)Cl[21] (0.61 Å) and Tl(TPP)Cl[36] (0.74 Å). Depsite the difference in the macrocyclic ligands, the trend toward increased displacement with increased size is apparent.

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Registry No. Ga(Pc)Cl, 19717-79-4; Al(Pc)Cl, 14154-42-8.

Supplementary Material Available: A detailed experimental section, listings of positional and thermal parameters and esd's (Tables II-S (Ga) and X-S (Al)), bond distances and angles (Tables III-S-V-S (Ga) and XI-S and XII-S (Al)), least-squares planes (Tables VI-S (Ga) and XIII-S (Al)), intermolecular contacts (Tables VII-S (Ga) and XIV-S (Al)), temperature factors (Table VIII-S (Ga) and XVI-S (Al)), and observed and calculated structure factor amplitudes (Tables IX-S (Ga) and XV-S (Al)), and a stereoview of the unit cell of Al(Pc)Cl (Figure 4-S) (95 pages). Ordering information is given on any current masthead page.

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(35) Perutz, M. F. *Sci. Am.* **1978**, *239*, 92.

(36) Henrick, K.; Matthews, R. W.; Tasker, P. A. *Inorg. Chem.* **1977**, *16*, 3293.

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Synthesis and Structural Characterization of Rhodium(I) and Iridium(I) Complexes of the Asymmetric Tetradentate PPNN Ligand 2,2′-Bis[[*o*-(diphenylphosphino)benzylidene]amino]-6,6′-dimethylbiphenyl

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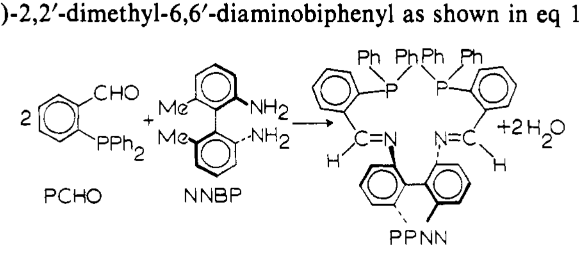
The new asymmetric ligand 2,2′-bis[[*o*-(diphenylphosphino)benzylidene]amino]-6,6′-dimethylbiphenyl, PPNN, was synthesized by the Schiff base reaction of *o*-(diphenylphosphino)benzaldehyde with 2,2′-dimethyl-6,6′-diaminobiphenyl. The *d* and *l* optical isomers of PPNN were also synthesized by the above reaction using the resolved enantiomers of 2,2′-dimethyl-6,6′-diaminobiphenyl. Specific and molecular rotations ($[\alpha]^{25}_D$, $[M]^{25}_D$ ($CHCl_3$)) for *d*-PPNN and *l*-PPNN were +198, 1493° and −193, −1457°, respectively. Rh(I) and Ir(I) complexes of PPNN were synthesized by the reactions of PPNN with $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ and $Ir(PPh_3)_2(N_2)Cl$, respectively, using CH_2Cl_2 as solvent. Both complexes were isolated in good yield as BPh_4 salts. The single-crystal X-ray structures of racemic $[Rh(PPNN)]BPh_4$ and $[Ir(PPNN)]BPh_4$ were determined. The two compounds are essentially isostructural. Crystal parameters for Rh: $P\bar{1}$, a = 13.473 (2) Å, b = 13.506 (2) Å, c = 17.424 (3) Å, α = 100.20 (1)°, β = 98.17 (1)°, γ = 91.41 (1)°, Z = 2, R (R_w) = 0.034 (0.047) for 6168 observations $[F_o^2 \geq 3\sigma(F_o^2)]$. Crystal parameters for Ir: $P\bar{1}$, a = 13.48 (1) Å, b = 13.551 (3) Å, c = 17.438 (8) Å, α = 100.28 (3)°, β = 98.00 (5)°, γ = 91.38 (4)°, Z = 2, R (R_w) = 0.055 (0.064) for 4483 observations $[F_o^2 \geq 2\sigma(F_o^2)]$. Both compounds have approximately square-planar P_2N_2 coordination core geometries with average Rh–P and Ir–P distances of 2.222 (1) and 2.244 (3) Å and with average Rh–N and Ir–N distances of 2.106 (3) and 2.09 (1) Å, respectively. The PPNN ligand is tetradentate in both complexes, and the twisted substituted biphenyl group imposes an asymmetry on the entire complex. The reactions of these complexes with CO and H_2 have been studied.

Introduction

In recent years there has been intense interest in the design and use of chiral transition-metal complexes for asymmetric catalysis.[1-5] The vast majority of these complexes have involved the use of chiral bidentate phosphines as ligands and Rh(I) as the metal. In very few cases have complex tetradentate chiral ligands been employed although such ligands should provide more stereochemically rigid complexes.[6] Higher optical yields may result from catalysts that use such ligands because a rigid arrangement of bulky substituents around the metal center should prevent significant changes in the asymmetric environment during the course of the catalytic cycle. In this paper we report the synthesis of the new tetradentate chiral ligand 2,2′-bis[[*o*-(diphenylphosphino)benzylidene]amino]-6,6′-dimethylbiphenyl, PPNN, from the reaction of *o*-(diphenylphosphino)benzaldehyde with (*R*)- or (*S*)-2,2′-dimethyl-6,6′-diaminobiphenyl as shown in eq 1.



(1)

The rhodium(I) and iridium(I) complexes, $[Rh(PPNN)]BPh_4$ (**1**) and $[Ir(PPNN)]BPh_4$ (**2**), have been synthesized and characterized. Single-crystal X-ray diffraction analyses were carried out on both racemic complexes in order to determine their stereochemistry and because the reactivity of the com-

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(1) Brown, J. M.; Chaloner, P. A. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; Chapter 4, p 137.

(2) Oliver, J. D.; Riley, D. P. *Organometallics* **1983**, *2*, 1032.

(3) Halpern, J. *Science* (*Washington, D.C.*) **1982**, *217*, 401 and references therein.

(4) MacNeil, P. R.; Roberts, N. K.; Bosnich, B. *J. Am. Chem. Soc.* **1981**, *103*, 2273.

(5) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.

(6) Brunner, H.; Rahman, A. F. M. M. *Chem. Ber.* **1984**, *117*, 710.

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plexes was found to be significantly different. Complex **1** did not react with H_2 and only partially with CO whereas complex **2** showed rapid and complex reactivity in solution with H_2 and CO. The CO adduct of **2** was found to have a bond between the iridium atom and a methyne carbon atom of the PPNN ligand to give an Ir(PPNC) coordination core. Complexes **1** and **2** were found to be isostructural in the solid state.

Experimental Section

Reagents and Solvents. 2-Amino-3-nitrotoluene was obtained from Fairfield Chemical Co. and used without further purification. *o*-Bromobenzaldehyde was obtained from Aldrich Chemical Co. and used without further purification. Chlorodiphenylphosphine was purchased from Aldrich Chemical Co. and freshly distilled under N_2 prior to use. All of the remaining organic starting materials were reagent grade and were used as obtained from their respective suppliers. All solvents were reagent grade and were used without further purification with the exception of tetrahydrofuran (THF), which was distilled under N_2 from potassium–benzophenone ketyl and used as needed.

Instrumentation. Infrared spectra were recorded on a Beckman Model 4250 grating spectrophotometer using NaCl plates and KBr pellets. Electronic absorption spectra were recorded with use of a Cary Model 17-d spectrometer. Mass spectra were obtained on a Finnigan 4000 mass spectrometer. Samples were introduced by means of the solid probe, and spectra were measured at an ion source temperature of 200–230 °C with an ionization energy of 70 eV. ^{1}H NMR spectra were obtained at 25 °C on a Varian HFT-80 or a Nicolet NT-300 spectrometer. ^{31}P NMR spectra were obtained at 121 MHz and 25 °C on a Nicolet NT-300 spectrometer. The chemical shifts are reported in ppm relative to the external standard 85% H_3PO_4 (δ 0) with positive shifts downfield. All polarimetric determinations were carried out on a Perkin-Elmer Model 241 polarimeter. The optical activity of each compound was measured at 25 °C in $CHCl_3$ or in 10% HCl solution in an all-glass cell (1 dm in length; 5 mL in volume) with sodium light. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis of the Compounds. 2,2′-Dimethyl-6,6′-diaminobiphenyl was prepared from 2-iodo-3-nitrotoluene that was made from 2-amino-3-nitrotoluene according to the literature procedures of Carlin and Foltz[7] and of O'Connor, Ernst, and Holm.[8] Pure 2,2′-dimethyl-6,6′-dinitrobiphenyl was obtained as pale yellow-green needles in 75% yield: mp 109–110 °C; IR (KBr pellet) ν(N–O) 1540, 1350 cm^{-1}, asymmetric and symmetric stretches; ^{1}H NMR (CD_2Cl_2, 80 MHz) aromatic H δ 6.9–7.4 (m, intensity 6), CH_3 δ 1.38 (s, intensity 7). 2,2′-Dimethyl-6,6′-dinitrobiphenyl (8 g) was added to 150 mL of absolute ethanol in a Parr pressure reaction flask. Platinum black catalyst (0.8 g) was then added to the flask under a purified atmosphere of N_2. The system was thoroughly purged with H_2 and then placed under 25 psi of H_2. The shaker was turned on and allowed to operate until the uptake of hydrogen had ceased. The spent platinum black catalyst was removed by vacuum filtration, and then 10 mL of distilled water was added to the solution. The solid crude product was precipitated from this solution upon slow evaporation of the solvent. This material was collected by vacuum filtration and washed with a small amount of cold distilled water. Pure 2,2′-dimethyl-6,6′-diaminobiphenyl was obtained as shiny white crystals in 75% yield upon recrystallization of the crude product from hot absolute ethanol: mp 134–135 °C; IR (KBr pellet) ν (N–H) 3420, 3330 cm^{-1}, asymmetric and symmetric stretches; ^{1}H NMR (CD_2Cl_2, 80 MHz) aromatic H δ 6.5–7.2 (m), NH_2 δ 3.3 (br s), CH_3 δ 1.8 (s).

Resolution of 2,2′-Dimethyl-6,6-diaminobiphenyl. The *d,l* base, 2,2′-dimethyl-6,6′-diaminobiphenyl, was resolved with the use of *d*-tartaric acid according to a modified method of Meisenheimer and Horing.[9] *d,l*-2,2′-Dimethyl-6,6′-diaminobiphenyl (30 g) was added to 150 mL of absolute ethanol in an Erlenmeyer flask, and the resultant mixture was gently heated until all of the solid material was dissolved. In a separate flask, *d*-tartaric acid (21 g) was added to 100 mL of absolute ethanol and also heated until the material was completely dissolved. The two solutions were added together while hot and mixed thoroughly. This solution was slowly cooled to room temperature and then chilled in a refrigerator to completely precipitate the *d*-tartrate salt. A 13.5-g sample of the pure D-tartrate was obtained upon five recrystallizations. Since this tartrate salt hydrolyzes in water, it was necessary to carry out all of the polarimetric determinations in 10% HCl solutions. The pure *d*-tartrate salt that was obtained was found to have a melting point of 164–165 °C, a specific rotation (in 10% HCl) of $[\alpha]_D = -11°$, and a molecular rotation of $[M]_D = -39°$. In order to separate the *l*-2,2′-dimethyl-6,6′-diaminobiphenyl from the *d*-tartrate salt, the 13.5 g of material was dissolved in 15 mL of 10% HCl and excess concentrated ammonia (7 mL) was added until the *l* base completely precipitated out of solution. Upon one recrystallization of this material from hot ethanol, 5.4 g of pure white crystalline *l*-2,2′-dimethyl-6,6′-diaminobiphenyl was obtained: mp 155–158 °C; specific rotation (10% HCl) $[\alpha]_D = -34°$; molecular rotation $[M]_D = -72°$. Literature values:[9] mp 156 °C; specific rotation (10% HCl) $[\alpha]_D = -35°$; molecular rotation $[M]_D = -74°$.

The mother liquid of the *d*-tartrate salt mentioned above contained concentrated salts of *d*-2,2′-dimethyl-6,6′-diaminobiphenyl. This material was obtained by evaporating off the solvent of the mother liquid until only a solid residue remained. This residue was dissolved in 20 mL of 10% HCl, and then excess concentrated ammonia (10 mL) was added until the *d* base was completely precipitated. The resulting solid material (7 g) was dissolved in 30 mL of boiling absolute ethanol. To this solution was added a solution of *l*-tartaric acid (5 g) in 25 mL of hot absolute ethanol. The combined solutions were mixed, allowed to cool, and then chilled to completely precipitate the *l*-tartrate salt. A 7.7-g sample of the pure *l*-tartrate salt was obtained upon one recrystallization of this material from hot ethanol: mp 164–165 °C; specific rotation (10% HCl) $[\alpha]_D = 13°$; molecular rotation $[M]_D = 46°$. In order to separate the *d*-2,2′-dimethyl-6,6′-diaminobiphenyl from the *l*-tartrate salt, the 7.7 g of material was dissolved in 15 mL of 10% HCl and excess concentrated ammonia (7 mL) was added until the *d* base completely precipitated out of solution. Upon one recrystallization of this material from hot ethanol, 3.4 g of pure *d*-2,2′-dimethyl-6,6′-diaminobiphenyl was obtained: mp 156–158 °C; specific rotation (10% HCl) $[\alpha]_D = 35°$; molecular rotation $[M]_D = 74°$. Literature values:[9] mp 156 °C; specific rotation (10% HCl) $[\alpha]_D = 36°$; molecular rotation $[M]_D = 77°$.

***o*-(Diphenylphosphino)benzaldehyde** was prepared according to the procedures of Sciemenz and Kaack[10] and of Rauchfuss.[11] Pure *o*-(diphenylphosphino)benzaldehyde was obtained as bright yellow crystals in 82% yield upon recrystallization of the crude product from hot methanol: mp 116–117 °C; IR (KBr pellet) ν(C=O) 1700 cm^{-1} (s str); ^{1}H NMR (acetone-d_6, 80 MHz) aromatic H δ 7.35 (m, intensity 15), C–H δ 10.44 (d, intensity 1, *J*(P–H) = 5.0 Hz); ^{31}P NMR (acetone) δ –9.5 (s).

2,2′-Bis[[*o*-(diphenylphosphino)benzylidene]amino]-6,6′-dimethylbiphenyl (PPNN). The PPNN ligand was prepared via a Schiff base reaction that was carried out under a purified N_2 atmosphere. *o*-(Diphenylphosphino)benzaldehyde (4.1 g, 14 mmol), *d,l*-2,2′-dimethyl-6,6′-diaminobiphenyl (1.5 g, 7 mmol), and 6 drops of concentrated sulfuric acid was added to 100 mL of benzene, and the resultant mixture was refluxed for 24 h. It was necessary to place a Dean–Stark trap filled with benzene in line with the condenser, in order to azeotropically remove the water that was produced during this reaction. Upon completion of this refluxing period, the solution was cooled to room temperature and then syringed into a side-arm flask that was attached to a high-vacuum Schlenk line. The remaining manipulations were carried out under a purified nitrogen atmosphere by using standard Schlenk-line techniques. The crude product was obtained from this solution by slowly evaporating the solvent until only an oil remained. Pure *d,l*-PPNN was obtained as a yellow powder in 96% yield upon recrystallization of this oil from degassed hot absolute ethanol: mp 78 °C (dec); IR (KBr pellet) ν(C=N) 1630 cm^{-1} (s str); ^{31}P NMR (acetone) δ –13.4 (s); ^{1}H NMR (acetone-d_6, 300 MHz) C–H δ 8.9 (d, intensity 2, *J*(P–H) = 5.0 Hz), aromatic H δ 6.3–7.7 (m, intensity 33), CH_3 δ 1.8 (s, intensity 6); mass spectrum, parent peak at *m/e* 756. Anal. Calcd for $C_{52}H_{42}P_2N_2$: C, 82.52; H, 5.59; N, 3.70; P, 8.18. Found: C, 82.29; H, 5.61; N, 3.57; P, 8.33. The synthesis of the *d*-PPNN and *l*-PPNN ligands was accomplished with the same procedure as described above, with the exception that

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(7) Carlin, R. B.; Foltz, G. E. *J. Am. Chem. Soc.* **1956**, *78*, 1997.

(8) O'Connor, M. J.; Ernst, R. E.; Holm, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 4561.

(9) Meisenheimer, J.; Horing, M. *Chem. Ber.* **1927**, *60*, 1425.

(10) Schiemenz, G. P.; Kaack, H. *Liebigs Ann. Chem.* **1973**, 1480.

(11) Hoots, J. E.; Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.* **1982**, *21*, 175.

the appropriate resolved base was substituted for the racemic mixture in each preparation. The resolved ligands were found to have the same infrared, ^1H NMR, and ^{31}P NMR spectra as the racemic PPNN ligand. The *d*-PPNN ligand was found to have a melting point of 85 °C (dec) and a specific rotation ($CHCl_3$) of $[\alpha]_D = {}^{+}198°$, which converts to a molecular rotation of $[M]_D = {}^{+}1493°$, and the *l*-PPNN ligand was found to have a melting point of 85 °C (dec), a specific rotation ($CHCl_3$) of $[\alpha]_D = -193°$, and a molecular rotation of $[M]_D = -1457°$.

In the following syntheses all manipulations were carried out under a purified N_2 atmosphere by using standard Schlenk techniques.

[*d,l*-Rh(PPNN)]BPh$_4$ (1) was prepared by slowly adding a solution of $[Rh(1,5\text{-cyclooctadiene})Cl]_2$[12] (0.10 g, 0.20 mmol) dissolved in 5 mL of CH_2Cl_2 to a solution of the *d,l*-PPNN ligand (0.34 g, 0.44 mmol) dissolved in CH_2Cl_2. The resulting dark red solution was stirred for 2 h at 25 °C and then slowly transferred to a flask that contained $NaBPh_4$ (0.14 g, 0.40 mmol) dissolved in 10 mL of methanol. The product was precipitated from this solution as an olive green powder upon the slow evaporation of the CH_2Cl_2. The powder was filtered and washed consecutively with methanol and pentane. Crystals were obtained in 80% yield by slow solvent diffusion with the use of CH_2Cl_2 and CH_3OH or $C_2H_5OC_2H_5$. Solutions of this compound were brown-green in color: IR (KBr pellet) ν(C=N) 1620 cm^{-1} (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 51.9 (d, *J*(Rh–P) = 172 Hz); ^1H NMR (CD_2Cl_2) CH_3 δ 2.1 (s), C–H resonance obscured by the aromatic peaks; electronic absorption spectrum (CH_2Cl_2) in the range 300–700 nm [λ_{max}, nm (log ϵ)] 422 (3.61), 563 (2.60). Anal. Calcd for $C_{76}H_{62}BN_2P_2Rh$: C, 77.42; H, 5.30; N, 2.38; P, 5.25. Found: C, 77.38; H, 5.13; N, 2.24; P, 5.45. The BF_4^- salt of **1** was synthesized by the reaction of PPNN with an acetone solution of $[Rh(ethylene)Cl]_2$ to which a stoichiometric amount of $AgBF_4$ had been added. This complex had spectroscopic properties identical with those of the BPh_4^- salt.

[*d,l*-Ir(PPNN)]BPh$_4$ (2) was prepared by slowly adding an ice-cold solution of $Ir(PPh_3)_2(N_2)Cl$[13] (0.13 g, 0.17 mmol) dissolved in 5 mL of CH_2Cl_2 to a cold solution of PPNN (0.14 g, 0.19 mmol) dissolved in 5 mL of CH_2Cl_2. The resulting solution was stirred for 1 h at 0 °C and then mixed with a solution of $NaBPh_4$ (0.60 g, 0.18 mmol) dissolved in 10 mL of methanol. This dark orange solution was stirred for 20 min at 0 °C. A dark brown solid was obtained upon the slow removal of the solvent via a vacuum. The solid product was filtered, washed with methanol and diethyl ether, and vacuum dried. Black crystals were obtained by slow solvent diffusion with use of CH_2Cl_2 and CH_3OH or $C_2H_5OC_2H_5$ in 55% yield. Solutions of this compound were red-brown in color: IR (KBr pellet) ν(C=N) 1620 cm^{-1} (s); $^{31}P\{^1H\}$ NMR (acetone-d_6) δ 19.5 (s); electronic absorption spectrum (CH_2Cl_2) in the range 300–700 nm [λ_{max}, nm (log ϵ)] 306 (4.16 sh), 367 (3.88), 507 (3.67), 630 (3.1). Anal. Calcd for $C_{76}H_{62}BN_2P_2Ir$: C, 71.97; H, 4.93; N, 2.21; P, 4.88. Found: C, 71.74; H, 4.93; N, 1.97; P, 5.22.

The *d* and *l* optical isomers were also synthesized for rhodium and iridium and were characterized by IR and NMR spectroscopy. However, the optical rotations could not be accurately measured, due to the highly absorbing nature of these complexes in the available wavelength region and because of their instability in very dilute solutions.

Reaction of [Ir(PPNN)]BPh$_4$ with CO and H$_2$. Carbon monoxide gas was bubbled through a CH_2Cl_2 solution of **2** for 1 h at room temperature. The solution gradually changed in color from dark orange to yellow-orange. Slow evaporation yielded a crystalline product: $^{31}P\{^1H\}$ NMR (CH_2Cl_2) two singlet resonances of equal intensity at δ 19.5 and −10.7 at 25 °C but several additional singlet peaks (δ −2.6, −32.7) when the spectrum was recorded at temperatures below 0 °C; IR (CH_2Cl_2) ν(CO) 2030 and 2130 cm^{-1}, ν(CN) 1608, and 1625 cm^{-1}. These data indicate the presence of several compounds. A single-crystal X-ray analysis was carried out on a crystal that was isolated from this reaction (see text).

An acetone solution of **2** (50 mg in 2 mL) was placed under 1 atm of H_2 at 25 °C with stirring. The color of the solution changed from orange to yellow in 6 h. Reduction of the volume and layering with CH_3OH at −40 °C afforded yellow microcrystals. $^{31}P\{^1H\}$ NMR (acetone solution) two singlets of equal intensity at δ 5.9 and −0.6; ^1H NMR (acetone-d_6) two multiplets of equal intensity at δ −9.0 (d of d of d, *J* = 3, 28, 148 Hz) and −18.6 (complex 11-line pattern); IR (KBr disk) ν(Ir–H) 2180 and 2000 cm^{-1}, ν(CN) 1640 (sh) and 1620 cm^{-1}, no N–H stretch observed.

Table I. Summary of Crystal Data and Intensity Collection for Compounds 1 and 2

	$[Rh(PPNN)]BPh_4 \cdot CH_3OH$ (1)	$[Ir(PPNN)]BPh_4 \cdot CH_3OH$ (2)
	crystal parameters	
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cryst dimens, mm^3	0.2 × 0.3 × 0.3	0.1 × 0.2 × 0.2
cell parameters		
a, Å	13.473 (2)	13.48 (1)
b, Å	13.506 (2)	13.551 (3)
c, Å	17.424 (4)	17.438 (8)
α, deg	100.20 (2)	100.28 (3)
β, deg	98.17 (2)	98.00 (5)
γ, deg	91.41 (2)	91.38 (4)
V, Å^3	3085 (3)	3099 (5)
Z	2	2
d(calcd), g cm^{-3}	1.304	1.394
abs coeff, cm^{-3}	3.69	22.42
max, min, av transmissn factors		1.0, 0.78, 0.88
formula	$C_{76}H_{62}BN_2P_2Rh \cdot CH_3OH$	$C_{76}H_{62}BN_2P_2Ir \cdot CH_3OH$
fw	1211.06	1300.36
	Measurement of Intensity Data	
diffractometer	CAD 4	CAD 4
radiation (λ, Å)	Mo K$\bar{\alpha}$ (0.71069) graphite monochromatized	Mo K$\bar{\alpha}$ graphite monochromatized
scan range in 2θ, deg	0–46	0–42
no. of unique reflcns measd (region)	8556 ($+h,\pm k,\pm l$)	6656 ($+h,\pm k,\pm l$)
obsd reflcns^a	6168 [$F_o^2 \geqslant 3\sigma(F_o^2)$]	4477 [$F_o^2 \geqslant 2\sigma(F_o^2)$]
	Refinement by Full-Matrix Least Squares	
no. of parameters	756	352
R^b	0.034	0.055
$R_w{}^b$	0.047	0.064
GOF^b	1.82	1.68
p^a	0.03	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 $I = [K/\mathrm{NPI})](C - 2B)$, where $K = 20.1166$(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 $[\sigma(I)]^2 = (K/\mathrm{NPI})^2[C + 4B + (pI)^2]$ 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 = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2[\sigma(I)/I]F_o$. [b] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma(F_o)]2$. The unweighted and weighted residuals are defined as $R = (||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [(\Sigma w(|F_o| - |F_c|)^2]^{1/2}$. The error in an observation of unit weight (GOF) is $[\Sigma w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

Collection and Reduction of X-ray Data. A summary of crystal and intensity collection data is presented in Table I. Crystals of the methanol solvates of **1** and **2** were secured to the end of glass fibers with 5-min epoxy resin. The crystals were found to belong to the triclinic crystal class by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing programs.[14] Background counts were measured at both ends of the scan range with the use of an ω–2θ scan,

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

(13) Collman, J. P. *Inorg. Synth.* **1970**, *12*, 8.

(14) All calculations were carried out on PDP 8A and 11/34 computers with use of the Enraf-Nonius CAD 4-SDP 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. "CAD 4 and SDP User's Manual"; Enraf-Nonius: Delft, Holland, **1978**.

Table II. Table of Positional Parameters and Their Estimated Standard Deviations for [Rh(PPNN)] BPh_4 (**1**)

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Rh	0.33016 (3)	0.05568 (3)	0.24150 (2)	2.437 (7)	C4F	0.3941 (4)	−0.3188 (4)	0.0190 (3)	4.9 (1)
P1	0.20569 (9)	0.01049 (8)	0.14144 (7)	2.52 (2)	C5F	0.3636 (4)	−0.3473 (4)	0.0833 (4)	5.1 (1)
P2	0.40763 (9)	−0.08620 (8)	0.24737 (7)	2.56 (2)	C6F	0.3686 (4)	−0.2802 (4)	0.1537 (3)	4.0 (1)
N1	0.2755 (3)	0.1986 (3)	0.2373 (2)	2.65 (8)	C1G	0.3753 (3)	0.1889 (3)	0.4018 (3)	2.8 (1)
N2	0.4236 (3)	0.1174 (3)	0.3486 (2)	2.67 (8)	C2G	0.3402 (4)	0.1582 (4)	0.4647 (3)	3.8 (1)
C1	0.1863 (3)	0.2283 (3)	0.2349 (3)	2.9 (1)	C3G	0.2934 (4)	0.2255 (4)	0.5148 (3)	4.5 (1)
C2	0.5113 (4)	0.0955 (4)	0.3779 (3)	3.4 (1)	C4G	0.2793 (4)	0.3216 (4)	0.5011 (3)	4.1 (1)
C3	0.2891 (4)	0.4565 (4)	0.4196 (3)	4.7 (1)	C5G	0.3124 (4)	0.3535 (3)	0.4376 (3)	3.2 (1)
C4	0.5433 (4)	0.4314 (4)	0.4040 (3)	4.7 (1)	C6G	0.3641 (3)	0.2870 (3)	0.3874 (3)	2.7 (1)
C1A	0.1639 (3)	−0.1180 (3)	0.0931 (3)	2.7 (1)	C1H	0.3557 (3)	0.2734 (3)	0.2440 (3)	2.7 (1)
C2A	0.1434 (4)	−0.1883 (3)	0.1389 (3)	3.3 (1)	C2H	0.3847 (4)	0.2969 (4)	0.1766 (3)	3.4 (1)
C3A	0.1100 (4)	−0.2852 (4)	0.1046 (3)	4.0 (1)	C3H	0.4633 (4)	0.3669 (4)	0.1835 (3)	4.0 (1)
C4A	0.0992 (4)	−0.3139 (4)	0.0237 (3)	4.3 (1)	C4H	0.5125 (4)	0.4096 (4)	0.2570 (3)	4.1 (1)
C5A	0.1199 (4)	−0.2460 (4)	−0.0221 (3)	4.6 (1)	C5H	0.4848 (3)	0.3856 (4)	0.3252 (3)	3.3 (1)
C6A	0.1520 (4)	−0.1476 (4)	0.0120 (3)	3.7 (1)	C6H	0.4029 (3)	0.3165 (3)	0.3186 (3)	2.6 (1)
C1B	0.0928 (3)	0.0621 (3)	0.1780 (3)	2.7 (1)	C1I	0.8923 (4)	0.4911 (4)	0.3164 (3)	3.8 (1)
C2B	0.0014 (4)	0.0082 (4)	0.1622 (3)	3.4 (1)	C2I	0.9621 (5)	0.4714 (4)	0.3783 (3)	5.2 (1)
C3B	−0.0841 (4)	0.0492 (4)	0.1881 (3)	4.5 (1)	C3I	0.9467 (6)	0.3969 (5)	0.4211 (4)	6.4 (2)
C4B	−0.0804 (4)	0.1460 (4)	0.2295 (4)	4.8 (1)	C4I	0.8619 (6)	0.3361 (5)	0.4028 (4)	7.2 (2)
C5B	0.0090 (4)	0.2030 (4)	0.2440 (3)	3.9 (1)	C5I	0.7930 (5)	0.3502 (5)	0.3418 (4)	6.7 (2)
C6B	0.0958 (3)	0.1618 (3)	0.2202 (3)	2.9 (1)	C6I	0.8068 (4)	0.4257 (4)	0.2988 (4)	5.0 (1)
C1C	0.2143 (3)	0.0751 (3)	0.0589 (3)	2.7 (1)	C1J	0.8244 (4)	0.5865 (3)	0.1970 (3)	3.6 (1)
C2C	0.1412 (4)	0.1367 (4)	0.0320 (3)	3.4 (1)	C2J	0.7296 (4)	0.6084 (4)	0.2177 (4)	4.7 (1)
C3C	0.1527 (4)	0.1858 (4)	−0.0299 (3)	4.0 (1)	C3J	0.6451 (4)	0.6107 (4)	0.1618 (4)	5.6 (2)
C4C	0.2356 (4)	0.1733 (4)	−0.0665 (3)	4.3 (1)	C4J	0.6537 (5)	0.5936 (4)	0.0829 (4)	6.2 (2)
C5C	0.3074 (4)	0.1111 (4)	−0.0421 (3)	4.6 (1)	C5J	0.7456 (5)	0.5766 (4)	0.0608 (4)	5.5 (2)
C6C	0.2980 (4)	0.0633 (4)	0.0206 (3)	3.9 (1)	C6J	0.8295 (4)	0.5742 (4)	0.1163 (3)	4.2 (1)
C1D	0.3767 (3)	−0.1547 (3)	0.3235 (3)	2.8 (1)	C1K	0.9406 (4)	0.6919 (4)	0.3208 (3)	3.4 (1)
C2D	0.2867 (4)	−0.1403 (4)	0.3511 (3)	3.4 (1)	C2K	0.9675 (4)	0.7714 (4)	0.2861 (3)	3.9 (1)
C3D	0.2597 (4)	−0.1932 (4)	0.4077 (3)	4.2 (1)	C3K	0.9950 (4)	0.8678 (4)	0.3294 (3)	4.6 (1)
C4D	0.3236 (4)	−0.2586 (4)	0.4363 (3)	4.2 (1)	C4K	0.9961 (4)	0.8871 (4)	0.4085 (3)	4.9 (1)
C5D	0.4140 (4)	−0.2726 (4)	0.4102 (3)	4.5 (1)	C5K	0.9672 (5)	0.8123 (5)	0.4447 (3)	5.3 (1)
C6D	0.4409 (4)	−0.2218 (4)	0.3543 (3)	3.8 (1)	C6K	0.9401 (4)	0.7161 (4)	0.4018 (3)	4.5 (1)
C1E	0.5430 (3)	−0.0589 (3)	0.2809 (3)	2.7 (1)	C1L	1.0217 (4)	0.5438 (3)	0.2331 (3)	3.1 (1)
C2E	0.6143 (4)	−0.1221 (4)	0.2519 (3)	3.5 (1)	C2L	1.1163 (4)	0.5865 (4)	0.2677 (3)	3.8 (1)
C3E	0.7153 (4)	−0.1061 (4)	0.2824 (3)	4.1 (1)	C3L	1.2040 (4)	0.5545 (4)	0.2415 (3)	4.6 (1)
C4E	0.7471 (4)	−0.0259 (4)	0.3427 (3)	4.7 (1)	C4L	1.2004 (4)	0.4782 (4)	0.1774 (3)	5.0 (1)
C5E	0.6780 (4)	0.0367 (4)	0.3720 (3)	4.4 (1)	C5L	1.1097 (4)	0.4316 (4)	0.1420 (3)	4.7 (1)
C6E	0.5768 (3)	0.0235 (4)	0.3413 (3)	3.3 (1)	C6L	1.0222 (4)	0.4624 (4)	0.1709 (3)	4.1 (1)
C1F	0.4051 (3)	−0.1821 (3)	0.1597 (3)	2.8 (1)	B	0.9181 (4)	0.5785 (4)	0.2662 (3)	3.4 (1)
C2F	0.4359 (4)	−0.1541 (4)	0.0938 (3)	3.5 (1)	O	0.5333 (3)	0.0952 (3)	0.1343 (2)	3.36 (8)
C3F	0.4315 (4)	−0.2223 (4)	0.0236 (3)	4.5 (1)	C	0.6223 (6)	0.1391 (6)	0.1745 (5)	8.4 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

equal, at each side, to one-fourth of the scan range of the peak. In this manner, the total duration of background measurements is equal to half 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. The effects of absorption were included for **2** by using the empirical absorption program EAC (ψ-scan data)[13] but not for **1**.

Solution and Refinement of the Structures. The structures were solved by conventional heavy-atom techniques. The metal atoms were 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,[15] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers'[16] values of $\Delta f'$ and $\Delta f''$. The final difference-Fourier maps did not reveal significant residual electron density for either compound. Hydrogen atom positions were calculated (C–H distance set at 0.95 Å) and included in the structure factor calculations but were not refined. The final positional and thermal parameters of the refined atoms appear in Tables II and III and as supplementary material.[17] The labeling scheme for the cation of **1** is presented in Figure 1. The labeling schemes are the same for **1** and **2**, and ORTEP drawings of the cations of **1** and **2** are shown in Figure 1 and as supplementary material,[17] respectively. Tables of observed and calculated structure factor amplitudes are included as supplementary material.[17]

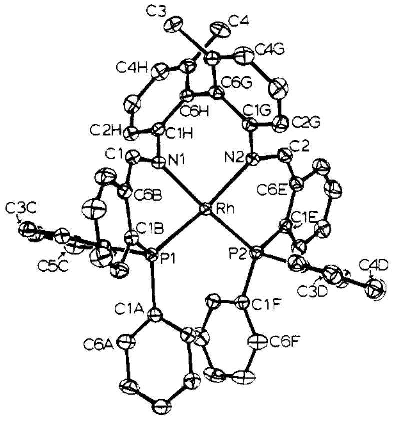

Figure 1. ORTEP drawing of the cation $[Rh(PPNN)]^+$ (**1**) showing the labeling scheme. The thermal ellipsoids show 35% probability surfaces. Compound **2** has the identical labeling scheme.

Results and Discussion

Synthesis and Characterization. The asymmetric ligand 2,2′-bis[[*o*-(diphenylphosphino)benzylidene]amino]-6-6′-dimethylbiphenyl (PPNN) was synthesized by the Schiff base

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(15) 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.

(16) Cromer, D. T.; Ibers, J. A. Reference 15.

(17) See paragraph at end of paper regarding supplementary material.

Table III. Table of Positional Parameters and Their Estimated Standard Deviations for [Ir(PPNN)] BPh_4 (2)

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
Ir	0.32962 (4)	0.05608 (4)	0.24157 (4)	3.31 (1)	C4F	0.394 (1)	−0.316 (1)	0.0198 (8)	5.4 (3)*
P1	0.2048 (3)	0.0114 (2)	0.1396 (2)	3.55 (9)	C5F	0.364 (1)	−0.345 (1)	0.0815 (8)	5.8 (4)*
P2	0.4079 (3)	−0.0861 (2)	0.2482 (2)	3.88 (9)	C6F	0.367 (1)	−0.280 (1)	0.1530 (8)	4.8 (3)*
N1	0.2738 (7)	0.1991 (7)	0.2377 (6)	3.8 (2)*	C1G	0.3741 (9)	0.1918 (9)	0.4011 (7)	3.6 (3)*
N2	0.4192 (7)	0.1184 (7)	0.3463 (5)	3.5 (2)*	C2G	0.340 (1)	0.160 (1)	0.4648 (8)	4.8 (3)*
C1	0.1855 (9)	0.2280 (9)	0.2323 (7)	3.5 (3)*	C3G	0.294 (1)	0.228 (1)	0.5160 (9)	5.9 (4)*
C2	0.509 (1)	0.0985 (9)	0.3776 (8)	4.5 (3)*	C4G	0.279 (1)	0.325 (1)	0.5019 (8)	4.9 (3)*
C3	0.287 (1)	0.457 (1)	0.4216 (8)	5.1 (3)*	C5G	0.3116 (9)	0.3544 (9)	0.4381 (7)	4.0 (3)*
C4	0.542 (1)	0.432 (1)	0.4019 (8)	5.6 (4)*	C6G	0.3636 (9)	0.2889 (8)	0.3861 (7)	3.2 (3)*
C1A	0.1656 (9)	−0.1172 (8)	0.0936 (7)	3.5 (3)*	C1H	0.3577 (9)	0.2749 (8)	0.2439 (7)	3.3 (3)*
C2A	0.1430 (9)	−0.1845 (9)	0.1397 (7)	4.0 (3)*	C2H	0.384 (1)	0.298 (1)	0.1753 (8)	4.7 (3)*
C3A	0.109 (1)	−0.283 (1)	0.1052 (8)	5.0 (3)*	C3H	0.462 (1)	0.368 (1)	0.1823 (8)	5.2 (3)*
C4A	0.102 (1)	−0.312 (1)	0.0272 (8)	4.8 (3)*	C4H	0.510 (1)	0.411 (1)	0.2560 (8)	5.0 (3)*
C5A	0.121 (1)	−0.248 (1)	−0.0212 (8)	5.7 (4)*	C5H	0.4843 (9)	0.3879 (9)	0.3256 (7)	3.8 (3)*
C6A	0.154 (1)	−0.1479 (9)	0.0140 (8)	4.5 (3)*	C6H	0.4011 (8)	0.3164 (8)	0.3187 (7)	3.0 (3)*
C1B	0.0917 (9)	0.0637 (8)	0.1759 (7)	3.3 (3)*	B	−0.084 (1)	−0.421 (1)	0.266 (1)	4.8 (4)*
C2B	0.000 (1)	0.0109 (9)	0.1597 (8)	4.5 (3)*	C1I	−0.109 (1)	−0.5091 (9)	0.3158 (7)	4.3 (3)*
C3B	−0.085 (1)	0.054 (1)	0.1881 (8)	5.0 (3)*	C2I	−0.039 (1)	−0.528 (1)	0.3761 (9)	6.1 (4)*
C4B	−0.080 (1)	0.149 (1)	0.2285 (9)	5.9 (4)*	C3I	−0.056 (1)	−0.606 (1)	0.4196 (9)	7.0 (4)*
C5B	0.009 (1)	0.205 (1)	0.2441 (8)	4.9 (3)*	C4I	−0.141 (1)	−0.662 (1)	0.4012 (9)	6.8 (4)*
C6B	0.0960 (9)	0.1626 (9)	0.2194 (7)	4.1 (3)*	C5I	−0.209 (1)	−0.649 (1)	0.3427 (9)	7.0 (4)*
C1C	0.2134 (9)	0.0751 (8)	0.0578 (7)	3.2 (3)*	C6I	−0.193 (1)	−0.575 (1)	0.2977 (9)	6.0 (4)*
C2C	0.1421 (9)	0.1362 (9)	0.0302 (7)	4.0 (3)*	C1J	−0.176 (1)	−0.4139 (9)	0.1964 (7)	4.3 (3)*
C3C	0.156 (1)	0.1861 (9)	−0.0307 (8)	4.6 (3)*	C2J	−0.272 (1)	−0.391 (1)	0.2182 (8)	5.5 (4)*
C4C	0.237 (1)	0.171 (1)	−0.0697 (8)	5.4 (3)*	C3J	−0.355 (1)	−0.389 (1)	0.1606 (8)	5.6 (4)*
C5C	0.309 (1)	0.109 (1)	−0.0437 (8)	5.6 (4)*	C4J	−0.346 (1)	−0.405 (1)	0.0858 (9)	6.2 (4)*
C6C	0.297 (1)	0.062 (1)	0.0177 (8)	4.9 (3)*	C5J	−0.257 (1)	−0.424 (1)	0.0613 (9)	6.4 (4)*
C1D	0.3766 (9)	−0.1543 (8)	0.3230 (7)	3.4 (3)*	C6J	−0.173 (1)	−0.427 (1)	0.1184 (8)	5.2 (3)*
C2D	0.285 (1)	−0.1423 (9)	0.3510 (8)	4.5 (3)*	C1K	−0.0601 (9)	−0.3102 (9)	0.3213 (7)	4.0 (3)*
C3D	0.259 (1)	−0.196 (1)	0.4069 (9)	5.9 (4)*	C2K	−0.0353 (9)	−0.2301 (9)	0.2854 (7)	4.0 (3)*
C4D	0.322 (1)	−0.260 (1)	0.4365 (8)	5.2 (3)*	C3K	−0.009 (1)	−0.133 (1)	0.3272 (8)	5.1 (3)*
C5D	0.415 (1)	−0.272 (1)	0.4108 (8)	5.7 (4)	C4K	−0.006 (1)	−0.115 (1)	0.4068 (8)	5.5 (3)*
C6D	0.442 (1)	−0.219 (1)	0.3554 (8)	5.3 (3)*	C5K	−0.032 (1)	−0.188 (1)	0.4442 (9)	6.0 (4)*
C1E	0.5423 (9)	−0.0582 (8)	0.2796 (7)	3.2 (3)*	C6K	−0.059 (1)	−0.285 (1)	0.4016 (8)	5.0 (3)*
C2E	0.614 (1)	−0.124 (1)	0.2520 (8)	4.6 (3)*	C1L	0.0201 (9)	−0.4589 (9)	0.2307 (7)	4.1 (3)*
C3E	0.713 (1)	−0.105 (1)	0.2840 (8)	5.0 (3)*	C2L	0.114 (1)	−0.416 (1)	0.2665 (8)	5.0 (3)*
C4E	0.744 (1)	−0.028 (1)	0.3428 (8)	5.4 (3)*	C3L	0.204 (1)	−0.449 (1)	0.2363 (8)	5.4 (3)*
C5E	0.676 (1)	0.038 (1)	0.3722 (8)	5.3 (3)*	C4L	0.197 (1)	−0.524 (1)	0.1721 (8)	5.3 (3)*
C6E	0.5730 (9)	0.0216 (9)	0.3400 (7)	3.8 (3)*	C5L	0.109 (1)	−0.571 (1)	0.1386 (9)	6.1 (4)*
C1F	0.4051 (9)	−0.1807 (8)	0.1589 (7)	3.5 (3)*	C6L	0.021 (1)	−0.5383 (9)	0.1699 (8)	4.6 (3)*
C2F	0.436 (1)	−0.153 (1)	0.0944 (8)	4.8 (3)*	O	0.526 (1)	0.0931 (9)	0.1351 (7)	7.6 (3)*
C3F	0.431 (1)	−0.222 (1)	0.0230 (8)	5.5 (3)*	C	0.621 (2)	0.142 (1)	0.176 (1)	10.0 (6)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

reaction of 2 equiv of *o*-(diphenylphosphino)benzaldehyde, PCHO, with 2,2′-dimethyl-6,6′-diaminobiphenyl, NNBP, as shown in eq 1. PCHO was prepared from *o*-bromobenzaldehyde as described by Shiemenz and Kaack[10] and by Rauchfuss et al.[11] The synthetic versatility of this compound with respect to the synthesis of new ligands has recently been demonstrated.[18] The preparation of *d,l*-NNBP was carried out by using the methods of Carlin and Foltz[7] and of Holm et al.[8] The resolution of the compound into its *d* and *l* enantiomers was accomplished by use of the method of Meisenheimer and Horing.[9] The specific rotations of *d*- and *l*-NNBP with use of 10% aqueous HCl as solvent were $[\alpha]_D$ = +35 and −34°, respectively, and are in good agreement with the literature values.[9] PCHO and NNBP were characterized by standard spectroscopic techniques and by their melting points, which were in good agreement with literature values (see Experimental Section). The Schiff base condensation reaction of PCHO with NNBP was carried out under a N_2 atmosphere with use of benzene as solvent to which a catalytic amount of H_2SO_4 had been added. The PPNN ligand was formed in 96% yield and was characterized by IR [ν(C=N) = 1630 cm^{-1}] and ^{31}P and ^{1}H NMR spectroscopy (see Experimental Section), elemental analysis, and mass spectroscopy [P$^+$, *m/e* 756]. The syntheses of the optically active ligands *d*-PPNN and *l*-PPNN were accomplished by the same procedure with the use of the resolved NNPB compounds. The specific and molecular rotations of the *d* and *l* enantiomers were ($CHCl_3$ solvent at 25 °C) as follows ($[\alpha]_D$, $[M]_D$: +198, +1493°; −193, −1457°. See the Experimental Section for details of the synthesis and characterization.

The [Rh(PPNN)]BPh_4 complex, **1**, was prepared by treating [Rh(cod)Cl]$_2$ with a 10% mol excess of PPNN ligand in the presence of the noncoordinating anion BPh_4^-. Complex **1** was isolated as olive green microcrystals in high yield and is slightly air sensitive in solution but stable in the solid state. The PPNN ligand is tetradentate in **1** (vide infra), giving rise to a four-coordinate complex of Rh(I). The ^{31}P NMR resonance of **1** [(CD_2Cl_2) δ 51.9 (d, J = 172 Hz)] is shifted downfield from that of the free PPNN ligand [δ −13.4 (s)]. A shift of this magnitude upon coordination is typical for Rh(I) complexes that have "PN" chelating ligands.[19-22] In addition, the magnitude of the Rh–P coupling constant is typical for a trans N–Rh–P coordination. For example, J(P–H) = 171

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(18) Rauchfuss, T. B. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, **1983**; Chapter 7, p 239.

(19) Anderson, M. P.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1983**, *22*, 2644.

(20) Anderson, M. P.; Pignolet, L. H. *Organometallics* **1983**, *2*, 1246.

(21) Anderson, M. P.; Tso, C. C.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1983**, *22*, 3267.

(22) Anderson, M. A. Ph.D. Dissertation, University of Minnesota, **1983**.

Hz in [Rh(PN)$_2$]BF$_4$ (PN = 1-(2′-pyridyl)-2-(diphenylphosphino)ethane, which has been shown to have a square-planar geometry with trans P–Rh–N bonding by single-crystal X-ray diffraction.[22] The ^{1}H NMR spectrum of **1** showed that the cod group of the starting material had been replaced by the PPNN ligand and that the methyl groups of the PPNN ligand are equivalent [CH$_3$ δ 2.1 (s)]. The signal for the methyne proton of **1** could not be resolved from the signals of the phenyl protons. The ν(C=N) vibration in **1** (1620 cm^{-1}) was unshifted from that of the free PPNN ligand. The spectroscopic results suggest that the PPNN ligand in **1** is tetracoordinate, which should give rise to an approximately planar coordination geometry. This has been confirmed by a single-crystal X-ray diffraction analysis (vide infra).

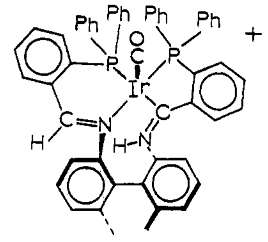
The [Ir(PPNN)]BPh$_4$ complex, **2**, was prepared from the reaction of Ir(PPh$_3$)$_2$(N$_2$)Cl with a slight molar excess of PPNN with the use of CH$_2$Cl$_2$ as solvent. Complex **2** was isolated as black microcrystals upon the addition of NaBPh$_4$ in MeOH solution. This complex was air sensitive in solution, and in the solid state a slow decomposition was observed at room temperature. The complex can be stored indefinitely at 0 °C under a N$_2$ atmosphere. The spectroscopic results for **2** are consistent with a tetracoordinated PPNN ligand and are similar to the results obtained with **1**. The ^{31}P NMR spectrum consisted of a singlet resonance [(CH$_2$Cl$_2$) δ 19.9], and in the ^{1}H NMR the methyl groups showed one resonance [(acetone-d_6) δ 2.1] that was shifted 0.3 ppm downfield from that of the free PPNN ligand. The signal assigned to the methyne proton was observed as a doublet [δ 8.7 (J = 10 Hz)].

The *d* and *l* optically active complexes of **1** and **2** were synthesized by the same procedure outlined above but with the use of the optically active PPNN ligands. These complexes had identical spectroscopic properties as observed for their racemic mixtures. It was not possible to measure accurate optical rotations for these complexes due to theiry very high optical densities in the wavelength region available on our polarimeter. However, approximate molecular rotations have been measured for **1** synthesized with *d* and *l*-PPNN (CHCl$_3$, 5×10^{-4} g/mL): $[M]_{578\text{nm}} = +8 \times 10^2, -6 \times 10^{2\,\circ}$, respectively. These values are not very accurate and decreased with time because the dilute solutions were unstable. The difference between the positive and negative rotations is not considered to be significant.

Complexes **1** and **2** were deeply colored in solid and solution. The electronic absorption spectra of these compounds recorded with use of CH$_2$Cl$_2$ as the solvent revealed several intense bands in the visible region (see Experimental Section). The dark green and red colors of these compounds, respectively, are typical for Rh(I) and Ir(I) complexes that contain conjugated N donor ligands such as bipyridine or *o*-phenanthroline.[23] Dark colors have also been noted for PPNN donor type complexes that contain nitrogen imine type functions.[6]

Reactivity of [M(PPNN)]$^+$ Complexes with H$_2$ and CO. The susceptibility of [M(PPNN)]$^+$ (M = Ph, Ir) toward oxidative addition of H$_2$ and carbonylation has been investigated. [Rh(PPNN)]$^+$ (**1**) was found to be unreactive toward H$_2$ at 50 psi in CDCl$_3$ solution as determined by ^{1}H and ^{31}P NMR analysis. Reaction of **1** as the BF$_4^-$ salt with CO at 1 atm in CHCl$_3$ solution occurred slowly and incompletely at room temperature. A new doublet resonance appeared in the ^{31}P NMR spectrum [(CHCl$_3$) δ 47.0 (J = 146 Hz)], but the doublet resonance of the starting complex remained. The reaction did not go to completion even after several hours, and the brown-green color of the starting solution persisted. A carbonyl absorption in the infrared spectrum was observed [(CHCl$_3$) ν(CO) v 2005 cm^{-1}]. These observations are consistent with the partial formation of a CO adduct of **1**. A singlet resonance also appeared in the ^{31}P NMR spectrum (δ 31.6) along with the resonance of the CO adduct. This resonance was apparently due to the formation of oxidized PPNN ligand, which most likely results from reaction with a molecular oxygen contaminant in the CO. A similar resonance has been observed from the reaction of PPNN with H$_2$O$_2$ in acetone solution.

The iridium complex **2** was found to be significantly more reactive toward CO and H$_2$ than complex **1**. Upon exposure to 1 atm of CO in CH$_2$Cl$_2$ solution at 25 °C the dark brown solution of **2** changed to a yellow-orange color. The reaction was complete after ca. 1 h. Two carbonyl stretches were present in the infrared spectrum [ν(CO) = 2030, 2130 cm^{-1}], and ^{31}P NMR data indicated that several compounds were present (see Experimental Section). It was not possible to analyze these spectra since several compounds were obviously present. A good quality crystal was isolated from this solution and was subjected to X-ray analysis.[25] The crystal structure consisted of a cocrystallized mixture of the starting complex, **2**, and a square-pyramidal five-coordinate CO adduct, **3**, in which one methyne carbon atom was coordinated to the Ir as shown in the drawing of compound **3**. The structure was refined by using a disordered model that included a 60:40 mixture of **3** and **2**, respectively. This ratio was determined by allowing the multiplicities of the disordered atoms to vary. Although the distances and angles within **3** are consistent with this formulation, the complicated nature of the disorder prevented a completely satisfactory result. However, the presence of the apical CO group and the methyne carbon–iridium bond is unambiguous. The details of this structure and of the chemistry of this compound will be published elsewhere when additional experiments have been completed. The presence of the Ir–C bond in **3** raises some interesting questions about the nature of PPNN complexes of iridium in general and is reminiscent of the Ir–C bond recently found in tris(2,2′-bipyridine)iridium(III) complexes.[26,27] A single-crystal X-ray analysis was carried out on **2** (vide infra) because of the possibility of Ir–C bonding in the parent complex.



3

The reaction of **2** with 1 atm of H$_2$ in acetone solution at 25 °C also occurred. The dark orange color of **2** changed to yellow as the reaction progressed. A yellow microcrystalline solid was isolated. ^{31}P and ^{1}H NMR analysis of an acetone-d_6

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(23) Mestroni, G.; Spogliarich, R.; Camus, A.; Martinelli, F.; Zassinovich, G. *J. Organomet. Chem.* **157**, 345. Mestroni, G.; Zassinovich, G.; Camus, A. *J. Organomet. Chem.* **1977**, *140*, 63.

(24) Martin, B.; McWhinnie, W. R.; Waind, G. M. *J. Inorg. Nucl. Chem.* **1961**, *23*, 207.

(25) Crystal parameters: $P1$; a = 13.442 (3), b = 13.749 (4), c = 17.212 (2) Å; α = 99.61 (2), β = 98.57 (1), γ = 91.87 (2)°; V = 3096 (2) Å^3; Z = 2. The crystal parameters are very similar to those of **1** and **2**. A total of 9676 unique reflections were collected in the 2θ range of 0–48°, and the structure was solved by conventional methods as described in the Experimental Section for **1** and **2**. Full-matrix least-squares refinement converged the structure to R = 3.5% and R_w = 4.6% for 523 variables and 6538 observations [$F_o^2 \geq 3\sigma(F_o^2)$].

(26) Nord, G.; Hazell, A. C.; Hazell, R. G.; Farver, O. *Inorg. Chem.* **1983**, *22*, 3429.

(27) Wickramasinghe, W. A.; Bird, P. H.; Serpone, N. *J. Chem. Soc., Chem. Commun.* **1981**, 1284.

Table **IV**. Selected Distances and Angles in [Rh(PPNN)]$BPh_4 \cdot CH_3OH$ (**1**) and [Ir(PPNN)]$BPh_4 \cdot CH_3OH$ (**2**)

	1	**2**		1	2
Distances, Å					
M–P1	2.228 (1)	2.257 (3)	C1B–C2B	1.382 (5)	1.38 (1)
M–P2	2.216 (1)	2.231 (2)	C2B–C3B	1.388 (5)	1.42 (1)
M–N1	2.092 (3)	2.11 (1)	C3B–C4B	1.373 (5)	1.35 (2)
M–N2	2.119 (3)	2.07 (1)	C4B–C5B	1.380 (5)	1.38 (2)
P1–C1A	1.827 (3)	1.82 (1)	C5B–C6B	1.392 (5)	1.40 (1)
P1–C1B	1.838 (3)	1.84 (1)	C6B–C1B	1.412 (5)	1.41 (1)
P1–C1C	1.825 (3)	1.81 (1)	C1E–C2E	1.390 (5)	1.41 (1)
P2–C1D	1.833 (3)	1.82 (1)	C2E–C3E	1.386 (5)	1.37 (1)
P2–C1E	1.841 (3)	1.83 (1)	C3E–C4E	1.381 (5)	1.35 (2)
P2–C1F	1.815 (3)	1.83 (1)	C4E–C5E	1.364 (5)	1.38 (2)
N1–C1	1.274 (4)	1.26 (1)	C5E–C6E	1.388 (5)	1.42 (1)
N1–C1H	1.439 (4)	1.49 (1)	C6E–C1E	1.407 (5)	1.38 (1)
N2–C2	1.282 (4)	1.32 (1)	C1G–C2G	1.376 (5)	1.39 (1)
N2–C1G	1.448 (4)	1.46 (1)	C2G–C3G	1.375 (5)	1.38 (2)
C1–C6B	1.461 (5)	1.45 (1)	C3G–C4G	1.374 (5)	1.40 (2)
C2–C6E	1.454 (5)	1.49 (1)	C4G–C5G	1.382 (5)	1.37 (1)
C6G–C6H	1.484 (5)	1.45 (1)	C5G–C6G	1.408 (5)	1.42 (1)
C5G–C3	1.510 (5)	1.50 (1)	C6G–C1G	1.399 (5)	1.39 (1)
C5H–C4	1.503 (5)	1.46 (2)	C1H–C2H	1.374 (5)	1.38 (1)
C5H–C6H	1.406 (5)	1.44 (1)	C2H–C3H	1.380 (5)	1.39 (2)
C6H–C1H	1.383 (4)	1.37 (1)	C3H–C4H	1.376 (5)	1.37 (2)
			C4H–C5H	1.382 (5)	1.39 (1)
Angles, deg					
P1–M–N1	82.11 (7)	81.7 (2)	N1–C1–C6B	124.8 (3)	125.0 (9)
P2–M–N2	86.72 (7)	87.4 (2)	N2–C2–C6E	127.6 (3)	124.9 (9)
P1–M–P2	103.11 (3)	103.6 (1)	P1–C1B–C6B	120.2 (3)	120.0 (8)
N1–M–N2	88.9 (1)	88.1 (3)	P2–C1E–C6E	120.3 (3)	118.7 (7)
P1–M–N2	167.13 (8)	166.5 (2)	C1–C6B–C1B	122.2 (3)	122.0 (9)
P2–M–N1	172.58 (8)	172.8 (3)	C2–C6E–C1E	124.2 (3)	127 (1)
M–P1–C1A	126.6 (1)	124.8 (3)	N1–C1H–C6H	118.1 (3)	115.8 (9)
M–P1–C1B	105.3 (1)	105.1 (3)	N1–C1H–C2H	119.3 (3)	118.1 (9)
M–P1–C1C	113.4 (1)	114.1 (3)	N2–C1G–C6G	119.2 (3)	119.1 (9)
M–P2–C1D	115.6 (1)	116.0 (3)	N2–C1G–C2G	119.3 (3)	117.9 (9)
M–P2–C1E	110.3 (1)	109.9 (3)	C1H–C6H–C6G	118.1 (3)	120.6 (9)
M–P2–C1F	120.7 (1)	119.4 (3)	C1H–C6H–C5H	118.2 (3)	116.5 (9)
M–N1–C1	130.4 (2)	131.1 (7)	C1G–C6G–C6H	119.6 (3)	119.8 (8)
M–N1–C1H	111.7 (2)	110.5 (6)	C1G–C6G–C5G	118.2 (3)	116.3 (9)
M–N2–C2	131.4 (2)	132.0 (7)	C4H–C5H–C6H	121.4 (3)	117 (1)
M–N2–C1G	114.0 (2)	116.8 (6)	C4H–C5H–C4	119.9 (3)	121 (1)
			C4G–C5G–C6G	119.2 (3)	122 (1)
			C4G–C5G–C3	120.6 (3)	118 (1)

solution of this product showed the presence of resonances (see Experimental Section) that are consistent with the *cis*-dihydrido complex $[Ir(H)_2(PPNN)]BPh_4$. The presence of the C–N stretching vibrations in the IR and the absence of an N–H resonance in the ^1H NMR shows that the imine function has not been hydrogenated. The formation of a *cis*-dihydrido complex suggests that this compound may have catalytic applications.

Preliminary experiments carried out thus far have not shown significant catalytic behavior for the hydrogenation of olefins using **1** or **2**. However, experiments currently being run that makes use of a variety of conditions and substrates should show if complexes **1** and **2** will function as catalysts for asymmetric induction. In any case, the reaction chemistry of **2** appears to be interesting and potentially important in light of recent reports on the unique reaction chemistry of Rh(I) complexes that contain nitrogen donor ligands.[28,29]

X-ray Structure Determinations. The single-crystal X-ray structures of **1** and **2** were determined. The complexes both crystallize as methanol solvates, and they are essentially isostructural. The unit cell dimensions of both compounds are very similar as are the crystallographic coordinates of all equivalent atoms (Tables I–III). The molecular structures of both cations and anions are labeled so that the structurally equivalent atoms have the same names. Figure 1 presents an ORTEP perspective of the molecular structure of the cation of **1**. A similar view of the cation of **2** and a stereoview of **1** are shown as supplementary material.[17] The ORTEP views of the cations of **1** and **2** are nearly identical and illutrate the isostructural nature of these compounds. Selected distances and angles within the cations of **1** and **2** are presented in Table IV. The equivalent distances and angles for the two cations are tabulated in adjacent columns so they may be easily compared. Most of the equivalent distances and angles are the same within experimental error except for those that involve the metal atoms. The carbon atoms of the four phenyl rings in the BPh_4^- anion are labeled C1I–C6I, C1J–C6J, C1K–C6K, and C1L–C6L. Distances and angles within the anions and solvate molecules are included as supplementary material, and the values are normal.[17] The cations, anions, and methanol solvate molecules are well separated. There are no unusually short intermolecular contacts.

The results of the X-ray structure determinations for both complexes show that the PPNN ligand is tetradentate and that the metal adopts a slightly distorted square-planar coordination geometry. The only significant differences between the two structures involve distances associated with the metals, and these differences reflect the slightly larger radius of iridium (1.36 Å) compared to that of rhodium (1.34 Å).[30] Since these

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(28) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302.

(29) Brunner, H.; Riepel, G. *Angew. Chem. Suppl.* **1982**, 769.

(30) Gordon, A. J.; Ford, R. A. "The Chemists Companion"; Wiley-Interscience: New York, **1972**; p 85.

two structures are so similar, they will be described as a single compound and all distances and angles subsequently quoted in the text will be for **1** and **2**, respectively, separated by commas. The slight deviation of the coordination geometry away from idealized square planar is evident from the dihedral angle between the planes MP1N1 and MP2N2 [10.9, 10.3°] and from the P1MN1 and P2MN2 "bite" angles [82.11(7), 81.7(2)° and 86.72(7), 87.4(2)°, respectively], which are significantly less than 90°. A table of least-squares planes is included as supplementary material.[17] The nonplanar nature of the coordination core geometry may be due to the large twist between the two phenyl rings of the biphenyl. The dihedral angle between the least-squares planes of the G and H phenyl rings is 69, 68°. This twist causes the chirality of the resolved complexes, and rotation about the C6H–C6G bond (racemization) is prevented by the repulsion between the 6,6′-methyl substituents. It is surprising that the coordination core geometry is so nearly planar because the twisted biphenyl causes phenyl rings B and E to be tilted significantly away from the plane of the coordination core. The dihedral angles between the P1P2N1N2 least-squares plane and planes of phenyl rings B and E are 50, 51° and −35, −35°, respectively. The phenyl rings within the cations are planar within experimental error, and the distances and angles for these rings are normal. The distances and angles within the substituted biphenyl groups are also normal and are similar to values observed in [Δ-2,2′-bis(salicylidenaminato)-D(+)-(*R*)-6,6′-dimethylbiphenyl]cobalt(II), which also contains a twisted 6,6′-dimethylbiphenyl group attached to a metal via the 2,2′ nitrogen atoms.[31] The lengths of the carbon–nitrogen double bonds [C1–N1 and C2–N2: 1.274 (4), 1.26 (1) Å, and 1.282 (4), 1.32 (1) Å] are also normal[31] and confirm the Schiff base nature of the ligand.

The M–P distances [M–P1 and M–P2: 2.228 (1), 2.257 (3) Å and 2.216 (1), 2.231 (2) Å] are short compared to those in complexes where the phosphorus atoms are mutually trans. Typical values for Rh and Ir complexes with trans phosphines are 2.30–2.34 Å.[21] In complexes **1** and **2** the phosphorus atoms are trans to nitrogen atoms [P1–M–N2 and P2–M–N1: 167.13 (8), 166.5 (2)° and 172.58 (8), 172.8 (3)°], and in such cases the M–P distances are usually short due to the weak trans influence of nitrogen compared with that of phosphorus. The average Rh–P distance trans to nitrogen in $[Rh(PN)_2]BF_4$ is 2.217 (1) Å,[22] and in $[Rh_2(CO)(\mu\text{-}PNP)_2](BPh_4)_2$ where PNP = 2-[bis(diphenylphosphino)methyl]pyridine, the average Rh–P distance trans to nitrogen is 2.233 (4) Å.[20] The Rh–P distances in these complexes are similar to the average distances in **1** and **2** [2.222 (1), 2.244 (3) Å]. The M–N distances in complexes **1** and **2** are similar and average 2.10 (1) Å. This distance is short compared with other Rh complexes with chelated PN type ligands where the nitrogen is trans to a phosphorus atom [2.129 (2) Å in $Rh(PN)_2^+$[22] and 2.15 (1) Å in $Rh_2(CO)(\mu\text{-}PNP)_2^{2+}$[20]].

The overall stereochemistry of complex **1** and **2** is best viewed in the stereoscopic drawing included as supplementary material.[17] The positioning of the phenyl rings creates a chiral pocket at the metal center such that entering substrates may bind in a stereospecific manner. Experiments in progress are designed to test this possibility.

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Registry No. **1**, 93565-23-2; **2**, 93565-26-5; **3**, 93565-29-8; [*d*-Ru(PPNN)]BPh_4, 93711-49-0; [*l*-Rh(PPNN)]BPh_4, 93711-51-4; NNBP, 20261-65-8; *l*-NNBP *d*-tartrate, 93711-52-5; *l*-NNBP, 3685-05-0; *d*-NNBP *l*-tartrate, 93711-53-6; *d*-NNBP, 3685-06-1; PPNN, 93565-30-1; [Rh(1,5-cyclooctadiene)Cl]$_2$, 12092-47-6; [*d*,*l*-Rh(PPNN)]BF_4, 93565-27-6; [Rh(ethylene)Cl]$_2$, 12122-73-5; $Ir(PPh_3)_2(N_2)Cl$, 15695-36-0; 2,2′-dimethyl-6,6′-dinitrobiphenyl, 55153-02-1; *o*-(diphenylphosphino)benzaldehyde, 50777-76-9.

Supplementary Material Available: ORTEP drawing of **2**, stereoview of **1**, and tables of distances and angles within the BPh_4 anions, general temperature factor expressions, positional parameters for the hydrogen atoms, weighted least-squares planes, and structure factor amplitudes for **1** and **2** (66 pages). Ordering information is given on any current masthead page.

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(31) Pignolet, L. H.; Taylor, R. P.; Horrocks, W. D., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 5457.