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Rhodium and Iridium Complexes with the PN Donor Ligand $(C_6H_5)_2P(CH_2)_2C_5H_4N$. Crystal and Molecular Structures of $Ir(PN)_2(CO)Cl$, $Ir(PN)(CO)Cl$, and $[Rh(PN)_2]PF_6$

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Several new PN [1-(2-pyridyl)-2-(diphenylphosphino)ethane] complexes of rhodium and iridium have been synthesized. $[Ir(PN)_2]^+$ (**1**) was synthesized from $[Ir(PN)(cod)]^+$ (cod = cyclooctadiene) and an excess of PN in acetone solution and characterized by IR, ^1H NMR, and ^{31}P NMR spectroscopy. **1** reacted with H_2 in acetonitrile solution to form the *cis*-dihydride $[Ir(PN)_2(H)_2]^+$ (**2**). $Ir(PN)_2(CO)Cl$ (**3**) and $Ir(PN)(CO)Cl$ (**4**) were synthesized from the reaction of 2-methoxyethanol solutions of $[Ir(CO)_2Cl_2]^-$ with 2 and 1 equiv of PN, respectively. These four-coordinate square-planar complexes were characterized by IR and ^{31}P NMR spectroscopy and by single-crystal X-ray analysis (**3**, monoclinic $P2_1/a$, $a = 13.178$ (2) Å, $b = 13.579$ (2) Å, $c = 9.672$ (2) Å, $\beta = 93.84$ (1)°, $Z = 2$, $R = 0.025$; **4**·Et_2O, triclinic $P\bar{1}$, $a = 11.079$ (3) Å, $b = 12.901$ (3) Å, $c = 8.377$ (3) Å, $\alpha = 101.95$ (3)°, $\beta = 109.50$ (3)°, $\gamma = 73.01$ (2)°, $Z = 2$, $R = 0.025$). In **3**, both PN ligands are monodentate coordinated through the phosphorus atom. $[Ir(PN)_2(CO)]^+$ (**5**) was synthesized from **3** with KPF_6 in acetone solution and characterized by IR and ^{31}P NMR spectroscopy as a four-coordinate square-planar complex with one PN ligand bidentate and one monodentate bonded through the phosphorus atom. The reactivity of **5** with H_2 and H^+ was also examined. The reaction of PN with an acetone solution of $[Rh(nbd)Cl]_2$ (nbd = norbornadiene) treated with $AgPF_6$ produced a new chelated complex, $[Rh(PN)_2]PF_6$ (**8**(PF_6)), which was characterized by IR and ^{31}P NMR spectroscopy and by single-crystal X-ray diffraction (monoclinic $P2_1/n$, $a = 10.714$ (2) Å, $b = 21.774$ (2) Å, $c = 15.915$ (4) Å, $\beta = 99.95$ (2)°, $Z = 4$, $R = 0.039$), and was shown to have a distorted square-planar cis geometry. Complex **8** reacted with CO to form the carbonyl adduct, $[Rh(PN)_2(CO)]^+$ (**9**). The reaction of the tridentate ligand 2-[bis(diphenylphosphino)methyl]pyridine (PNP) with $[Rh(CO)_2Cl_2]^-$ under refluxing conditions of 2-methoxyethanol/toluene produced the 4-coordinate complex $Rh(PN')(CO)Cl$ (**11**). The ligand PN′ = 2-[(diphenylphosphino)methyl]pyridine resulted from P–C bond cleavage of PNP. The PN analogue of **11**, $Rh(PN)(CO)Cl$ (**10**), was also synthesized by reaction of $[Rh(CO)_2Cl_2]^-$ with PN in 2-methoxyethanol/toluene solution. Complexes **9**–**11** were characterized by IR and ^{31}P NMR spectroscopy. The activities for the decarbonylation of benzaldehyde with use of **1**(PF_6) and **8**(BF_4) were found to be 9 and 10 turnovers/h, respectively, at 150 °C in neat benzaldehyde, and their catalytic properties were studied. The results are discussed and compared to the catalytic activity and proposed mechanism of the decarbonylation reaction using $[M(dppp)_2]^+$ (M = Rh, Ir; dppp = 1,3-bis(diphenylphosphino)propane).

Introduction

We report in this paper the synthesis, characterization, and reactivity of several new rhodium and iridium complexes containing the potentially bidentate PN ligand (PN = 1-(2-pyridyl)-2-(diphenylphosphino)ethane).[1] Our initial interest in this ligand arose from studies of the catalytic decarbonylation of aldehydes using diphosphine complexes of rhodium and iridium, $[M(PP)_2]^+$ ($PP = Ph_2P(CH_2)_nPPh_2$, $n = 1$–4).[2-5] These cationic complexes of rhodium have been shown to give good catalytic activities, produce high product yields, be highly selective and robust, and be of general utility in organic synthesis.[2-6] The iridium analogues of these complexes, however, displayed much lower catalytic activities.[5] Mechanistic studies with the catalysts $[Rh(dppe)_2]^+$ and $[Rh(dppp)_2]^+$ (dppe and dppp are PP ligands where $n = 2$ and 3, respectively) had suggested that M–P bond rupture was an important and rate-limiting step in the catalytic decarbonylation cycle.[3-5] Since M–N bonds are known to be more labile than M–P bonds in some complexes,[7-10] it was hoped that the use of a bidentate ligand that contained one phosphorus and one nitrogen donor would lead to higher catalytic activities. It was also expected that the resulting $[M(PN)_2]^+$ complex may be more electron rich than the dppp analogue and thereby facilitate oxidative addition. Both of these factors should have an important effect on the rate and mechanism of the catalytic decarbonylation of aldehydes.[5] Unfortunately, the PN complexes of rhodium were not good catalysts for the decarbonylation of benzaldehyde: $[Rh(PN)_2]BF_4$ showed an activity for the formation of benzene of 10 turnovers/h at 150 °C compared to 1.1×10^2 turnovers/h for $[Rh(dppp)_2]BF_4$. The opposite trend was observed for the iridium analogues. A thorough discussion of the results for the decarbonylation of benzaldehyde using $[M(PN)_2]^+$ (M = Rh, Ir) will be presented. As part of this general investigation and in order to obtain a better understanding of the differences in structure and reactivity between PN and PP complexes, a study of the synthesis and reactivity of various rhodium and iridium PN complexes was also initiated.[1]

There is also general interest in complexes containing unsymmetrical bidentate PN donor ligands because of their potential as catalysts[10-15] and their proven usefulness in the construction of heterobimetallic species.[16-20] In such complexes the PN type donor ligand can act as a chelating bidentate ligand, a monodentate ligand coordinated through the phosphorus atom, or a bridging ligand in dimeric species. Because PN could adopt any of these bonding modes, single-crystal X-ray diffraction analysis was utilized in the characterization of the new PN complexes Ir(P-

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N)$_2$(CO)Cl (**3**) and Ir(PN)(CO)Cl (**4**). Both **3** and **4** were shown to be mononuclear square-planar complexes, with two trans monodentate PN ligands in **3**, and one bidentate ligand in **4**. In addition to the synthesis, characterization, and reactivity of **3** and **4**, we report the synthesis, characterization, and reactivity of $[Ir(PN)_2]^+$ (**1**). The Rh analogue of **1**, $[Rh(PN)_2]BF_4$ (**8**(BF_4)), was also prepared, and its catalytic, structural and chemical properties were investigated.

Experimental Section

Physical Measurements and Reagents. ^1H and ^{31}P NMR spectra were recorded at 300 and 121.5 MHz, respectively, with the use of a Nicolet NT-300 spectrometer. ^{31}P NMR spectra were run with ^1H decoupling and are reported in ppm relative to the external standard H_3PO_4 (85%) with positive shifts downfield and at ambient probe temperature, unless otherwise noted. IR spectra were recorded on a Beckman Model 4250 grating spectrophotometer and mass spectra on a Finnigan 4000 mass spectrometer. Analytical data were determined by Galbraith Laboratories. 1-(2-pyridyl)-2-(diphenyl-phosphino)ethane (PN),[1] [Ir(PN)(cod)]PF_6,[1] Li[Ir(CO)$_2$Cl$_2$],[21] [Rh(nbd)Cl]$_2$,[22] [Rh(C_2H_4)Cl]$_2$,[23] and 2-[bis(diphenylphosphino)methyl]pyridine (PNP)[24] were prepared as described elsewhere. 1,5-Cyclooctadiene (cod) was purchased from Aldrich Chemical Co. and used without further purification. D_2 and CO were obtained from the Matheson Co. All solvents were reagent grade, and 2-methoxyethanol was distilled over $MgSO_4$. HBF_4 was obtained from the J. T. Baker Chemical Co. as a 48–50% aqueous solution. Norbornadiene (nbd), $AgBF_4$, $AgPF_6$, and $NaBH_4$ were purchased from Aldrich Chemical Co. and used without further purification. Benzaldehyde was obtained from Mallinckrodt, Inc., purified by vacuum distillation, and stored in the dark under N_2 and over Na_2CO_3 or K_2CO_3 and neutral alumina after distillation. All manipulations were carried out under a purified N_2 atmosphere by using standard schlenk techniques. Catalytic decarbonylation measurements were performed in the same manner as described previously.[2]

Synthesis of Compounds. $[Ir(PN)_2]PF_6$ (1(PF_6)). A red-orange solution of [Ir(PN)(cod)]PF_6 (100 mg, 0.14 mmol) in 1 mL of acetone was added to 199 mg of PN (0.68 mmol). This solution was stirred at 50 °C for 30 min, during which time the solution color faded to a light orange. Opaque, dome-shaped orange crystals were obtained by layering this solution with Et_2O. Recrystallization of these crystals from CH_2Cl_2/Et_2O afforded transparent platelike orange crystals (76% yield). Anal. Calcd for $IrC_{38}H_{36}N_2P_3F_6{\cdot}0.45CH_2Cl_2$: C, 48.19; H, 3.88; N, 2.92. Found: C, 48.19; H, 4.05; N, 2.92. The presence of the CH_2Cl_2 solvate was verified by ^1H NMR. ^{31}P NMR (CH_2Cl_2): δ 14.1 (singlet). IR (KBr): ν(py CN) = 1610 cm^{-1}.

$[Ir(PN)_2(H)_2]PF_6$ (2(PF_6)) was generated in situ by bubbling H_2 through an orange CD_3CN solution of **1**(PF_6) for 15 min at 25 °C. No immediate color change was observed; however, after standing for 24 h under an H_2 atmosphere, the solution became colorless. The ^1H NMR spectrum of the CD_3CN solution showed hydride resonances due only to **2**; however, the ^{31}P NMR spectrum indicated the presence of another non-hydride species (see Discussion). ^{31}P NMR (CD_3CN): δ 12.8 and 12.5 (two overlapping doublets, $J_{P-P} \approx 40$ Hz). ^1H NMR (CD_3CN): δ −8.21 (H_X, d of d of d, $J_{transP-H} = 144$ Hz, $J_{cisP-H} = 19$ Hz, $J_{cisH-H} = 4$ Hz, int = 1), −20.22 (H_A, d of d of d, $J_{cisP-H} = 19$ and 12.5 Hz, $J_{cisH-H} = 4$ Hz, int = 1).

$Ir(PN)_2(CO)Cl$ (3). A solution of PN (496 mg, 1.70 mmol) in 3 mL of 2-methoxyethanol was added to a pale yellow solution of Li[Ir(CO)$_2$Cl$_2$] (0.85 mmol) in 4 mL of 2-methoxyethanol. The resulting bright yellow solution was stirred for 12 h during which time a yellow powder precipitated from the solution. This powder was filtered and washed with acetone. Recrystallization from CH_2Cl_2/Et_2O afforded yellow crystals in 78% yield. Anal. Calcd for $IrC_{39}H_{36}P_2N_2ClO$: C, 55.88; H, 4.33; N, 3.34. Found: C, 56.23; H, 4.75; N, 3.26. ^{31}P NMR (CH_2Cl_2): δ 20.3 (singlet). IR (CH_2Cl_2): ν(CO) = 1958 cm^{-1}; ν(py CN) = 1591 cm^{-1}.

[Ir(PN)(CO)Cl]·Et_2O (4·Et_2O). The preparation of **4** was identical with that of **3** with only 1 equiv of PN used. However, even with the use of 1 equiv of PN, 2-methoxyethanol solutions of **4** were found to be contaminated with **3**. **3** had a much lower solubility in 2-methoxyethanol than **4** and was precipitated by heating the stirred solution at 45 °C for 2 h. **3** was separated by filtration, and Et_2O was added to the yellow filtrate to precipitate crude **4** as a yellow powder. This crude product was dissolved in CH_2Cl_2 and filtered to remove insoluble salts. Recrystallization from CH_2Cl_2/Et_2O gave yellow crystals (yield 35–40%). The Et_2O solvate was removed in vacuo prior to the elemental analysis. Anal. Calcd for $IrC_{20}H_{18}PNOCl$: C, 43.91; H, 3.32; N, 2.56. Found: C, 43.58; H, 3.26; N, 2.49. ^{31}P NMR (CH_2Cl_2): δ 15.9 (singlet). IR (KBr): ν(CO) = 1976 cm^{-1}; ν(py CN) = 1607 cm^{-1}.

$[Ir(PN)_2(CO)]PF_6$ (5(PF_6)). In a typical preparation, a 10-fold excess of KPF_6 (220 mg, 1.2 mmol) was added to a stirred suspension of powdered $Ir(PN)_2(CO)Cl$ (**3**) (100 mg, 0.12 mmol) in 10 mL of acetone. After 30 min, **3** had almost completely dissolved, giving a yellow solution. This solution was filtered, and the resulting filtrate was concentrated in vacuo until the acetone was completely removed. The remaining yellow residue was redissolved in CH_2Cl_2 and filtered to remove insoluble potassium salts. CH_2Cl_2 was removed from this yellow filtrate in vacuo, yielding a flaky, yellow precipitate (yield 90–95%). ^{31}P NMR (CH_2Cl_2, −95 °C, standard = internal trimethyl phosphate (TMP)): δ 23.0 and 19.8 (AB quartet, $J_{P-P} = 265$ Hz). IR (CH_2Cl_2): ν(CO) = 1995 cm^{-1}; ν(py CN) = 1612, 1592 cm^{-1}; ν(PF) = 850 cm^{-1}.

$[Ir(PN)_2(H)_2(CO)]PF_6$ (6(PF_6)). A 75-mg sample of **5**(PF_6) was dissolved in 3 mL of CH_2Cl_2, giving a yellow solution, which was stirred under 1 atm of H_2 for 6 h, during which time the solution faded to a very pale yellow. CH_2Cl_2 was removed by passing a rapid stream of H_2 over this solution while heating it to ca. 35 °C. **6** was left as a sticky, pale yellow residue. Yield: >90% by IR and NMR spectroscopy. ^{31}P NMR ($CDCl_3$): δ 11.9 and 6.3 (AB quartet, $J_{P-P} = 280$ Hz). ^1H NMR ($CDCl_3$): δ −8.29 (d of d of d, $J_{H-H} = 3.9$ Hz, $J_{P-H} = 14.2$ and 18.6 Hz, int = 1), −19.11 (d of d of d, $J_{H-H} = 3.9$ Hz, $J_{P-H} = 10.9$ and 16.3 Hz, int = 1). IR (CH_2Cl_2): ν(IrH) = 2190 (m), 2110 (s) cm^{-1}; ν(CO) = 2010 cm^{-1}; ν(py CN) = 1610, 1595 cm^{-1}.

$[Ir(PN)_2(D)_2(CO)]PF_6$ was synthesized in a manner identical with that used for **6** by using D_2 instead of H_2. IR (CH_2Cl_2): ν(CO) = 2045 cm^{-1}; ν(IrD) = 1590 cm^{-1} (detected with an unusual intensity and broadening in two partially overlapping absorptions). The second ν(IrD) was not detected.

$[Ir(PN)_2H(CO)](BF_4)_2$ (7(BF_4)$_2$). To a stirring solution of 50 mg of **5**(BF_4) in 1 mL of acetone was added 20 μL of HBF_4 (48–50% aqueous solution). No immediate color change was observed; however, after this yellow solution was stirred for 12 h, the color slowly faded to colorless. Large, rectangular, colorless crystals were obtained by layering this solution with *i*-PrOH (80% yield). ^{31}P NMR (acetone-d_6): δ 14.0 and 8.5 (AB quartet, $J_{P-P} = 272$ Hz). ^1H NMR (acetone-d_6): δ −14.88 (d of d, $J_{P-H} = 8.3$ and 10.7 Hz). IR (KBr): ν(IrH) = 2210 cm^{-1}; ν(CO) = 2060 cm^{-1}; ν(py CN) = 1611 cm^{-1}.

$[Rh(PN)_2]X$ (8X, X = PF_6^-, BF_4^-). In a typical synthesis, an acetone solution of $AgPF_6$ (0.290 g, 1.15 mmol) was added to a slurry of [Rh(nbd)Cl]$_2$ (0.252 g, 1.09 mmol of Rh) in acetone, and a white AgCl precipitate formed. This mixture was refluxed for 30 min and then filtered. The yellow filtrate was added to a 2-fold excess of PN (0.670 g, 2.30 mmol) dissolved in toluene, resulting in a yellow solution. The acetone was removed during reflux, and a yellow precipitate formed that was filtered and washed with Et_2O. Recrystallization from CH_2Cl_2/Et_2O yielded large yellow crystals in 67% yield. ^{31}P NMR (CH_2Cl_2): δ 48.2 (d, $J_{Rh-P} = 171$ Hz). IR (KBr): ν(py CN) = 1610 cm^{-1}. Anal. Calcd for $RhC_{38}H_{36}N_2P_3F_6$: C, 54.99; H, 4.37; N, 3.37. Found: C, 54.81; H, 4.55; N, 3.46.

$[Rh(PN)_2(CO)]PF_6$ (9(PF_6)). Complex **8**(PF_6) (0.110 g, 0.133 mmol) was placed in a side-arm flask equipped with a gas dispersion tube. Dry THF (20 mL) was added, and CO was bubbled through the suspension until the mixture became clear yellow (ca. 1 min). The solution was stirred under a CO atmosphere for an additional 10 min at which time the THF was removed in vacuo, yielding a flaky, glasslike residue. Attempts to recrystallize **9**(PF_6) were unsuccessful and resulted in the formation of oils. Yield: 75 mg (66%). ^{31}P NMR (THF): δ 29.2 (d, $J_{Rh-P} = 125$ Hz). IR (KBr): ν(CO) = 1995 cm^{-1}; ν(py CN) = 1607 cm^{-1}; ν(PF) = 837 cm^{-1}. UV/vis (CH_2Cl_2): λ = 374 (ϵ = 1500), 252 nm (ϵ = 17 000). Anal. Calcd for $RhC_{39}H_{36}N_2OP_3F_6$: C, 54.55; H, 4.37; N, 3.26. Found: C, 54.18; H, 4.38; N, 3.25.

Rh(PN)(CO)Cl (10). $RhCl_3{\cdot}3H_2O$ (0.527 g, 2.00 mmol) and LiCl (0.222 g, 5.22 mmol) were dissolved in 10 mL freshly distilled 2-methoxyethanol in a Kontes Griffin–Worden pressure apparatus. The suspension was placed under 50 psi CO at 140–145 °C for 60–90 min, yielding the yellow $[Rh(CO)_2Cl_2]^-$ anion.[25] This solution was filtered into a 100-mL round-bottomed flask. Slow addition of the PN ligand (0.584 g, 2.00 mmol) dissolved in toluene to this filtrate gave vigorous evolution of CO with no noticeable color change. Et_2O was then added to precipitate the crystalline product in 71% yield. Recrystallization from CH_2Cl_2/Et_2O resulted in large yellow crystals. ^{31}P NMR (CH_2Cl_2): δ 43.4 (d, $J_{Rh-P} = 168$ Hz). IR (KBr): ν(CO) = 1990 cm^{-1}, ν(py CN)

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Table I. Summary of Crystal Data and Intensity Collection for **3**, **4**, and **8**(PF_6)

	$[Ir(PN)_2(CO)Cl]$ (**3**)	$[Ir(PN)(CO)Cl]\cdot Et_2O$ (**4**·Et_2O)	$[Rh(PN)_2]PF_6$ (**8**(PF_6))
	Crsytal Parameters and Measurement of Intensity Data		
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/a$	$P\bar{1}$	$P2_1/n$
cryst dimens, mm^3	0.1 × 0.2 × 0.3	0.2 × 0.2 × 0.3	0.15 × 0.25 × 0.25
cell params			
T, °C	23	23	23
a, Å	13.178 (2)	11.079 (3)	10.714 (2)
b, Å	13.579 (2)	12.901 (3)	21.774 (2)
c, Å	9.672 (2)	8.377 (3)	15.915 (4)
α, deg	90	101.95 (3)	90
β, deg	93.84 (1)	109.50 (3)	99.95 (2)
γ, deg	90	73.01 (2)	90
V, Å^3	1726.9 (9)	1071 (1)	3657 (2)
Z	2	2	4
d_{calcd}, g/cm^3	1.612	1.925	1.508
abs coeff, cm^{-1}	42.9	67.9	6.5
max, min, av transmissn factors	1.00, 0.83, 0.91	1.00, 0.93, 0.97	
formula	$IrC_{39}H_{36}ClN_2OP_2$	$IrC_{24}H_{28}ClNO_2P$	$RhC_{38}H_{36}F_6N_2P_3$
fw, amu	838.3	621.1	830.5
diffractometer	CAD4	CAD4	CAD4
radiation	Mo K$\bar{\alpha}$ (λ = 0.170 69 Å) graphite monochromatized		
scan type; range (2θ), deg	$\omega-2\theta$; 0–56	$\omega-2\theta$; 0–50	$\omega-2\theta$; 0–52
no. of unique reflcns measd (region)	4573 ($\pm h,+k,+l$)	4032 ($\pm h,\pm k,+l$)	7760 ($+h,+k,\pm l$)
no. of obsd reflcns^a	3045 [$F_o^2 \geq \sigma(F_o^2)$]	3421 [$F_o^2 \geq 2.0\sigma(F_o^2)$]	5611 [$F_o^2 \geq 2.5\sigma(F_o^2)$]
	Refinement by Full-Matrix Least Squares		
no. of params	211	246	451
R^b	0.025	0.025	0.039
$R_w{}^b$	0.033	0.033	0.047
GOF^b	1.038	1.050	1.75
p^a	0.05	0.05	0.03

[a] The intensity data were processed as described in: *CAD4 and SDP-PLUS User's Manual*; B. A. Frenz & Associates: College Station, TX, 1982. The net intensity I = $[K/\text{NPI}](C - 2B)$, where K = 20.1166 × (attenuator factor), NPI = ratio of fasted 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 $[\sigma(I)]^2 = (K/\text{NPI})^2[C + 4B + (pI)^2]$ 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 $\sum W(|F_o| - |F_c|)^2$, 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 is an observation of unit weight (GOF) is $[\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

= 1610 cm^{-1}. Anal. Calcd for $RhC_{20}H_{18}PNOCl\cdot 0.54CH_2Cl_2$: C, 48.99; H, 3.82; N, 2.78; P, 6.15. Found: C, 49.31; H, 3.80; N, 2.78; P, 6.38.

Rh(PN′)(CO)Cl (11) was prepared from the reaction of $[Rh(CO)_2Cl_2]^-$, as prepared in the synthesis of **10**, with the PNP ligand in a 2-methoxyethanol/toluene (10 mL, 1:1 mixture) solution. This red solution turned yellow during refluxing for ca. 40 min; it was then cooled and filtered. Large yellow crystals were produced upon the slow addition of Et_2O (65% yield). ^{31}P NMR (CH_2Cl_2): δ 58.8 (d, J_{Rh-P} = 164 Hz). IR (KBr): ν(CO) = 1980 cm^{-1}; ν(py CN) = 1607 cm^{-1}. Anal. Calcd for $RhC_{19}H_{16}PNOCl$: C, 51.44; H, 3.63; N, 3.16; P, 6.98; Cl, 7.99. Found: C, 51.22; H, 3.83; N, 3.11; P, 7.81; Cl, 8.65. Unit cell dimensions were determined by X-ray crystallography at 23 °C with use of Mo K$\bar{\alpha}$ (λ = 0.71069 Å) radiation: triclinic, $P\bar{1}$, a = 8.602 (4) Å, b = 9.178 (3) Å, c = 13.155 (2) Å, α = 98.62 (2)°, β = 96.50 (3)°, γ = 113.91 (3)°, V = 921 Å^3, R = 0.027.[26]

Isolation of Metallo Products from Decarbonylation Experiments. In a typical experiment, the catalyst was heated in benzaldehyde at 150 °C with a N_2 purge for the desired time (1–12 h). After this time, a large amount of degassed decane was injected into the hot solution and the reaction flask was quickly immersed in an ice bath. The inorganic components immediately precipitated from the solution and eventually formed an oily residue. The colorless mother liquor was then decanted from the reaction flask. ^{31}P NMR and IR analyses of the oily residue were obtained by dissolving it in CH_2Cl_2.

X-ray Structure Determinations. Collection and Reduction of X-ray Data. A summary of crystal data is presented in Table I. Crystals of $Ir(PN)_2(CO)Cl$ (**3**) (thick plate), $[Ir(PN)(CO)Cl]\cdot Et_2O$ (**4**·Et_2O) (well-shaped prism), and $[Rh(PN)_2]PF_6$ (**8**(PF_6)) (well-shaped prism) were secured to the ends of glass fibers with 5-min epoxy resin. The crystals of all three compounds remained stable at room temperature during data collection. The crystals of **3** and **8** were found to belong to the monoclinic crystal class by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing programs and by a Delaunay reduction calculation.[27] The space groups were chosen from the systematic absences observed during data collection and were verified by successful solution and refinement. The crystal of **4** was found to belong to the triclinic crystal class by the methods described above, and the space group was verified by successful solution and refinement. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure time for all three compounds, and no decay with time was noted. The data were corrected for Lorentz, polarization, and background effects. Empirical absorption corrections were applied to compounds **3** and **4** with use of ψ-scan data and the program EAC.[27] No absorption correction was applied to **8** (μ = 6.5 cm^{-1}) since ψ scans showed it to be unnecessary.

Solution and Refinement of the Structures. All three structures were solved by conventional heavy-atom techniques. The Rh and Ir atoms were located by Patterson syntheses. 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,[28] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers' values of $\Delta f'$ and $\Delta f''$.[29] Corrections for extinction were applied. For **4** and **8**, all of the non-hydrogen atoms, except those from the Et_2O solvate in **4**, were refined with anisotropic thermal parameters, while for **3**, all of the non-hydrogen atoms except the disordered carbonyl C and O and Cl were refined anisotropically (vide infra). Hydrogen atom positions were calculated in idealized positions (C–H distance set at 0.95 Å) and included in the structure factor calculations but were not refined. The final difference Fourier maps did not reveal chemically significant residual electron

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(26) Anderson, M. P. Ph.D. Thesis, University of Minnesota, 1983.

(27) All calculations were carried out on a PDP 8A and 11/34 computers with use of the Enraf-Nonius CAD4-SDP programs. This crystallographic computing package is described by: Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthoff-Hazekamp, R., van Koningsveld, H.; Bassi, G. C. Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. See also: *CAD4 User's Manual*; Enraf-Nonius: Delft, Holland, 1978.

(28) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.4.

(29) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table II. Positional Parameters and Their Estimated Standard Deviations for [Ir(PN)$_2$(CO)Cl] (**3**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ir	0.000	0.000	0.000	2.059 (3)
P	−0.14391 (7)	0.09078 (7)	0.0435 (1)	2.36 (2)
C1A	−0.1227 (3)	0.2108 (3)	0.1261 (4)	2.68 (7)
C2A	−0.1970 (3)	0.2560 (3)	0.1998 (4)	3.51 (8)
C3A	−0.1786 (4)	0.3500 (3)	0.2585 (5)	4.2 (1)
C4A	−0.0900 (4)	0.3969 (3)	0.2423 (5)	4.4 (1)
C5A	−0.0162 (4)	0.3531 (3)	0.1690 (5)	4.3 (1)
C6A	−0.0320 (3)	0.2601 (3)	0.1117 (5)	3.40 (8)
C1B	−0.2225 (3)	0.0254 (3)	0.1609 (5)	2.88 (7)
C2B	−0.2006 (4)	0.0316 (4)	0.3024 (5)	4.00 (9)
C3B	−0.2564 (5)	−0.0233 (4)	0.3923 (6)	5.4 (1)
C4B	−0.3320 (4)	−0.0853 (4)	0.3415 (6)	6.0 (1)
C5B	−0.3534 (4)	−0.0922 (4)	0.2026 (7)	5.8 (1)
C6B	−0.2988 (4)	−0.0384 (4)	0.1106 (6)	4.3 (1)
N	−0.3586 (4)	0.1474 (3)	−0.3491 (4)	5.5 (1)
C7	−0.2235 (3)	0.1196 (3)	−0.1148 (4)	3.51 (8)
C8	−0.3183 (4)	0.1802 (4)	−0.1037 (5)	4.2 (1)
C9	−0.3687 (4)	0.2095 (3)	−0.2436 (5)	3.53 (9)
C13	−0.4042 (5)	0.1737 (4)	−0.4721 (5)	6.1 (1)
C12	−0.4585 (5)	0.2581 (4)	−0.4929 (5)	5.1 (1)
C11	−0.4677 (5)	0.3186 (4)	−0.3846 (6)	5.3 (1)
C10	−0.4214 (5)	0.2946 (4)	−0.2588 (5)	4.8 (1)
Cl	0.0661 (2)	0.0428 (2)	0.2248 (2)	3.61 (4)*
C	0.0487 (9)	0.0248 (8)	0.170 (1)	4.7 (2)*
O	0.0779 (6)	0.0427 (7)	0.2827 (8)	5.4 (2)*

[a] An asterisk denotes *B* values for atoms that were isotropically refined due to disorder (see text). *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

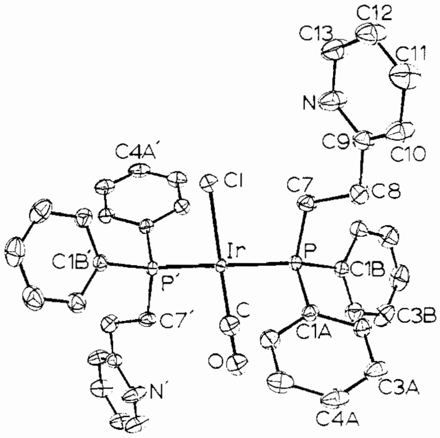

Figure 1. ORTEP drawing of **3**. Ellipsoids are drawn with 50% probability boundaries. Selected distances (Å) are as follows: Ir–P, 2.324 (1); Ir–C, 1.76 (2); Ir–Cl, 2.361 (4); C–O, 1.16 (2); P–C1A, 1.828 (4); P–C1B, 1.819 (4); P–C7, 1.839 (4); C7–C8, 1.506 (6); C8–C9, 1.520 (6); N–C9, 1.338 (6); N–C13, 1.345 (6). Selected angles (deg) are as follows: P–Ir–C, 88.9 (4) and 91.1 (4); P–Ir–Cl, 87.59 (7) and 92.41 (7); Cl–Ir–C, 176.8 (4); Ir–C–O, 178 (1); C–P–C, average 105.1. Two angles are reported for P–Ir–C and P–Ir–Cl because of the disorder between the Cl and CO ligands. The nature of the disorder (i.e., the Ir atom is located on an inversion center) requires that these angles be complementary.

density for any of the compounds. For **3**, the Ir atom was located on a crystallographic center of symmetry, and as a result, the CO and Cl ligands were randomly disordered. The carbonyl C and O and Cl positions were refined with 0.5 multiplicities and showed reasonable thermal parameters, distances, and angles. The location of the N atom in complex **3** was determined by least-squares refinement of the atoms in the pyridyl ring (C9–C13) using carbon atomic scattering factors. The N atom was then identified by its small thermal parameter (B = 3.8 Å^2) relative to the C atoms (average B = 4.6 Å^2). Further refinement using nitrogen atomic scattering factors for N gave reasonable thermal parameters (for N, B = 5.5 Å^2; for pyridyl C, average B = 5.3 Å^2) and consistent distances and angles within the pyridyl ring. In **4**, the Et$_2$O solvate was disordered due to its proximity to a crystallographic inversion center and was refined by using a disordered model. The final positioal and thermal parameters of the refined atoms appear in Tables II–IV.

Table III. Positional Parameters and Their Estimated Standard Deviations for [Ir(PN)(CO)Cl]·Et$_2$O (**4**·Et$_2$O)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ir1	−0.01555 (1)	−0.18700 (1)	0.05211 (2)	3.269 (3)
P	0.1055 (1)	−0.24862 (9)	−0.1278 (1)	3.37 (2)
Cl	−0.1565 (1)	−0.1115 (1)	0.2297 (1)	4.61 (3)
N	−0.1863 (3)	−0.1662 (3)	−0.1633 (4)	3.88 (9)
O	0.2212 (4)	−0.2144 (5)	0.3546 (5)	7.9 (1)
C	0.1287 (5)	−0.2059 (5)	0.2364 (6)	4.9 (1)
C1	0.0357 (4)	−0.1706 (4)	−0.3126 (5)	4.0 (1)
C2	−0.0843 (5)	−0.0789 (4)	−0.2979 (5)	3.9 (1)
C3	−0.1973 (4)	−0.1190 (4)	−0.2975 (5)	3.9 (1)
C4	−0.3132 (5)	−0.1093 (5)	−0.4346 (6)	5.1 (1)
C5	−0.4155 (5)	−0.1492 (6)	−0.4311 (7)	6.3 (2)
C6	−0.4024 (5)	−0.1973 (6)	−0.2945 (7)	6.2 (2)
C7	−0.2871 (5)	−0.2056 (5)	−0.1626 (6)	5.2 (1)
C1A	0.2758 (4)	−0.2367 (4)	−0.0415 (5)	3.8 (1)
C2A	0.2995 (5)	−0.1332 (4)	−0.0105 (7)	5.0 (1)
C3A	0.4285 (5)	−0.1206 (5)	0.0691 (8)	6.2 (1)
C4A	0.5296 (5)	−0.2100 (6)	0.1138 (7)	6.3 (2)
C5A	0.5073 (6)	−0.3096 (6)	0.0853 (9)	7.2 (2)
C6A	0.3806 (5)	−0.3253 (5)	0.0062 (8)	5.9 (2)
C1B	0.1220 (4)	−0.3916 (4)	−0.2183 (6)	3.8 (1)
C2B	0.0846 (5)	−0.4616 (4)	−0.1493 (7)	5.2 (1)
C3B	0.0968 (6)	−0.5704 (5)	−0.2130 (9)	6.4 (2)
C4B	0.1472 (5)	−0.6111 (4)	−0.3445 (8)	5.8 (1)
C5B	0.1851 (5)	−0.5459 (5)	−0.4167 (7)	6.0 (2)
C6B	0.1723 (5)	−0.4343 (4)	−0.3539 (7)	5.0 (1)

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

Table IV. Positional Parameters and Their Estimated Standard Deviations for Selected Atoms of [Rh(PN)$_2$]PF$_6$ (**8**(PF$_6$))

atom	*x*	*y*	*z*	*B*,[a] Å^2
Rh	0.29058 (3)	0.10969 (1)	0.22813 (2)	2.328
P1	0.32968 (9)	0.05412 (4)	0.34700 (6)	2.571
P2	0.22129 (9)	0.03483 (4)	0.13828 (6)	2.532
N1	0.3150 (3)	0.1852 (1)	0.3147 (2)	2.866
N2	0.2970 (3)	0.1712 (1)	0.1253 (2)	2.830
C1	0.4875 (4)	0.0789 (2)	0.4036 (3)	3.636
C2	0.5186 (4)	0.1455 (2)	0.3831 (3)	3.783
C3	0.4101 (4)	0.1889 (2)	0.3831 (2)	3.245
C4	0.4016 (5)	0.2291 (2)	0.4497 (3)	4.426
C5	0.2981 (5)	0.2662 (2)	0.4465 (3)	5.014
C6	0.2036 (5)	0.2639 (2)	0.3759 (3)	4.428
C7	0.2151 (4)	0.2229 (2)	0.3116 (3)	3.647
C8	0.1284 (4)	0.0670 (2)	0.0382 (2)	3.602
C9	0.0961 (4)	0.1356 (2)	0.0453 (2)	3.756
C10	0.2125 (4)	0.1745 (2)	0.0516 (2)	3.007
C11	0.2367 (4)	0.2099 (2)	−0.0161 (2)	3.863
C12	0.3476 (5)	0.2429 (2)	−0.0091 (3)	4.136
C13	0.4331 (4)	0.2403 (2)	0.0654 (3)	3.698
C14	0.4055 (4)	0.2043 (2)	0.1317 (2)	3.486

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Parameters for the remaining atoms are included as supplementary material.

ORTEP drawings of the complexes with selected distances and angles are shown in Figures 1–3. A complete listing of thermal parameters, calculated hydrogen atom positions, distances, angles, least-squares planes, and structure factor amplitudes is included as supplementary material.[30]

Results and Discussion

Iridium Complexes with the PN Donor Ligand. A series of iridium complexes with the ligand PN have been synthesized and characterized as follows.

[Ir(PN)$_2$]PF$_6$ (1(PF$_6$)). The synthesis of [Ir(PN)(cod)]PF$_6$ was reported previously, and shown to be the product of the reaction of 1 equiv of PN with [Ir(cod)(acetone)$_2$]$^+$ in acetone solution.[1] Under the appropriate conditions, [Ir(PN)(cod)]PF$_6$

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[30] See paragraph at end of paper regarding supplementary material.

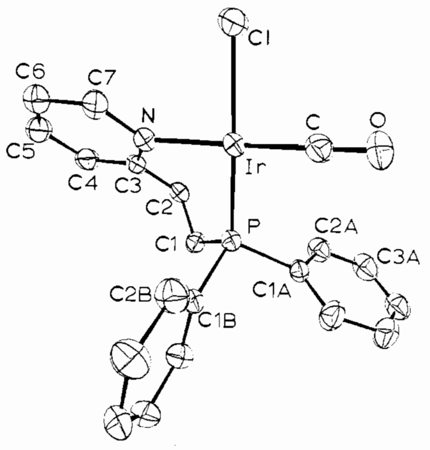


Figure 2. ORTEP drawing of **4**. Ellipsoids are drawn with 50% probability boundaries. Selected distances (Å) are as follows: Ir–P, 2.221 (1); Ir–N, 2.129 (4); Ir–C, 1.811 (5); Ir–Cl, 2.380 (1); C–O, 1.159 (7); P–C1A, 1.822 (4); P–C1B, 1.824 (4); P–C1, 1.844 (5); C1–C2, 1.520 (7); C2–C3, 1.490 (7); N–C3, 1.341 (6); N–C7, 1.357 (6). Selected angles (deg) are as follows: P–Ir–N, 88.1 (1); P–Ir–C, 92.4 (2); N–Ir–Cl, 88.3 (1); Cl–Ir–C, 91.3 (2); P–Ir–Cl, 175.59 (4); N–Ir–C, 179.2 (2); C–P–C, average 104.3.

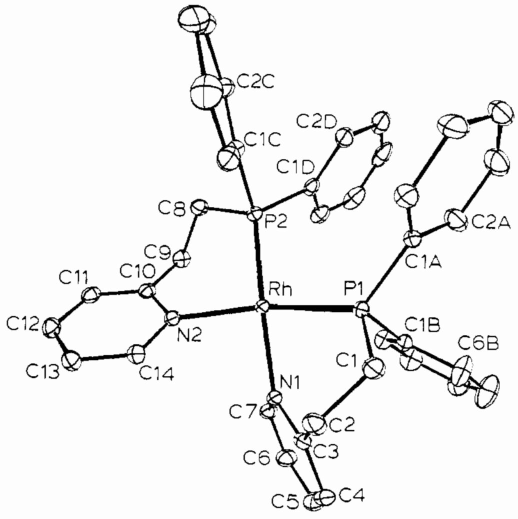
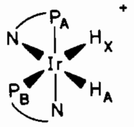


Figure 3. ORTEP drawing of the coordination core of **8**(PF_6). Ellipsoids are drawn with 50% probability boundaries. Selected distances (Å) are as follows: Rh–P1, 2.224 (1); Rh–P2, 2.210 (1); Rh–N1, 2.133 (2); Rh–N2, 2.125 (2); P1–C1A, 1.832 (3); P1–C1B, 1.825 (3); P1–C1, 1.854 (3); P2–C1C, 1.824 (3); P2–C1D, 1.831 (3); P2–C8, 1.863 (3); C1–C2, 1.536 (4); C2–C3, 1.497 (4); C8–C9, 1.542 (4); C9–C10, 1.497 (4); N1–C3, 1.359 (4); N1–C7, 1.343 (4); N2–C10, 1.354 (4); N2–C14, 1.356 (4). Selected angles (deg) are as follows: P1–Rh–P2, 98.17 (3); P1–Rh–N1, 83.43 (7); P1–Rh–N2, 166.33 (7); P2–Rh–N1, 167.62 (7); P2–Rh–N2, 91.08 (7); N1–Rh–N2, 89.70 (9); C–P–C, average 102.2.

reacted with a 4- to 5-fold excess of PN to form the bis chelate $[Ir(PN)_2]PF_6$ (**1**(PF_6)). The related $[Ir(dppe)_2]^+$ and $[Ir(dppp)_2]^+$ complexes (vide infra) have been synthesized in a similar fashion except that only 1 equiv of the diphosphine ligand was needed. However, attempts to synthesize **1** from $[Ir(PN)(cod)]PF_6$ by using only 1 equiv of PN were unsuccessful. It is possible that an equilibrium exists that requires the use of a large excess of PN to drive the reaction, or, alternatively, that the phosphorus atoms from the excess PN ligands are needed to displace coordinated cod. There is evidence to suggest that nitrogen donors are ineffective at displacing coordinated cod in Ir(I)/cod complexes. For example, attempts to synthesize $[Ir(NN)_2]^+$ complexes (NN = 1,10-phenanthroline or 2,2′-bipyridine) from $[Ir(NN)(cod)]^+$ and NN (1 equiv or excess) were unsuccessful and left the starting complexes unchanged.[31] NN ligands have also been reported to be unable to displace cod in $[Rh(NN)(cod)]^+$ complexes.[32]

The coordination of both PN ligands as bidentate in **1** was confirmed by the observation of ν(py CN) at 1610 cm^{-1} in the IR spectrum (KBr), a shift of ca. 20 cm^{-1} from that of free PN (1589 cm^{-1}).[1] Also, the ^{31}P NMR spectrum recorded with the use of CH_2Cl_2 as solvent consisted of a singlet at δ 14.1, and resonances due to cod were absent from the ^1H NMR spectrum of **1**. Therefore, **1** is presumed to have a square-planar geometry; however, the cis or trans stereochemistry could not be unambiguously determined from this data. It is likely that **1** has a cis configuration similar to that of the X-ray determined structure of the analogous rhodium complex, $[Rh(PN)_2]^+$ (**8**) (vide infra). The possibility that both cis and trans isomers of **1** are present in solution and are rapidly interconverting on the NMR time scale, however, could not be ruled out even though low-temperature (−60 °C) ^{31}P NMR studies did not show any evidence of such an equilibrium. Compound **1** is an active catalyst for the decarbonylation of benzaldehyde (vide infra). The activity exhibited by this catalyst is somewhat higher than that exhibited by $[Ir(dppp)_2]PF_6$, which may be due to the greater lability of an Ir–N bond relative to an Ir–P bond.

An acetonitrile solution of **1** slowly turned colorless after 24 h under 1 atm of H_2. The ^1H NMR spectrum of this colorless solution was consistent with the formation of the dihydride complex *cis*-$[Ir(PN)_2(H)_2]^+$ (**2**); however, the ^{31}P NMR spectrum indicated that another species was also present. The structure proposed for **2** is as follows:



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Two hydride resonances of equal intensity were present in the ^1H NMR spectrum of a CD_3CN solution of **2** (δ −8.21 and −20.22). The splitting patterns (d of d of d) and coupling constants ($J_{transP-H_X}$ = 144 Hz, J_{cisP-H_X} = 19 Hz, J_{cisP-H_A} = 19 and 12.5 Hz, $J_{cisH_X-H_A}$ = 4 Hz) are within the normal ranges[33,34] and support the proposed stereochemistry. The ^{31}P NMR spectrum of this solution showed two signals at δ 12.7 and 7.5. The resonance at δ 12.7 was interpreted to be due to partially overlapping doublets of an AB system at δ 12.8 and 12.5 (J_{cisP-P} = 40 Hz). Although this interpretation is uncertain, it is consistent with the proposed structure of **2**. The singlet at δ 7.5 was presumably due to a non-hydride iridium species, but the identity of this species was not determined.

The diphosphine complexes $[Ir(dppe)_2]^+$ and $[Ir(dppp)_2]^+$ are known to react readily with H_2 to form analogous *cis*-dihydride complexes.[35,36] However, $[Rh(PN)_2]^+$ (**8**) is unreactive toward H_2 (vide infra), which is not unusual since Ir(I) complexes are known to undergo oxidative-addition reactions more easily than their rhodium analogues. Attempts to synthesize a CO adduct of **1** by the addition of CO gas to CH_2Cl_2 solutions of **1** led to a complex mixture of products that could not be separated and characterized. However, a CO adduct of **1**, $[Ir(PN)_2(CO)]^+$ (**5**), was prepared by another route (vide infra).

$Ir(PN)_2(CO)Cl$ (3) was synthesized in good yield by the addition of 2 equiv of PN to a 2-methoxyethanol solution of $[Ir(CO)_2Cl_2]^-$ and was characterized by the usual spectroscopic methods and by single-crystal X-ray diffraction. Relevant crystallographic data are presented in Tables I and II. The structure consisted of discrete molecules of **3** with no unusually short intermolecular contacts. Figure 1 shows an ORTEP drawing of the molecular structure of **3** with selected distances and angles. The primed and unprimed atoms are related by an inversion center

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(31) Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.

(32) Cocevar, C.; Mestroni, G.; Camus, A. *J. Organomet. Chem.* **1972**, *35*, 389.

(33) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

(34) Chatt, J.; Coffey, R. S.; Shaw, B. L. *J. Chem. Soc.* **1965**, 7391.

(35) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324.

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with the iridium atom located on the center of symmetry. Consequently, the CO and Cl ligands were randomly disordered, which is not uncommon for this type of compound and has been reported for a similar *trans*-$Ir(PR_3)_2(CO)Cl$ complex.[37]

Compound **3** is a four-coordinate complex with a slightly distorted square-planar coordination core with trans phosphorus atoms. The Ir–N distance of 5.970 (4) Å is very long and well outside the range of bonding distances reported for nitrogen donor complexes of iridium and rhodium (2.10–2.20 Å) (vide infra).[11,26] Thus, both PN ligands are monodentate with dangling pyridine arms similar to other complexes that contain monodentate PN type donor ligands bound to a transition metal through the phosphorus atom.[7,9,10,16,17,38,39] All of the cis L1–Ir–L2 (L1, L2 = P, CO, Cl) angles are very close to orthogonal (90 ± 2°) while the trans Cl–Ir–CO angle of 176.7 (4)° deviates only slightly from the ideal. The Ir–P bond distance of 2.324 (1) Å is within the range (2.305–2.365 Å)[37,40,41] commonly reported for mutually trans phosphorus atoms of an Ir(I) square-planar complex. The Ir–Cl and Ir–CO bonds are 2.361 (4) and 1.76 (2) Å, respectively, both of which are in the ranges (Ir–Cl (2.34–2.43 Å), and Ir–CO (1.67–1.91 Å)) commonly observed in other square-planar *trans*-Cl–Ir–CO complexes.[37,41–43] The carbonyl C–O distance is normal, and the Ir–C–O angle is consistent with terminal coordination. All distances and angles within the PN ligands are in good agreement with those in other PN complexes.[1,26] The ^{31}P NMR and IR spectra of **3** were consistent with the solid-state X-ray structure of this complex (see Experimental Section). Of particular note is that the highest frequency deformation mode of the pyridyl ring (ν(py CN) = 1591 cm^{-1}) was very similar to that observed in the free PN ligand (1589 cm^{-1})[1] and supports the assignment of two noncoordinated pyridine arms.

Not unexpectedly, **3** could also be synthesized directly from Ir(PN)(CO)Cl (**4**) (vide infra) by the addition of 1 equiv of PN. A similar displacement of the coordinated nitrogen donor end by a phosphorus donor was reported for the iridium analogue of **3** by using *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline.[10] The greater bond strength of an Ir–P bond relative to an Ir–N bond is an important factor in this reaction; however, the stability derived from a trans arrangement of phosphorus atoms and a trans arrangement of the CO and Cl ligands may also be important. The addition of the PN ligand to the Rh analogue of **4**, Rh(PN)(CO)Cl (**10**), did not result in the isolation of a product in which the nitrogen donor was displaced but left the starting complex unchanged (vide infra). This somewhat surprising result may be due to a combination of the chelate effect and a smaller difference in Rh–P and Rh–N bond strengths relative to Ir–P and Ir–N. It is noteworthy that no examples of the PN ligand bound in a monodentate manner to rhodium were found in this study.

[Ir(PN)(CO)Cl]·Et$_2$O (4·Et$_2$O) was synthesized in moderate yield by the addition of 1 equiv of PN to a 2-methoxyethanol solution of $[Ir(CO)_2Cl_2]^-$ and characterized by spectroscopy and by a single-crystal X-ray analysis. Relevant crystallographic data is presented in Tables I and III. The structure consisted of discrete molecules of **4** and disordered Et_2O solvate molecules with no unusually short intermolecular contacts. Figure 2 shows an ORTEP drawing of the molecular structure of **4** and includes the atom labeling scheme with selected distances and angles.

Compound **4** is a monomeric, slightly distorted square-planar complex, in which both the phosphorus and nitrogen atoms of the PN ligand are coordinated to the iridium. The chloride and phosphorus atoms are trans, as are the nitrogen atom and CO ligand. The same stereochemistry has been reported for the analogous iridium complex with *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline[11] and for Rh(PN′)(CO)Cl (**11**) (vide infra).[26] The angles about Ir(I) show the coordination geometry of a slightly distorted square. The PN bite angle of 88.1 (1)° is very close to the idealized square-planar angle of 90° and is within the range of bite angles observed for other PN complexes (83.4–93.7°) (vide infra).[1,11,26] The remaining *cis*-L–Ir–L′ angles are nearly orthogonal and fall within the range 88–92°. The *trans*-L–M–L′ angles deviate only slightly from 180°. The Ir–Cl and Ir–CO distances, 2.380 (1) and 1.811 (5) Å, respectively, are similar to the distances found in analogous complexes.[11,26] The Ir–N distance is 2.129 (4) Å and falls within the range observed for other PN complexes of rhodium and iridium (2.09–2.14 Å) (vide infra).[1,26] The Ir–P distance, 2.221 (1) Å, is short compared to Ir–P distances observed in square-planar *trans*-$Ir(PR_3)_2(CO)Cl$ complexes (2.305–2.365 Å)[37,40,41] but is similar to the M–P distances (M = Rh, Ir) observed in four-coordinate complexes of Rh(I) and Ir(I) where the phosphorus atom is trans to a chloride (2.20–2.22 Å).[11,44,45] The carbonyl C–O distance is normal, and the Ir–C–O angle is consistent with a terminal CO ligand. Within the PN ligand, the distances and angles are normal. The IR and ^{31}P NMR spectra of **4** were consistent with its solid-state structure (see Experimental Section).

Several factors are involved in determining the nuclearity of $[M(LL')(CO)Cl]_x$ complexes (M = Rh, Ir; LL′ = diphosphines or PN type donor ligands; x = 1, 2). One important factor is the stability of the chelate ring formed in mononuclear M(LL′) complexes compared to the stability of a bridging arrangement in binuclear $M(LL')_2M$ complexes. Consider the anomalous behavior of the diphosphine ligand dppe. Unlike all other diphosphine ($Ph_2P(CH_2)_nPPh_2$, n = 1–6) analogues, which are dimers with bridging diphosphine ligands, Rh(dppe)(CO)Cl is a mononuclear complex.[18] This may be due to the greater relative stability of a five-membered chelate ring since dppe generally shows a strong preference to act as a chelating ligand. Therefore, since dppe and the phosphorus-nitrogen donor ligands *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline and 2-[(diphenylphosphino)methyl]pyridine all contain a two-carbon backbone, a similar effect may have been important in the generation of the iridium and rhodium mononuclear M(LL′)(CO)Cl complexes containing these ligands.[11,26] The ligand PN, however, contains a three-carbon backbone and exhibits a range of P–M–N "bite angles" that are similar to those of the diphosphine dppp (typical ranges: dppp, 87.9–93.4°; PN, 83.4–93.7°).[1,11,26] Thus, the formation of **4** as a mononuclear complex was somewhat unexpected. However, the mononuclear Rh/PN analogue of **4** was also synthesized (vide infra), as were various other complexes of the same formulation using the PN type donor ligands dimethyl(3-(diphenylphosphino)propyl)amine and dimethyl(*o*-(diphenylphosphino)benzyl)amine, which have a three-carbon backbone.[10,11,46]

The stereochemical arrangement of ligands about the metal center may also be an important factor in the determination of the nuclearity of these complexes. Since a mononuclear M(LL′)(CO)Cl complex must have a cis stereochemistry while the dimers with bridging LL′ ligands adopt a trans geometry, the relative stabilities of these two configurations must be considered. It may be that the electronic differences between nitrogen and phosphorus donor atoms favor the formation of cis complexes with PN type donor ligands and trans complexes with diphosphines. Note that in **4** the π-acceptor ligands, CO and P, are positioned trans to the σ donors. This is a particularly stable arrangement not possible with PP ligands. To explore this premise, the reaction of $Ir(PN)_2(CO)Cl$ and $[Rh(CO)_2(\mu\text{-}Cl)]_2$ was carried out and found to lead to the exclusive formation of the mononuclear

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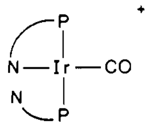
complexes Ir(PN)(CO)Cl and Rh(PN)(CO)Cl by transfer of PN from the iridium complex to the rhodium complex. A similar reaction between $[Rh(CO)_2(\mu\text{-}Cl)]_2$ and $Rh(LL')_2(CO)Cl$ (LL' = the PN type donor ligand 2-(diphenylphosphino)pyridine) in which both PN type donor ligands are monodentate yielded the dimer $Rh_2(\mu\text{-}LL')_2(\mu\text{-}CO)Cl_2$.[38] However, another factor is important to consider in this latter case since it is well-known that four-membered chelate rings, such as are found in monomeric complexes of dppm and this PN type donor ligand, are less stable than their bridging analogues.

$[Ir(PN)_2(CO)]PF_6$ (5(PF_6)). A suspension of $Ir(PN)_2(CO)Cl$ (3) in acetone rapidly dissolved upon the addition of excess KPF_6 to give a yellow solution of the new complex $[Ir(PN)_2(CO)]^+$ (5)



5

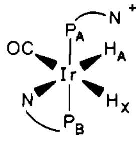
in good yield. Compound **5** was characterized by IR and variable-temperature ^{31}P NMR spectroscopy. This data was consistent with the formation of a four-coordinate square-planar complex in which one PN ligand is bidentate and the other PN ligand is monodentate and coordinated through the phosphorus atom. The presence of both coordinated and noncoordinated pyridyl rings was confirmed by the observation of two pyridyl ring vibrations, ν(py CN), of approximately equal intensity at 1612 and 1592 cm^{-1} in the IR spectrum of a CH_2Cl_2 solution of **5**. A single CO stretch was observed at 1995 cm^{-1}, which represents a shift of approximately 37 cm^{-1} to higher energy relative to the value for the parent complex $Ir(PN)_2(CO)Cl$ and is consistent with the net positive charge on **5**. The ^{31}P NMR spectrum of **5** recorded at 25 °C with use of CH_2Cl_2 as solvent showed only a singlet at δ 21.3 relative to the internal standard trimethyl phosphate (TMP). Low-temperature ^{31}P NMR spectra revealed, however, that a rapid exchange of coordinated and noncoordinated nitrogen atoms was occurring on the NMR time scale at 25 °C. The spectrum recorded at −95 °C was very close to the slow exchange limit and consisted of an AB quartet at δ 23.0 and 19.8 (J_{P-P} = 265 Hz), which is consistent with trans stereochemistry.[18,47]

It has been shown that complexes of the type $M(CO)_4(LL')$ (M = Cr, Mo, W; LL' = PN type donor ligands) undergo dissociation of the nitrogen donor to form an unsaturated 16e intermediate.[7] It seems unlikely that such a dissociative process is occurring in this case, since this would require the formation of a 14e intermediate. It is more likely that an associative mechanism that involves an undetected five-coordinate 18e intermediate is involved in the exchange process in **5**.

The structure of **5** is surprising when compared to the structures of the diphosphine analogues $[Ir(dppe)_2(CO)]^+$,[35,48] $[Ir(dppp)_2(CO)]^+$,[49] and $[Ir(dppm)_2(CO)]^+$[49] and the rhodium analogue $[Rh(PN)_2(CO)]^+$ (**9**) (vide infra). Although the crystal structures of all of these compounds have not been determined, it is believed that they are 18e five-coordinate complexes. In particular, IR and variable-temperature ^{31}P NMR spectroscopic studies of **9** did not reveal any evidence for monodentate PN coordination (vide infra). The precise reasons for the difference between **5** and its rhodium analogue are not well understood but may be a reflection of the relatively weaker Ir–N interaction.

Compound **5** was also found to be present in high concentrations in the benzaldehyde solutions of catalytic decarbonylation experiments in which **1** was used as a catalyst or catalyst precursor (vide infra). Since **5** may be the active catalyst in this system, it was important to establish whether it could undergo an oxidative-addition reaction. Thus the reaction of **5** with H_2 was explored.

A yellow CH_2Cl_2 solution of **5** slowly faded to a very pale yellow color during 6 h of stirring under 1 atm of H_2 at 25 °C. The IR, ^1H NMR, and ^{31}P NMR spectra of this solution were consistent with the formation of the *cis*-dihydride, *cis*-$[Ir(PN)_2(H)_2(CO)]^+$ (**6**) in good yield. The ^1H NMR spectrum of **6** in $CDCl_3$ showed

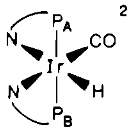


6

two hydride resonances attributable to H_A and H_X (see Experimental Section). The observed splitting patterns (d of d of d) and coupling constants (cis P–H and H–H) were consistent with hydride ligands that are coupled to three nonequivalent I = $^1/_2$ nuclei. The presence of two nonequivalent trans phosphorus atoms was confirmed by the observation of an AB quartet at δ 11.9 and 6.3 (J_{P-P} = 280 Hz) in the ^{31}P NMR spectrum of **6** with use of $CDCl_3$ as solvent. The IR spectrum of **6** in CH_2Cl_2 solution showed two pyridyl ring vibrations attributable to coordinated and noncoordinated nitrogen atoms at 1610 and 1595 cm^{-1}, respectively. Two absorptions characteristic of terminal hydrides were detected at 2190 (m) and 2110 cm^{-1} (s). The intense IrH stretch at 2110 cm^{-1} is characteristic of a hydride trans to a CO and results from a Fermi resonance interaction between the vibrational states of the IrH and CO stretching motions.[50] A single CO stretch characteristic of a terminal CO was observed at 2010 cm^{-1}. These assignments were verified by the synthesis and characterization of the deuteride analogue $[Ir(PN)_2(D)_2(CO)]^+$. The two IrH stretches were absent in the IR spectrum (CH_2Cl_2) of this compound and the IrD stretch appeared as expected as a broad peak at 1590 cm^{-1} (ν(IrH)/ν(IrD) = 1.39 for the IrH stretch at 2190 cm^{-1}) and the usual high energy shift in ν(CO) was observed (ν(CO) = 2045 cm^{-1}).[50]

The structure of **6** is consistent with the simple cis addition of H_2 to the parent complex **5** and further supports the structure proposed for **5**. Compound **6** resembles the structure of one of the Rh(III) intermediates postulated in the mechanism for the catalytic decarbonylation of aldehydes by $[Rh(dppe)_2]^+$ and $[Rh(dppp)_2]^+$ complexes[3] that is believed to contain one bidentate and one monodentate diphosphine.

Complex **5** also reacted with H^+ to yield the dicationic iridium hydride $[Ir(PN)_2H(CO)]^{2+}$ (**7**). Treatment of **5**(BF_4) with excess



7

HBF_4 in acetone caused the originally yellow solution to slowly turn colorless over a 12 h period. The complex $[Ir(PN)_2H(CO)](BF_4)_2$ (**7**(BF_4)$_2$) was isolated in high yield from this solution and characterized by IR, ^{31}P NMR, and ^1H NMR spectroscopy. Consistent with this structure, a single hydride resonance (δ −14.88) was observed in the ^1H NMR spectrum with use of acetone-d_6 as solvent. The P–H coupling constants (8.3 and 10.7 Hz) are consistent with the assignment of a hydride that is cis to two nonequivalent phosphorus atoms,[33,34] and the second-order pattern of an AB quartet at δ 14.0 and 8.5 (J_{P-P} = 272 Hz) observed in the ^{31}P NMR spectrum (acetone) is consistent with the proposed trans stereochemistry of the phosphorus atoms.[18,47] An IrH stretch characteristic of a terminal hydride was observed at 2210 cm^{-1} in the IR spectrum (KBr), and the coordination of both pyridyl rings was confirmed by the presence of a single ν(py CN) stretching frequency at 1611 cm^{-1}. No evidence of N–H bond formation was apparent in the IR or ^1H NMR spectra. The coordination of a terminal CO ligand was confirmed by the observation of a single ν(CO) stretch at 2060 cm^{-1}, a shift of 65 cm^{-1}

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to higher frequency relative to ν(CO) of the parent complex **5**, consistent with the increased charge and higher formal oxidation state of Ir in **7**.

Rhodium Complexes with the PN Donor Ligand. A series of rhodium complexes with the ligands PN and PN′ have been synthesized and characterized as follows. **[Rh(PN)$_2$]$^+$** was synthesized as the BF_4^- and PF_6^- salts (**8**(BF_4) and **8**(PF_6)) in good yield upon treatment of [Rh(nbd)Cl]$_2$ in acetone solution with $AgBF_4$ or $AgPF_6$, respectively, followed by the addition of a toluene solution of 2 mol of the PN ligand per mole of rhodium. The molecular structure of **8**(PF_6) was determined by single-crystal X-ray analysis and shown to consist of discreet cations and anions with no unusually short intermolecular contacts. Relevant crystallographic data is presented in Tables I and IV. An ORTEP drawing of the coordination core of the cation along with selected distances and angles is shown in Figure 3.

Complex **8** is a PN bis chelate with the phosphorus atoms trans to the nitrogen atoms. The geometry of the cation is approximately square planar with a moderate tetrahedral distortion due to steric crowding. Thus, the angles at the metal atom between trans ligands are 167.62 (7)° for P2–Rh–N1 and 166.33 (7)° for P1–Rh–N2. Another measure of this distortion is provided by the dihedral angle between the planes formed by oppositely oriented [Rh–P–N] triangles, which for an idealized square-planar geometry would be 0° and is 17° in **8**. This distortion is not as severe as that found in [Rh(dppb)$_2$]$^+$, in which case these angles are 37 and 39°,[51] and is most likely due to intramolecular phosphine–phosphine repulsions. The orientation of the phosphorus atoms trans to the nitrogen atoms is in agreement with trans-effect arguments and is analogous to the X-ray-determined structures of other square-planar complexes with two PN type donor ligands.[39,52] The Rh–P distances in **8** (average 2.217 (1) Å) are short compared to the Rh–P distances in [Rh(dppb)$_2$]$^+$ (average 2.329 (2) Å)[51] and [Rh(dppe)$_2$]$^+$ (average 2.306 (7) Å)[53] due possibly in part to the greater structural trans influence of the phosphorus bound ligand compared to the nitrogen bound ligand. The average Rh–N distance (2.129 (2) Å) compares well with the Rh–N distance in Rh(PN′)(CO)Cl (2.135 (2) Å) (**11**)[26] and with those of other rhodium–pyridine complexes.[38,54] All other distances and angles are normal. The spectroscopic and analytical data are consistent with the solid-state structure. The IR spectrum of **8** contained a pyridyl CN stretch at 1610 cm^{-1}, which indicates pyridine coordination.[1] The ^{31}P NMR spectrum with use of CH_2Cl_2 as solvent showed a simple doublet with normal Rh–P coupling (δ 48.2, J_{Rh-P} = 171 Hz).

Compound **8**(PF_6) did not react with H_2, even at 100 psi after 12 h. This same result has been noted for [Rh(dppe)$_2$]$^+$ [55] but is in contrast to the reactions of H_2 with [Rh(dppp)$_2$]$^+$ [56] and [Ir(PN)$_2$]PF$_6$ (vide supra), in which case *cis*-dihydrides were formed. The pale yellow complex **[Rh(PN)$_2$(CO)]PF$_6$ (9(PF$_6$))** was the only isolated product formed by the reaction of [Rh(PN)$_2$]PF$_6$ (**8**(PF_6)) with CO (1 atm), unlike the analogous reaction with [Ir(PN)$_2$]PF$_6$ (**1**(PF_6)), which formed a mixture of products (vide supra). The IR spectrum of **9**(PF_6) with use of CH_2Cl_2 as solvent had a very strong CO band at 2004 cm^{-1} and a pyridyl CN stretch at 1607 cm^{-1} indicative of coordinated nitrogen atoms. In the solid state (KBr), these features did not change significantly: ν(CO) = 1995 cm^{-1} and ν(py CN) = 1607 cm^{-1}. Therefore, in both the solution and the solid state the nitrogen atoms are coordinated. The ^{31}P NMR spectrum with use of THF or CH_2Cl_2 as solvent consisted of a doublet with J_{Rh-P} = 125 Hz, indicative of equivalent phosphorus atoms. The low-temperature (−90 °C) ^{31}P NMR spectrum with use of CH_2Cl_2 as solvent was identical with the room-temperature spectrum. Therefore, a possible structure is that of a trigonal bipyramid with both phosphorus atoms either axial or equatorial and the CO ligand in an equatorial position. This postulated structure is similar to the X-ray determined structure of [Rh(dppm)$_2$(CO)]$^+$ [57] and the analogous complex [Rh(dppp)$_2$(CO)]$^+$ [58] but is in contrast to the iridium analogue [Ir(PN)$_2$CO]$^+$ (**5**) (vide supra). Another possibility is a fluxional molecule with the PN ligands rapidly rearranging on the NMR time scale to give an averaged ^{31}P NMR spectrum. It is interesting to note that the nitrogen atoms of other complexes with PN type donor ligands are generally displaced by CO,[7-9] but in this study no monodentate Rh–PN complexes were formed. Of particular note is the reaction between CO and [Rh(LL′)$_2$]$^+$ containing the PN type donor ligand *o*-(diphenylphosphino)-*N*,*N*-dimethylaniline, which formed a four-coordinate dicarbonyl complex with the dimethylamino arms of both chelates displaced by CO.[9]

The reaction of a stoichiometric amount of PN ligand dissolved in a minimal amount of toluene with the lithium salt of [Rh(CO)$_2$Cl$_2$]$^-$ in 2-methoxyethanol yielded the immediate formation of **Rh(PN)(CO)Cl (10)** and an effervescent loss of CO. Its formulation is based on IR and ^{31}P NMR spectroscopy and, by analogy, to the structures of Ir(PN)(CO)Cl (**4**) (vide supra) and Rh(PN′)(CO)Cl (**11**) (vide infra),[26] which were determined by single-crystal X-ray diffraction. The ^{31}P NMR of **10** with use of CH_2Cl_2 as solvent showed a single doublet resonance at δ 43.4 with J_{Rh-P} = 168 Hz, and the IR spectrum (KBr) contained a CO stretch at 1990 cm^{-1} and a pyridyl CN stretch at 1610 cm^{-1}. This data is consistent with a structure similar to that of **4**. As stated previously, **10** did not appear to react further with PN.

The yellow complex **Rh(PN′)(CO)Cl (11)** is a product of the reaction of the PNP ligand, which has been shown to be susceptible to P–C bond cleavage at elevated temperatures,[59] with the lithium salt of [Rh(CO)$_2$Cl$_2$]$^-$ in a 2-methoxyethanol/toluene solution. This reaction yielded a red solution that turned yellow upon refluxing for ca. 30 min. Slow addition of diethyl ether produced large yellow crystals in ca. 65% yield. The formulation of this complex is based on IR data (KBr, ν(CO) = 1980 cm^{-1}, ν(py CN) = 1607 cm^{-1}), ^{31}P NMR data (CH_2Cl_2, δ 58.8, d, J_{Rh-P} = 164 Hz), and a single-crystal X-ray diffraction analysis.[26] The molecular structure showed a four-coordinate planar geometry about the rhodium atom. The compound is monomeric with the PN′ ligand chelated through both the phosphorus and pyridyl nitrogen atoms. The phosphorus atom is trans to the chloride, and the nitrogen atom is trans to the carbonyl ligand as postulated in **4**. This is in agreement with trans effect arguments.

Catalytic Decarbonylation of Aldehydes. The catalytic decarbonylation of aldehydes using [Rh(PP)$_2$]$^+$ complexes as catalysts has been thoroughly discussed elsewhere.[2-5] A proposed pathway in the catalytic reaction cycle using [Rh(dppp)$_2$]$^+$ involves Rh–P bond rupture as the rate-determining step, followed by fast aldehyde association and oxidative addition giving a hydride acyl species [Rh(dppp)(dppp*)(H)(COR)]$^+$, where dppp* is monodentate.[5] This pathway is consistent with kinetic data.[5] In order to test the hypothesis that Rh–P bond dissociation is a kinetically important step in the decarbonylation of aldehydes using [Rh(PP)$_2$]$^+$ complexes, specifically [Rh(dppp)$_2$]$^+$, the activities of the catalysts [Rh(PN)$_2$]BF$_4$ (**8**(BF_4)), [Ir(PN)$_2$]PF$_6$ (**1**(PF_6)), and [Ir(dppp)$_2$]PF$_6$[60] for the decarbonylation of neat benzaldehyde were measured at 150 °C. The results of these experiments are presented in Table V along with the activities of a number of other rhodium(I) and iridium(I) diphosphine catalysts. The rhodium and iridium bis(diphosphine) catalysts have been reported to have

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(60) [Ir(dppp)$_2$]PF$_6$ can by synthesized in a manner analogous to that reported for the dppe complex in ref 35. Alternatively these bis(diphosphine) complexes can and often were synthesized from [Ir(cod)Cl]$_2$ and $AgPF_6$ in acetone solution, followed by the addition of 2 equiv of the appropriate ligand dissolved in toluene and by refluxing for several hours.

Table V. Catalytic Decarbonylation of Benzaldehyde

catalyst	ref	catalytic activity,[c] (mol of benzene/mol of catalyst)/h	temp, °C	conditions
$[Ir(PN)_2]PF_6$ (**1**(PF_6))	*b*	9 (2)	150	N_2
$[Ir(dppp)_2]PF_6$	*b*	1.5 (5)	150	N_2
$[Ir(dppe)_2]^+$	5	2.5	178	N_2
$[Ir(dppp)_2]^+$	5	4.4	178	N_2
$[Ir(dppb)_2]^+$	5	4.2	178	N_2
$[Ir(dppp)_2CO]^+$	5	4.6	178	N_2
$[Ir(PPh_3)_2]PF_6$[a]	36	17	150	H_2/N_2
$[Ir(dppe)]BF_4$[a]	36	28	150	H_2/N_2
$[Ir(dppp)]BF_4$[a]	5	39	150	H_2/N_2
$[Ir(dppb)]BF_4$[a]	36	16	150	H_2/N_2
$[Rh(dppp)_2]BF_4$	4	110	150	N_2
$[Rh(dppe)_2]BF_4$	4	25	150	N_2
$[Rh(PN)_2]BF_4$ (**8**(BF_4))	*b*	10 (2)	150	N_2
$[Rh(dppp)(PN)]BF_4$	*b*	14 (3)	150	N_2

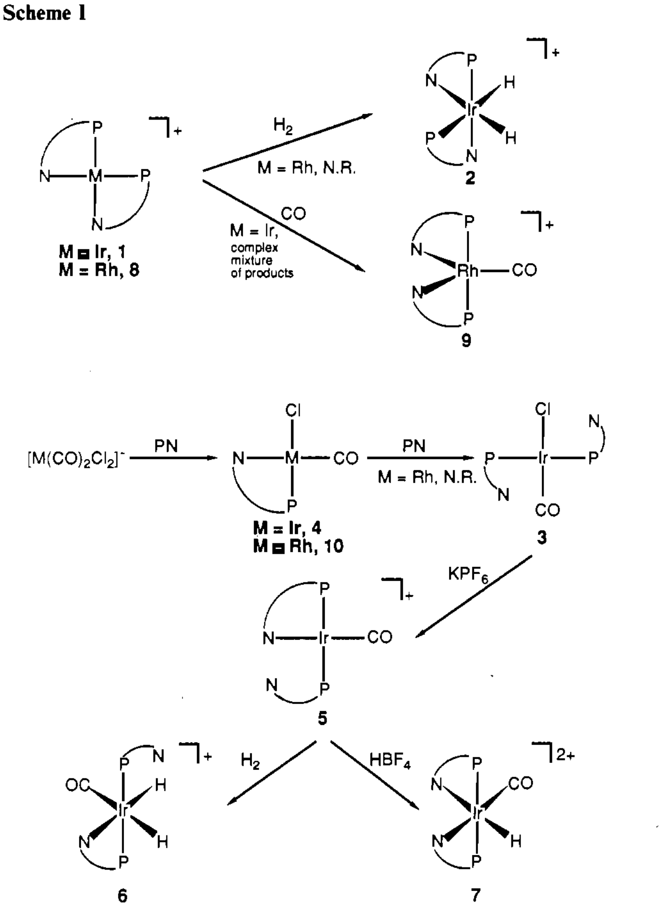
[a] Made in situ from [IrL(cod)]X by first purging the system for 1 min with H_2 to hydrogenate the cod (1,5-cyclooctadiene) to cyclooctane and then purging with purified N_2. [b] This work. [c] The values in parentheses are esd's. The previously determined activities are within ±15% as determined by repetitive experiments.[2]

good stability, with activities remaining constant over at least 48 h at 178 °C.[2-5] The catalytic activity of the PF_6^- salt of **1** and the BF_4^- salt of **8** were relatively constant during the first 5–6 h at 150 °C; however, for **1** a slow deactivation was noted during the next 12 h, and only ca. 5–10% of the original activity remained after this time. The activities reported for both **1** and **8** have therefore been averaged over the first 5–6 h.

As shown in Table V, complex **1** gave higher rates for the decarbonylation of benzaldehyde than did $[Ir(dppp)_2]PF_6$. In fact, inspection of Table V shows that **1** has a higher activity than any of the bis(diphosphine)iridium catalysts, even though these latter activities were measured at 178 °C. If a mechanism similar to that proposed for $[Rh(dppp)_2]^+$[5] (vide supra) is operative for the bis-chelated iridium catalysts, then this trend may be attributed to the increased lability of the Ir–N bond relative to the Ir–P bond. Also, note that the mono(diphosphine) complexes of iridium are better catalysts than the bis(diphosphine) complexes, which is consistent with M–P bond rupture being the rate-limiting step for the iridium bis(diphosphine) complexes. The complexes $Ir(PN)_2(CO)Cl$ (**3**), $[Ir(PN)_2(CO)]^+$ (**5**), and $[Ir(PN)_2(H)_2(CO)]^+$ (**6**) all contain monodentate PN ligands in which the PN ligand is coordinated through the phosphorus atom. In fact, **5** undergoes a rapid exchange of the coordinated and noncoordinated nitrogen end of the ligand (vide supra). The analogous diphosphine compounds $[Ir(dppe)_2(CO)]^+$, $[Ir(dppp)_2(CO)]^+$, $[Ir(dppm)_2(CO)]^+$ are 5-coordinate, 18e complexes that do not undergo detectable Ir–P bond rupture at 25 °C.[35,36,49]

The opposite trend was observed for the catalytic activity of the rhodium catalysts: $[Rh(PN)_2]BF_4 < [Rh(dppe)_2]BF_4 < [Rh(dppp)_2]BF_4$ (see Table V). The catalytic activity of **8**(BF_4) was determined to be 10 turnovers/h at 150 °C. This low catalytic activity was unexpected, and the reason for it is unclear; however, this trend suggests that the rhodium atom in **8** may not be "electron rich" enough to promote facile oxidative addition to an intermediate containing only two coordinated phosphorus atoms. Therefore, the rate-limiting step is oxidative addition. In support of this argument, the bis(diphosphine) catalysts $[Rh(PP)_2]^+$ have been found to be more active than their mono(diphosphine) analogues $[Rh(PP)]^+$,[5] and $[Rh(dppp)(PN)]^+$[61] is more active than complex **8** (see Table V). With $[Ir(PN)_2]^+$ (**1**), oxidative addition to an intermediate containing only two coordinated phosphorus atoms is apparently not rate limiting. This makes sense because iridium complexes are well-known to undergo oxidative addition more readily than their rhodium analogues. Also, **8**(PF_6) was shown to be unreactive toward H_2 (vide supra), whereas $[Rh(dppp)_2]^+$ readily reacted with H_2.[56]

Scheme I



A solution of **8**(PF_6) (75 mg) in 3 mL of neat benzaldehyde was heated to 178 °C for 3 h and rapidly quenched with 15 mL of cold decane. The ^{31}P NMR spectrum of the residue showed only **8**(PF_6) as the major resonance, along with a trace amount of $[Rh(PN)_2(CO)]^+$ (**9**). The absence of any Rh(III) species and the presence of only a trace amount of **9** are similar to the results obtained with $[Rh(dppp)_2]^+$.[5] This demonstrates that **9** could be part of the catalytic cycle, similar to the findings with $[Rh(dppp)_2]^+$. Also, due to the lack of buildup of Rh(III) species, migration and reductive elimination can be ruled out as rate-limiting steps. If **9** is a part of the catalytic cycle, CO lability and slow regeneration of the catalyst can also be ruled out as the reason for the low decarbonylation activity of **8**, since **9** loses CO readily upon standing in solution at room temperature, as did $[Rh(dppp)_2(CO)]^+$.[5]

Conclusion. In this paper we have discussed the synthesis, characterization, and reactivity of several new rhodium and iridium complexes containing the PN ligand, in an effort to obtain a better understanding of the differences in structure and reactivity between PN and PP complexes. As stated earlier, our interest in the PN ligand arose because mechanistic studies with the catalysts $[Rh(dppe)_2]^+$ and $[Rh(dppp)_2]^+$ suggested that M–P bond rupture was an important and rate-limiting step in the catalytic decarbonylation cycle. Also, M–N bonds are generally more labile than M–P bonds, and the resulting $[M(PN)_2]^+$ complex was thought to be more electron rich than the dppp analogue and would thereby facilitate oxidative addition. With this in mind, $[Ir(PN)_2]^+$ (**1**) and $[Rh(PN)_2]^+$ (**8**) were synthesized and their reactivities studied. As summarized in Scheme I, complex **1** reacted with H_2 to form the *cis*-dihydride $[Ir(PN)_2(H)_2]^+$ (**2**), as do $[Ir(dppe)_2]^+$ and $[Ir(dppp)_2]^+$; however, complex **8** proved to be unreactive toward

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(61) $[Rh(dppp)(PN)]^+$ was synthesized in two steps. The first step was analogous to the synthesis of **1** but with a 1:1 mole ratio of Rh to PN, forming orange crystals of $[Rh(nbd)(PN)]^+$. This product was then reacted with 1 mol of dppp in acetone solution. ^{31}P NMR (acetone): δ_3 33.7 (d of d of d, $J_{Rh-P3} = 154$ Hz, $J_{P3-P2} = 57$ Hz, $J_{P3-P1} = 34$ Hz); δ_2 15.3 (d of d of d, $J_{Rh-P2} = 140$ Hz, $J_{P2-P1} = 290$ Hz, $J_{P2-P3} = 57$ Hz); δ_1 30.9 (d of d of d, $J_{Rh-P1} = 134$ Hz, $J_{P1-P2} = 289$ Hz, $J_{P1-P3} = 34$ Hz).

H_2. Complex **8** reacted with CO to form the carbonyl adduct, $[Rh(PN)_2(CO)]^+$ (**9**), whereas the iridium analogue reacted with CO to form a complex mixture of products. The carbonyl adduct of **1**, $[Ir(PN)_2(CO)]^+$ (**5**), however, was synthesized from $Ir(PN)_2(CO)Cl$ (**3**) with KPF_6, which was synthesized from the reaction of $[Ir(CO)_2Cl_2]^-$ with 2 equiv of PN. The structure of **5** was determined to be four-coordinate with one monodentate PN ligand, which is surprising when compared to the five-coordinate structures of the diphosphine analogues $[Ir(dppe)_2(CO)]^+$, $[Ir(dppp)_2(CO)]^+$, and $[Ir(dppm)_2(CO)]^+$ and the rhodium analogue $[Rh(PN)_2(CO)]^+$ (**9**). The reactivity of **5** with H_2 and H^+ was also examined since compound **5** was found to be present in the benzaldehyde solutions of catalytic decarbonylation experiments using complex **1**.

Unfortunately, the PN complexes of rhodium were not good catalysts for the decarbonylation of benzaldehyde: $[Rh(PN)_2]BF_4$ showed an activity for the formation of benzene of 10 turnovers/h at 150 °C compared to 1.1×10^2 turnovers/h for $[Rh(dppp)_2]BF_4$. The opposite trend was observed for the iridium analogues; compound **1** was found to be a better catalyst for the decarbonylation of benzaldehyde than the iridium bis(diphosphine)catalysts. This trend is consistent with the mechanism proposed for the $[Rh(dppp)_2]^+$ catalyst system, and the increased rate results from the increased lability of the Ir–N bond relative to Ir–P. Also, the most probable reason for the slower decarbonylation rate for **8** relative to $[Rh(dppp)_2]^+$ is the slower rate for oxidative addition; however, slow Rh–N bond rupture can not be totally ruled out.

These conclusions should be treated with some caution, however, since they are based on the assumption that the mechanisms of these two catalyst systems are identical with that postulated for $[Rh(dppp)_2]^+$. Detailed kinetic studies have not been carried out for the iridium complexes. Seemingly slight changes in the electronic and steric properties of a complex can drastically affect the activity and mechanism of a catalyst. Furthermore, the observation of intermediates can be misleading when studying mechanisms of catalytic reactions. For example, in the case of **1**, it is possible that $[Ir(PN)_2(CO)]^+$ (**5**) is the active catalyst and undergoes oxidative addition of the aldehyde without prior loss of CO. This is a reasonable proposal since **5** will oxidatively add H_2 at 1 atm and 25 °C to form $[Ir(PN)_2(H)_2(CO)]^+$ (**6**). If this mechanism were operative for **1**, then the true rate-determining step might be Ir–N bond rupture or oxidative addition. Clearly, more kinetic and chemical studies are needed to understand the mechanism of these reactions.

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Registry No. **1**(PF_6), 113705-90-1; **2**(PF_6), 113705-92-3; **3**, 113705-93-4; **4**·Et_2O, 113705-95-6; **5**(PF_6), 113705-97-8; **6**(PF_6), 113705-99-0; **7**(BF_4)$_2$, 113706-01-7; **8**(PF_6), 113706-02-8; **8**(BF_4), 107810-34-4; **9**-(PF_6), 113706-04-0; **10**, 113706-05-1; **11**, 113706-06-2; PN, 60398-55-2; $[Ir(PN)(cod)]PF_6$, 112021-45-1; H_2, 1333-74-0; $Li[Ir(CO)_2Cl_2]$, 55095-92-6; $[Rh(nbd)Cl]_2$, 12257-42-0; D_2, 7782-39-0; $[Ir(dppp)_2]PF_6$, 113706-08-4; $[Ir(cod)Cl]_2$, 12112-67-3; $[Rh(dppp)(PN)]^+$, 113706-09-5; benzaldehyde, 100-52-7.

Supplementary Material Available: Listings of general temperature factor expressions, final positional and thermal parameters for all atoms including solvate molecules, calculated hydrogen atom positions, distances and angles, and least-squares planes (25 pages); listings of observed and calculated structure factor amplitudes (52 pages). Ordering information is given on any current masthead page.

Notes

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^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR Investigation of the Platinum(0)-Tetraphosphine Complexes $Pt[CH_3C(CH_2PPh_2)_3]PR_3$

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Platinum(IV) and platinum(II) complexes have been investigated extensively by ^{195}Pt NMR spectroscopy, usually by use of INDOR techniques; in contrast, the amount of ^{195}Pt NMR data available on mononuclear platinum(0) complexes is limited.[1,2] Data concerning the magnitudes of Pt–P coupling constants and ^{195}Pt and ^{31}P chemical shifts for Pt(0)–phosphine complexes are particularly limited due to the tendency of $Pt(PR_3)_4$ compounds to dissociate in solution. By use of the chelating triphosphine ligand $CH_3C(CH_2PPh_2)_3$ ("tripod") a series of dissociatively stable $Pt(tripod)PR_3$ complexes (PR_3 = PMe_2Ph, $PMePh_2$, PPh_3, $P(4\text{-}FC_6H_4)_3$, $P[3,5\text{-}(CF_3)_2C_6H_3]_3$, $P(CH_2CH_2CN)_3$, $P(OMe)Ph_2$, $P(OMe)_2Ph$, $P(OMe)_3$, $P(OPh)_3$, and $P(OCH_2CF_3)_3$) has been prepared and the ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR data obtained. These data have allowed us to expand the data base available for platinum(0) complexes and to draw empirical relationships from the platinum chemical shifts and platinum–phosphorus coupling constants.

Experimental Section

General Procedures. All reactions and sample preparations were carried out by use of standard Schlenk and inert-atmosphere-box techniques. Reagent grade solvents were dried by conventional methods[3] and distilled under argon. Distilled water and absolute ethanol were purged with an Ar stream for 20 min prior to use. Deuteriated THF, all phosphines and phosphites (all liquids were received under Ar) and $NaBH_4$ were used without further purification.

Synthesis of Complexes. The $Pt(tripod)PR_3$ complexes (PR_3 = $PPhMe_2$, PPh_2Me, PPh_3, $P(4\text{-}FC_6H_4)_3$, and $P(CH_2CH_2CN)_3$) were synthesized according to a published procedure.[4] The analogous phosphite complexes, $Pt(tripod)P(OR)_3$ ($P(OR)_3$ = $P(OMe)_3$, $P(OPh)_3$, and $P(OCH_2CF_3)_3$) were prepared by the same procedure; one must be careful to substitute the corresponding alcohol or THF for ethanol as the reaction solvent to prevent exchange of alkoxide groups. The complexes $Pt(tripod)P(OMe)Ph_2$ and $Pt(tripod)P(OMe)_2Ph$ were prepared in an NMR tube by adding the appropriate ligand ($P(OMe)Ph_2$ or $P(OMe)_2Ph$) to $Pt(tripod)PPh_2Me$ to displace PPh_2Me. The other complex, $Pt(tripod)P[3,5\text{-}(CF_3)_2C_6H_3]_3$, was prepared by refluxing a solution containing 0.2499 g (0.2806 mmol) of $PtCl_2(tripod)$ and 0.1885 g (0.2812 mmol) of $P[3,5\text{-}(CF_3)_2C_6H_3]_3$[5] in 35 mL of THF for 1 h. The resultant solution was concentrated to half its initial volume in vacuo; then 0.0341 g (0.830 mmol) of $NaBH_4$ dissolved in 10 mL of distilled water was added dropwise. The solvent was removed from the resulting orange slurry, and 20 mL of absolute ethanol and 10 mL of distilled water were added to the orange paste. The resultant orange solid was collected on a Schlenk frit, washed with 2 × 5 mL aliquots of distilled water, and dried in vacuo. Yield: 0.30 g.

Instrumentation. The ^{195}Pt{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded at 296 K on a Bruker MSL-300 spectrometer operating at 64.386 and 121.497 MHz, respectively. The ^{31}P{^{1}H} NMR spectra are referenced to external 85% H_3PO_4, and the ^{195}Pt{^{1}H} NMR spectra are referenced to external H_2PtCl_6 in D_2O/HCl with a correction made for the

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