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Synthetic and Structural Studies of the Coordination Behavior of 2-Pyridylbis(diphenylphosphino)methane

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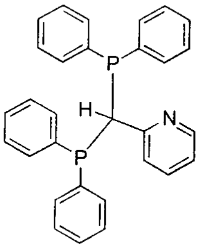
The coordination chemistry of the potentially semilabile tridentate ligand 2-pyridylbis(diphenylphosphino)methane (NPP) has been investigated. Bidentate (N, P) coordination occurs in $CoCl_2(NPP)$ (**1**) and $[CdX(\mu\text{-}X)(NPP)]_2$ (X = Cl (**2**); OAc (**3**)), prepared from the corresponding metal salts, in *fac*-$Re(CO)_3Br(NPP)$ (**4**) and in $Fe(CO)_2(MA)(NPP)$ (**6**). The last is one of three products from the reaction of $Fe(CO)_4(MA)$ (MA = maleic anhydride) with NPP, the other two being $Fe(CO)_3(NPP)$ (**7**; P, P coordinated) and the unusual cyclic ylid $Ph_2PC(2\text{-}C_5H_4N)PPh_2C(CH_2CO_2H)C({=}O)$ (**5**). The ligand shows tridentate coordination in $Cr(CO)_3(NPP)$ (**9**), $RuCl_2(PPh_3)(NPP)$ (**10**), and possibly in $PtCl_2(NPP)$ (**8**). Carbon monoxide displaces one phosphorus arm of the ligand in **10**. Anhydrous $NiCl_2$ and NPP react in the presence of methanol to give $NiCl_2(P(OMe)Ph_2)(Ph_2PCH_2py)$ (**12**) in which the NPP ligand has been cleaved. This in turn reacts with O_2 to form *trans*-$NiCl_2(Ph_2P(O)CH_2py)_2$ (**13**). The methine proton of NPP is transferred to the metal on reaction with $Pt(C_2H_4)(PPh_3)_2$ and $[Ir(COD)(NPP)]BF_4$ to form the hydride complexes $Pt(H)(PPh_3)(NPP{-}H)$ (**14**) and $[Ir(H)(NPP)(NPP{-}H)]BF_4$ (**15**). In **15** the intact NPP ligand is tridentate. The structures of **1** − **7** and **12** − **15** have been determined.

Introduction

There has been a continuing interest in the synthesis and chemistry of complexes of "hemilabile" ligands, for example $Ph_2PCH_2CH_2NMe_2$[1] (a PN donor set), because of their potential for stabilizing the active sites of resting catalyst species in homogeneous systems.[2] The vast majority of studies reported to date concern bidentate ligands of this type, and, given our continuing work in the area of dinuclear complexes, we considered it of interest to explore the coordination behavior of tridentate ligands having the P_2N donor set to determine if similar "semilabile" behavior might be observed in dinuclear species. A suitable ligand appeared to be 2-pyridylbis(diphenylphosphino)methane (NPP).



NPP

This and an analogue methylated on the pyridyl group have been the subjects of a limited number of reports[3−7] but it does not appear that there has been any systematic study of the chemistry of NPP-type ligands. To address this we sought first to determine the extent to which NPP would promote the formation of dinuclear complexes from mononuclear precursors as is well-established for its "parent" ligand bis(diphenylphosphino)methane (DPPM)[8] and as has been found to occur with Rh(I) and Ir(I) systems.[6,9] A second goal of the study was to ascertain if monometallic NPP complexes could function as metalloligands in the synthesis of *hetero*bimetallic complexes. Additionally it was of interest to confirm the coordination mode of NPP in examples of its complexes where this had been only inferred from limited spectroscopic data.[3] To complement earlier work, the coordination behavior of NPP toward metals from Groups 7−12 should provide an adequate study of its capabilities as a ligand. However, the known sensitivity of NPP to cleavage under photochemical[7] and severe thermal conditions[8] significantly limits the range of starting complexes that can be used to those with readily replaceable ligands.

Experimental Section

All reactions were carried out using a purified nitrogen atmosphere and a standard Schlenk-type apparatus. Dry, oxygen-free solvents were used throughout, and other reagents, including metal salts, were used

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as purchased. Literature methods were used to prepare NPP,[9] $\mathrm{Re(CO)_3Br(MeCN)_2}$,[10] $\mathrm{Fe(CO)_4(MA)}$ (MA = maleic anhydride),[11] $\mathrm{PtCl_2(PhCN)_2}$,[12] $\mathrm{Cr(CO)_3(C_7H_8)}$,[13] $\mathrm{RuCl_2(PPh_3)_3}$,[14] $\mathrm{[Ir(COD)(NPP)]BF_4}$ (COD = 1,5-cyclooctadiene),[15] and $\mathrm{Pt(C_2H_4)(PPh_3)_2}$.[16] NMR spectra were obtained on an IBM/Bruker AF200 NMR spectrometer at 200.132 MHz (^{1}H, $\mathrm{Me_4Si}$ standard) and 81.015 MHz (^{31}P, 85% $\mathrm{H_3PO_4}$ standard). High-field proton spectra of the hydride complexes were also recorded on a GE Ω 400 MHz spectrometer by Dr. Michael Player of the Tulane University Chemistry Department (key to NMR peak multiplicities: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; td, triplet of doublets; ddd, doublet of doublets of doublets; sept, septet; py*H* refers to a hydrogen atom on the pyridyl ring). IR spectra were recorded on a Mattson-Cygnus 100 Fourier Transform Spectrometer (key to infrared absorption intensities: vs, very strong; s, strong; m; medium; w, weak; sh, shoulder), and electronic spectra were recorded on an H.P. diode array spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

$\mathrm{CoCl_2(NPP)}$ (1). A total of 0.258 g (1.08 mmol) of $\mathrm{CoCl_2{\cdot}6H_2O}$ and 0.500 g (1.08 mmol) of NPP were dissolved in 10 mL portions of ethanol, and 4 mL of 2,2-dimethoxypropane was added to the ligand solution. The two solutions were combined, and dark blue needles of the product were obtained by dilution with diethyl ether and cooling. The analytical sample was recrystallized from 1,2-dichloroethane/diethyl ether. Anal. Calcd for $\mathrm{C_{30}H_{25}P_2Cl_2NCo}$: C, 60.93; H, 4.27. Found: C, 60.5; H, 4.3.

$\mathrm{Cd_2Cl_2(\mu\text{-}Cl)_2(NPP)_2}$ (2). A solution of 0.434 g (0.94 mmol) of NPP in 2 mL of dichloromethane was added to a solution of 0.172 g (0.94 mmol) of anhydrous $\mathrm{CdCl_2}$ in 12 mL of methanol. After an immediate change in color to bright green an insoluble white precipitate was obtained. This was collected via filtration, washed with a mixture of methanol and diethyl ether, and dried in vacuo. Larger crystals of the complex could be obtained by carrying out the reaction in pure methanol followed by slow vapor diffusion of diethyl ether into the reaction mixture. Anal. Calcd for $\mathrm{C_{60}H_{50}P_4N_2Cl_4Cd_2}$: C, 55.88; H, 3.91; Cl, 11.00. Found: C, 55.4; H, 4.3; Cl, 10.8. IR (Nujol mull): 1599(m) (ν_{pyCN}) cm^{-1}.

$\mathrm{Cd_2(OAc)_2(\mu\text{-}OAc)_2(NPP)_2}$ (3). Anhydrous $\mathrm{Cd(OAc)_2}$ (0.063 g, 0.274 mmol) and NPP (0.126 g, 0.274 mmol) were mixed in 15 mL of acetone. Sufficient dry methanol was added to dissolve all the solid, and the reaction mixture was warmed briefly. Following reduction of the volume by about 50% in vacuo, the resulting solution was layered with diethyl ether and cooled to −30° C to produce white crystals of X-ray quality. Despite the successful solution of the structure, elemental analyses on the sample repeatedly gave low values for carbon. IR (Nujol mull): 1595(m) (ν_{pyCN}), 1555(s), 1442(s) (ν_{OAc}) cm^{-1}.

$\mathrm{Re(CO)_3Br(NPP){\cdot}0.75acetone}$ (4). To a solution of 0.468 g (1.08 mmol) of $\mathrm{Re(CO)_3Br(MeCN)_2}$ in 8 mL of THF was added a solution of 0.500 g (1.08 mmol) of NPP in 4 mL of THF. The reaction mixture was then stirred for 1 h followed by precipitation with diethyl ether. The white powder was isolated by filtration and recrystallized from acetone/diethyl ether as colorless crystals. Anal. Calcd for $\mathrm{C_{34.25}H_{29.5}NP_2O_{3.75}BrRe}$: C, 48.78; H, 3.53; N, 1.66. Found: C, 49.4; H, 3.8; N, 1.4. IR (Nujol mull): 2027(vs), 1939(vs), 1877(vs) ($\nu_{\mathrm{C\equiv O}}$) cm^{-1}. ^{1}H NMR (acetone d$_6$): δ 9.01 (m, 1H, py*H*), 7.60−6.90 (m, 23 H, $\mathrm{C_6}H_5$, py*H*), 5.82 (dd ($J_{\mathrm{P-H}}$ = 10.8, 2.1 Hz), 1 H, $\mathrm{P_2C}H$). ^{31}P{^{1}H} NMR (acetone d$_6$): δ 43.2 (d), −6.3 (d) ($J_{\mathrm{P-P}}$ = 107.0 Hz).

Reaction of NPP with $\mathrm{Fe(CO)_4(MA)}$. To a solution of 0.324 g (1.22 mmol) of $\mathrm{Fe(CO)_4(MA)}$ in 10 mL of acetone was added 0.562 g (1.22 mmol) of NPP dissolved in 15 mL of acetone, and the mixture was refluxed for 2 h. Three products (**5**−**7**) were formed which were separated by fractional crystallization as described below.

$\mathrm{Ph_2\overline{PC(2\text{-}C_5H_4N)PPh_2C(CH_2CO_2H)C}({=}O)}$ (5). This was obtained as pale yellow crystals when the original reaction mixture was allowed to stand at room temperature overnight. These were collected by filtration and recrystallized from chloroform/hexane. The same compound can also be prepared by the direct reaction of NPP with an equimolar quantity of maleic anhydride. Anal. Calcd for $\mathrm{C_{34}H_{27}NO_3P_2}$: C, 72.98; H, 4.86; N, 2.50. Found: C, 72.6; H, 5.1; N, 2.5. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 7.99−7.48 (m, 22 H, $\mathrm{C_6}H_5$, COO*H*, py*H*), 7.13 (td (J = 7.7, 1.9 Hz), 1 H, py*H*), 6.55−6.44 (m, 2 H, py*H*), 3.15 (d (J(P−H) = 9.9 Hz), 2 H, CH_2). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 24.4 (d), 7.0 (d) ($J_{\mathrm{P-P}}$ = 71.1 Hz).

$\mathrm{Fe(CO)_2(MA)(NPP)}$ (6). This was obtained as yellow orange crystals upon addition of diethyl ether to the filtrate remaining after removal of **5** and cooling at −30° C overnight. These were isolated by filtration and recrystallized from dichloromethane/diethyl ether. Anal. Calcd for $\mathrm{C_{36}H_{27}NO_5P_2Fe}$: C, 64.39; H, 4.05;. Found: C, 63.5; H, 5.3. IR (Nujol mull): 1979(s), 1925(s) ($\nu_{\mathrm{C\equiv O}}$); 1724(ms), 1699(ms) ($\nu_{\mathrm{C=O}}$); 1599(w) (ν_{pyCN}) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.45 (m, 1 H, py*H*) 7.64−7.04 (m, 21 H, $\mathrm{C_6}H_5$), 6.74 (m, 2 H, py*H*), 6.29 (m, 1 H, py*H*), 5.12 (dd ($J_{\mathrm{P-H}}$ = 12.6, 3.4 Hz), 1 H, $\mathrm{P_2C}H$), 4.10 (m, 1H, C═C*H*), 3.59 (m, 1 H, C═C*H*). ^{31}P{^{1}H} NMR (acetone d$_6$): δ (P$_1$) 80.0 (d), δ (P$_2$) −10.8 (d) ($J_{\mathrm{P1-P2}}$ = 91.0 Hz).

$\mathrm{Fe(CO)_3(NPP)}$ (7). This was obtained as analytically pure, orange crystals from the filtrate produced in the previous step followed by addition of more diethyl ether and further cooling. These were collected by filtration, washed with diethyl ether and dried in vacuo. Anal. Calcd for $\mathrm{C_{33}H_{25}NO_3P_2Fe}$: C, 65.91; H, 4.19; N, 2.32. Found: C, 65.7; H, 4.3; N, 2.4. IR ($\mathrm{CH_2Cl_2}$ soln): 1989(s), 1915(m), 1904(m) ($\nu_{\mathrm{C\equiv O}}$); (Nujol mull) 1588(m) (ν_{pyCN}) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 8.50 (m, 1 H, py*H*) 7.71−7.15 (m, 20 H, $\mathrm{C_6}H_5$), 6.92 (m, 1 H, py*H*), 6.69 (m, 1 H, py*H*), 6.43 (m, 1 H, py*H*), 4.83 (m, 1 H, $\mathrm{P_2C}H$). ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 36.8 (s).

$\mathrm{PtCl_2(NPP)}$ (8). To 0.292 g (0.618 mmol) of $\mathrm{PtCl_2(PhCN)_2}$ dissolved in 6 mL of dichloromethane was added 0.285 g of NPP dissolved in 4 mL of dichloromethane. The solvent was then removed in vacuo and the residual solid was washed with diethyl ether and recrystallized from dichloromethane/diethyl ether. Anal. Calcd for $\mathrm{C_{30}H_{25}P_2NCl_2Pt{\cdot}0.75CH_2Cl_2}$: C, 46.68; H, 3.38. Found: C, 46.4; H, 3.9. IR (Nujol mull): 1607(m) cm^{-1} (ν_{pyCN}). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −44.4 (s with ^{195}Pt satellites, $J_{\mathrm{Pt-P}}$ = 3138.4 Hz).

$\mathrm{Cr(CO)_3(NPP){\cdot}acetone}$ (9). Solid NPP (0.500 g,1.08 mmol) was added to a solution of 0.247 g (1.08 mmol) of $\mathrm{Cr(CO)_3(C_7H_8)}$ dissolved in 15 mL of acetone. The solution was refluxed for ca. 20 h and filtered to remove a small quantity of green precipitate. Dilution of the filtrate with diethyl ether and cooling afforded the product as a bright orange, microcrystalline solid. This was isolated by filtration, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $\mathrm{C_{33}H_{25}P_2O_3NCr{\cdot}C_3H_6O}$: C, 66.56; H, 4.81; N, 2.16. Found: C, 65.6; H, 4.5; N, 2.3. IR (Nujol mull): 1902(vs), 1798(vs) ($\nu_{\mathrm{C\equiv O}}$); 1713(m) ($\nu_{\mathrm{C=O}}$); 1593(w) (ν_{pyCN}) cm^{-1}. ^{1}H NMR (acetone d$_6$): δ 9.01 (m, 1H, py*H*), 7.87−7.07 (m, 23H, $\mathrm{C_6}H_5$, py*H*), 6.27 (t ($J_{\mathrm{P-H}}$ = 4.7 Hz), 1H, $\mathrm{P_2C}H$). ^{31}P{^{1}H} NMR (acetone d$_6$): δ 66.1 (s).

$\mathrm{RuCl_2(PPh_3)(NPP)}$ (10). $\mathrm{RuCl_2(PPh_3)_3}$ (0.416 g, 0.433 mmol) and NPP (0.200 g, 0.433 mmol) were combined in 20 mL of dichloromethane. The solution was then gently refluxed for ca. 1 h during which time a light orange precipitate formed. Precipitation was completed by the addition of diethyl ether to the cooled reaction mixture, and the product was collected by filtration, washed with diethyl ether, and recrystallized from dichloromethane/diethyl ether as fibrous yellow orange needles. Anal. Calcd for $\mathrm{C_{48}H_{40}P_3Cl_2NRu{\cdot}0.1CH_2Cl_2}$: C, 63.89; H, 4.49; Cl, 8.62. Found: C, 62.7; H, 4.9; Cl, 8.3. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 9.55 (m, 1H, py*H*), 8.05−6.48 (m, 38 H, $\mathrm{C_6}H_5$, py*H*), 5.84 (t ($J_{\mathrm{P-H}}$ = 6.1 Hz), 1H, $\mathrm{P_2C}H$). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$): δ (P$_1$, P$_{1'}$) 36.9 (d), 42.2 (P$_2$) (t) ($J_{\mathrm{P1-P2}}$ = 24.0 Hz).

$\mathrm{RuCl_2(CO)(PPh_3)(NPP){\cdot}CH_2Cl_2}$ (11). Dry CO gas was bubbled through a solution of **10** in dichloromethane for about 0.5 h during which time the color of the solution changed from orange yellow to bright yellow. Dilution with diethyl ether and cooling overnight at −30° C provided the product as yellow crystals. Anal. Calcd for $\mathrm{C_{50}H_{51}P_3OCl_4NRu}$: C, 51.48; H, 3.65. Found: C, 50.5; H, 4.0. IR (Nujol

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mull): 1960(vs) ($\nu_{C\equiv O}$) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 9.10 (m, 1 H, py*H*), 8.50−6.50 (m, 47 H, C_6H_5, py*H*), 4.95 (d ($J_{P-H} = 13.3$ Hz), 1H, P_2CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ ($P_{1'}$) −3.8 (d, $J_{P1-P1'} = 62.9$ Hz), δ (P_2) 36.2 (d, $J_{P1-P2} = 24.2$ Hz), δ (P_1) 58.9 (dd, $J_{P1-P1'} = 62.9$, $J_{P1-P2} = 24.2$ Hz).

$NiCl_2(Ph_2POMe)(Ph_2PCH_2py)$ (12). Anhydrous $NiCl_2$ (0.136 g, 1.05 mmol) was suspended in 15 mL of THF and 0.486 g (1.05 mmol) of NPP was added. Subsequent addition of 6 mL of dry methanol caused the pinkish suspension to become dark brown as the majority of the solid dissolved. After stirring at room temperature overnight, the mixture was filtered and the filtrate diluted with diethyl ether. Large brown crystals were obtained after cooling for several days at −30° C. These were isolated by removing the mother liquor via syringe following which they were dried in vacuo. Anal. Calcd for $C_{31}H_{29}NOP_2Cl_2Ni$: C, 59.75; H, 4.70; Cl, 11.38. Found: C, 59.1; H, 4.8; Cl, 11.7. IR (Nujol mull): 1609(m) (ν_{pyCN}) cm^{-1}.

$NiCl_2(Ph_2P(O)CH_2py)_2 \cdot 2H_2O$ (13). A solution of **12** in 1,2-dichloroethane was exposed to the atmosphere for several days resulting in significant bleaching of the color of the solution and the formation of light green crystals. The supernatant was removed via syringe and the crystals dried in vacuo. Anal. Calcd for $C_{36}H_{32}N_2O_2P_2Cl_2Ni \cdot 2H_2O$: C, 57.47; H, 4.83. Found: C, 57.8; H, 4.9.

$PtH(PPh_3)(NPP-H)$ (14). A solution of 0.154 g (0.334 mmol) of NPP in 6 mL of acetone was added to a suspension of 0.250 g (0.334 mmol) of $Pt(C_2H_4)(PPh_3)_2$ in 10 mL of acetone, resulting in a yellow solution from which the product precipitated after approximately 30 s. This was collected by filtration, washed with acetone and diethyl ether, and recrystallized from dichloromethane/diethyl ether. Anal. Calcd for $C_{48}H_{40}P_3NPt$: C, 62.74; H, 4.40; N, 1.52. Found: C, 62.3; H, 4.5; N, 1.4. IR (Nujol mull): 1994(w) (ν_{Pt-H}), 1578(m) (ν_{pyCN}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.98−6.24 (m, C_6H_5, py*H*), −5.93 (ddd, Pt-*H*, J_{P-H} = 9.3 Hz, 23.0 Hz, 167.7 Hz. $J_{Pt-H} = 1076.7$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (P_1) 30.5(dd), δ (P_2) −29.2(dd), δ (P_3) −26.9(dd) ($J_{P1-P2} = 12.8$, $J_{P2-P3} = 20.6$, $J_{P1-P3} = 351.2$, $J_{Pt-P1} = 2623.4$, $J_{Pt-P2} = 1406.6$, $J_{Pt-P3} = 2195.4$ Hz).

$[IrH(NPP-H)(NPP)]BF_4$ (15). Solid NPP (0.606 g,1.31 mmol) was added to a solution of 1.115 g (1.31 mmol) of $[Ir(COD)(NPP)]BF_4$ in 30 mL of acetone. The reaction mixture was then refluxed for 1.5 h during which time a yellow precipitate formed. This was collected by filtration and washed with acetone followed by diethyl ether. The analytical sample was recrystallized from dichloromethane/diethyl ether. Anal. Calcd for $C_{60}H_{50}N_2P_4BF_4Ir$: C, 59.96; H, 4.19; N, 2.33; F, 6.32. Found: C, 58.8; H, 4.7; N, 1.9; F, 6.8. ^1H NMR (CD_2Cl_2): δ −18.6 (sept, $J_{P-H} = 15.1$, 7.4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 1.9 (d), −51.8 (d) ($J_{P-P} = 302.7$ Hz).

Reaction of DPPM with MA. The off white precipitate rapidly formed on mixing acetone solutions of DPPM and MA shows $^{31}P\{^1H\}$ NMR resonances ($CDCl_3$ soln) at δ 13.6(d), −27.6 (d) ($J_{P-P} = 63.6$ Hz) and ^1H NMR resonances ($CDCl_3$ soln) at δ 7.64−7.20 (m, 20 H, C_6H_5), 3.72 (d ($J_{P-H} = 14.3$ Hz), 2 H, PCH_2P), 3.1 (s, 2 H, $-CH_2-$).

Synthesis of $(Ph_2P)_2CDpy$. A solution of NPP in dry THF was treated dropwise with 1 equiv of *n*-BuLi (in hexane) at 0 °C. The dark red-orange solution was quenched with D_2O and the solvent removed in vacuo. Extraction of the residue with dichloromethane followed by filtration, dilution with hexane, and concentration under reduced pressure gave white crystals whose ^1H and ^{31}P NMR spectra were identical with those of NPP except for the absence of the resonance attributable to the methine proton and a significant broadening of the single phosphorus resonance.

X-ray Crystallography. Crystals of **2**, **3**, **12**, and **13** were obtained directly from the respective reaction mixtures as described above. The remainder of the crystals used were chosen from the recrystallized samples used for elemental analyses. All except for **2** and **5** were mounted on thin glass fibers with a coat of epoxy cement. For compound **2** the crystal was wedged into a nitrogen-filled, thin-walled quartz capillary which was then flame-sealed. All crystallographic data for complexes, with the exception of **5**, were obtained on an Enraf-Nonius CAD-4 diffractometer. In the case of **5**, the data were collected at 100 K on a Nonius Kappa CCD instrument using a crystal mounted on a glass fiber with Paratone oil. We thank Dr. Frank Fronczek of the Chemistry Department, Louisiana State University, for this data set. General procedures for crystal alignment, unit cell determination and refinement, and collection of intensity data have been published.[17] Final unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 high order (typically with $18.0° \le \theta \le 24.0°$) which were determined by the SET4 routine of the CAD-4 software. For **3**, **4**, **6**, and **13**−**15** the space groups were uniquely determined by the observed systematic absences while in **1** and **2** the intensity statistics strongly indicated the centric space group. For **5** and **12**, no symmetry higher than monoclinic was indicated by either the CAD-4 software or SHELXPREP[18] and preliminary data collection results clearly showed the chosen unit cells to be, respectively, primitive and C-centered. In both instances, the intensity statistics had very nearly the ideal values for an acentric structure which provided a basis for the choice of the acentric space groups here. The successful refinement with no unusually high correlations between least-squares parameters supports this. In the case of **7**, both the CAD-4 software and SHELXPREP strongly indicated the primitive triclinic cell chosen initially to be correct, and the intensity statistics strongly favored the acentric space group. While recognizing that P1 is an infrequently encountered space group, the above criteria plus the satisfactory refinement of the structure and the absence of unusual geometrical or other derived parameters strongly suggest that it is correct. All intensity data were corrected for Lorentz and polarization effects and, where warranted, for decay in the intensity monitors and for absorption using ψ scans on several reflections with χ near 90°. Structure solutions and refinements were performed using the SHELXTL-PLUS[18] package. Typically, hydrogen atoms attached to carbon were placed in calculated positions and allowed to ride except for the methine proton in intact NPP ligands and the protons of the maleic anhydride ligand in **6** which were refined. For **15**, low angle $\Delta\rho$ maps provided a reasonable location for the hydride ligand which was subsequently included as a fixed contribution since attempts at refinement proved to be unsatisfactory. In **14**, the $\Delta\rho$ map calculated after inclusion of all the ligand hydrogen atoms showed a residual peak of moderate size located in the region expected for the hydride ligand but at a distance of 2.12 Å from the platinum. The source of this peak is not clear as it is too large and too distant from the metal to be the hydride ligand but too close to be a chloride ligand (a plausible alternative since hydride complexes are known to react with halogenated solvents to give the corresponding chloro complexes[19] and during the slow crystallization of **14** in the presence of dichloromethane some conversion to the chloro analogue and cocrystallization of the two could have occurred). It is, however, close to that reported for a Pt−OH moiety,[20] and attempted refinement as such proceeded satisfactorily, converging with a 25% occupancy for oxygen. Despite this, it is much less clear how partial conversion of the hydride complex to a hydroxide complex could have occurred under the conditions employed and as there was an insufficient quantity of the sample used for the structure determination for a detailed analysis, it was considered best to leave the peak in question unaccounted for. This does not appear to have any significant effect on the rest of the structure. Further crystallographic details on the individual structures are provided in the Supporting Information.

Results and Discussion

Reaction of hydrated Co(II) chloride with NPP under conditions used for the preparation of first-row transition element complexes of the closely related ligand 2-bis(diphenylphosphino)methyl-6-methylpyridine (ppn)[3] readily afforded a dark blue crystalline product analyzing as $CoCl_2(NPP)$ (**1**). Complex **1** exhibits an electronic absorption spectrum typical of tetrahedral Co(II)[21] with bands at 18 450(sh), 17 544, 15 385, and 14 409 cm^{-1} ($C_2H_4Cl_2$ soln) which compare favorably with those

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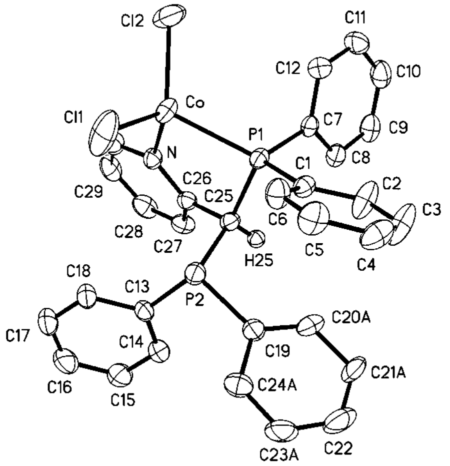

Figure 1. Perspective view of $CoCl_2$(NPP) (**1**). Only one orientation of the disordered phenyl group containing C19 is shown and hydrogen atoms are omitted for clarity.

reported for $CoCl_2$(ppn).[3] In the latter complex and related species, coordination of ppn in the N,P mode was inferred from shifts in the frequency of the highest energy deformation vibration of the pyridine ring upon coordination. In our hands, this infrared band could not always be identified with confidence so the structure of **1** was determined to confirm the coordination mode of NPP. As shown in Figure 1, it is coordinated in N,P fashion with the cobalt in a distorted tetrahedral environment. The major distortion results from the N−Co−P1 angle being 82.63(8)° as the result of chelate ring formation. All other angles about cobalt are in the range 112−117°, and the remaining metrical parameters are unexceptional.

Application of this synthetic methodology to hydrated zinc and cadmium salts did not yield any tractable products and a similar lack of success was had with anhydrous zinc salts as well. However, with anhydrous cadmium chloride and acetate, white crystalline products (**2** and **3**) were prepared. Complex **2** analyzes as $CdCl_2$(NPP) and the identification of the deformation band at 1599 cm^{-1} suggests N,P coordination for the ligand. This was confirmed by the structure determination which also showed the molecule to be dimeric with bridging chloride ligands and crystallographically imposed centrosymmetry (Figure 2). Overall, the structure is quite similar to that found for $[CdCl_2(Ph_2PCH_2CH_2NEt_2)]_2$[22] with the coordination about cadmium being a distorted trigonal bipyramid in which Cl(1) and N are the axial ligands (see Table 2). The $\{Cd_2Cl_2\}$ moiety here is more nearly equilateral than in the example cited but the nonbonding Cd···Cd distance of 3.834 Å is about the same. Also found in the crystal sample of **2** are two molecules of solvent methanol but these serve only to fill voids in the structure. A complex of formula $CdBr_2$(ppn) in which N,P coordination of the ligand was proposed has been reported[3] but a 4-coordinate monomeric structure was postulated. On the basis of the present work, that species is probably dimeric. In the case of **3**, microanalytical data for hydrogen and nitrogen were consistent with the composition determined from the crystal structure analysis but carbon values were consistently low. We have no ready explanation for this but feel that the structure represents the nature of the bulk sample. The structure of **3** consists of acetate-bridged dinuclear molecules having crystallographically imposed centrosymmetry (Figure 3). The nonbridging acetate ligands show highly asymmetric coordination with the difference in the two Cd−O distances (see Table 2) larger than that found in $[Cd(O_2C(o\text{-}C_6H_4OH))_2(H_2O)_2]_2$ (2.322(2), 2.429(1) Å)[23] but smaller than that in $[Cd(bipy)(O_2CCH_2NHS(O)_2(p\text{-tol}))_2]_2$ (2.265(6), 2.657(6) Å).[24] However, since the longer distance here is much less than the sum of the van der Waals radii (3.10 Å) we consider that this acetate should be considered to be chelating. A similar situation is obtained with the bridging acetate ligands where the Cd−O3 and Cd−O4A distances differ by considerably more than the corresponding distance in the two complexes cited above. There the bridging carboxylates are considered to chelate to one metal and to also coordinate to the second via one oxygen, but in the present case, this description is more tenuous. On the other hand, the Cd−O4A distance is considerably shorter than what would be the corresponding distance in $[Cd(OAc)_2(imidazole)_2]_n$ (3.117 Å) where each oxygen atom of the bridging acetate ligand is within bonding distance of only one cadmium atom.[25] For these reasons, it is difficult to arrive at a good description of the coordination number and geometry of cadmium in **3** but a seven-coordinate structure is not likely.

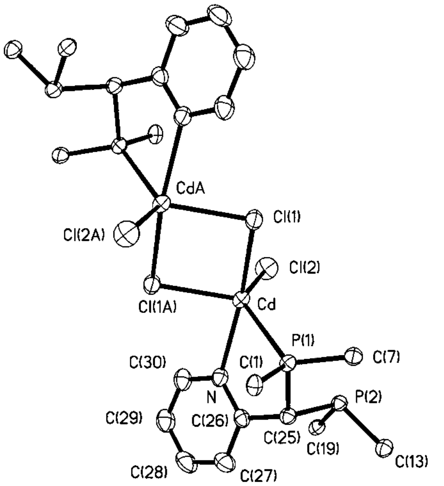

Figure 2. Perspective view of $[CdCl(\mu\text{-}Cl)(NPP)]_2$ (**2**). Only the *ipso* carbon atoms of the phenyl groups are shown and the hydrogen atoms are omitted for clarity. Unlabeled atoms and those labeled with an "A" are related to the atoms with normal labels by the center of symmetry.

The NPP ligand readily replaces acetonitrile in $ReBr(CO)_3(MeCN)_2$ to form colorless crystals analyzing as $ReBr(CO)_3(NPP)\cdot 0.75$acetone (**4**) whose infrared spectrum indicates the presence of a $\{fac\text{-}Re(CO)_3\}$ moiety with lower than C_{3v} symmetry and whose $^{31}P\{^1H\}$ NMR spectrum shows the presence of one coordinated and one uncoordinated phosphorus atom. The NPP ligand is thus N,P coordinated and this is confirmed by the crystal structure (Figure 4). By contrast, reaction of NPP with $MnBr(CO)_3(MeCN)_2$ repeatedly gave mixtures of products that could not be satisfactorily separated or characterized.

Reaction of NPP with $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, or $Co_2(CO)_8$ under a variety of conditions typically gave a mixture of products which we were unable to satisfactorily separate. However, with $Fe(CO)_4$(MA) a more tractable system resulted as indicated in the Experimental Section and three products, **5**−**7**, were separated and characterized. Complex **6** has been

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Table 1. Crystal Data and X-ray Experimental Details

	1	2	3	4	5	6	7
formula	$C_{30}H_{25}NP_2Cl_2Co$	$C_{62}H_{58}N_2P_4Cl_2Cd_2{\bullet}2CH_3OH$	$C_{68}H_{64}N_2O_8P_4Cd_2$	$C_{33}H_{25}NO_3P_2BrRe{\bullet}0.75C_3H_6O$	$C_{34}H_{27}NO_3P_2$	$C_{36}H_{27}NO_5P_2Fe$	$C_{33}H_{25}NO_3P_2Fe$
fw	591.3	1417.6	1383.9	855.2	559.51	671.4	601.33
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)	$P1$ (No. 1)
a, Å	8.5451(7)	11.167(2)	11.765(2)	17.006(2)	9.7170(6)	9.8996(7)	9.228(1)
b, Å	11.1705(8)	11.957(2)	13.253(2)	10.8139(7)	16.752(2)	13.8066(7)	9.304(2)
c, Å	15.907(1)	15.079(3)	19.801(2)	20.678(2)	9.3600(7)	23.283(1)	9.442(13)
α, deg	90.286(6)	87.71(1)	90	90	90	90	114.05(1)
β, deg	100.529(6)	68.52(2)	94.59(1)	114.178(9)	103.81(5)	93.549(5)	93.11(1)
γ, deg	110.489(6)	62.25(2)	90	90	90	90	104.44(1)
V, $Å^3$	1394.4(2)	1637.2(5)	3077.3(8)	3469.3(5)	1400.4(2)	3176.2(3)	705.7(2)
Z	2	1	2	4	2	4	1
D_{calc}, mg m^{-3}	1.408	1.438	1.493	1.637	1.327	1.404	1.415
μ, mm^{-1}	0.94	0.96	0.85	4.783	0.19	0.62	0.68
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T, K	293	293	293	293	−173	293	293
R^a	0.040	0.033	0.044	0.037	0.039	0.037	0.031
$R_{w2}{}^b$	0.085	0.083	0.114	0.087	0.068	0.080	0.076
wgt par a, b^b	0.031, 1.145	0.045, 0.700	0.046, 5.261	0.048, 0.0	0.022, 0.0	0.033, 2.123	0.053, 0.0

	12	13	14	15
formula	$C_{31}H_{29}NOP_2Cl_2Ni$	$C_{32}H_{32}N_2O_2P_2Cl_2Ni$	$C_{48}H_{40}NP_3Pt$	$C_{60}H_{50}N_2P_4BF_4Ir{\bullet}C_4H_{10}O$
fw	623.1	716.2	918.8	1276.0
space group	Cc (No. 9)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	14.992(1)	9.378(2)	18.088(1)	15.184(1)
b, Å	11.407(1)	14.559(2)	12.8836(9)	21.329(2)
c, Å	17.417(2)	12.510(2)	18.423(2)	18.365(3)
α, deg	90	90	90	90
β, deg	105.390(9)	104.30(1)	112.975(8)	99.081(9)
γ, deg	90	90	90	90
V, $Å^3$	2871.8(5)	1655.0(4)	3952.6(5)	5873(1)
Z	4	2	4	4
D_{calc}, mg m^{-3}	1.441	1.437	1.544	1.443
μ, mm^{-1}	1.00	0.88	3.71	2.44
λ, Å	0.71073	0.71073	0.71073	0.71073
T, K	293	293	293	293
R^a	0.038	0.037	0.029	0.033
$R_{w2}{}^b$	0.094	0.078	0.073	0.080
wgt par a, b^b	0.063, 0.0	0.034, 0.900	0.043, 1.543	0.045, 1.439

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{w2} = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = {}^1/_3[F_o^2 + 2F_c^2]$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $[CdX(\mu\text{-}X)(NPP)]_2$ (X = Cl (**2**), OAc (**3**))[a]

2		3	
Cd−Cl(2)	2.4099(10)	Cd−O(3)	2.253(3)
Cd−N	2.442(3)	Cd−O(4)	2.272(3)
Cd−Cl(1)#1	2.5372(11)	Cd−O(2)	2.322(3)
Cd−P(1)	2.5925(11)	Cd−N	2.491(4)
Cd−Cl(1)	2.6515(11)	Cd−O(1)	2.618(5)
Cl(1)−Cd#1	2.5372(11)	Cd−P(1)	2.6357(12)
		Cd−O(4)#2	2.648(4)
Cl(2)−Cd−N	97.20(8)	O(3)−Cd−O(4)	110.03(14)
Cl(2)−Cd−Cl(1)#1	112.02(4)	O(3)−Cd−O(2)	125.58(13)
N−Cd−Cl(1)#1	87.59(7)	O(4)−Cd−O(2)	83.31(12)
Cl(2)−Cd−P(1)	126.43(4)	O(3)−Cd−N	80.94(13)
N−Cd−P(1)	73.30(7)	O(4)−Cd−N	83.05(12)
Cl(1)#1−Cd−P(1)	119.83(4)	O(2)−Cd−N	153.14(13)
Cl(2)−Cd−Cl(1)	99.43(4)	O(3)−Cd−P(1)	110.98(10)
N−Cd−Cl(1)	163.29(7)	O(4)−Cd−P(1)	126.24(10)
Cl(1)#1−Cd−Cl(1)	84.73(4)	O(2)−Cd−P(1)	99.42(10)
P(1)−Cd−Cl(1)	97.80(4)	N−Cd−P(1)	70.81(9)
Cd#1−Cl(1)−Cd	95.27(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 = −*x* + 2, −*y* + 1, −*z* + 1; #2 = −*x* + 2, −*y* + 2, −*z* + 1.

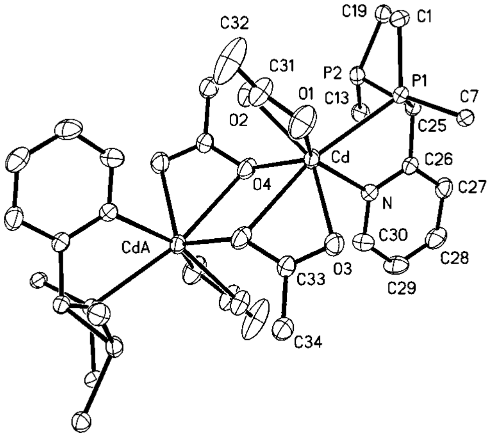

Figure 3. Perspective view of $[Cd(OAc)(\mu\text{-}OAc)(NPP)]_2$ (**3**). Only the *ipso* carbon atoms of the phenyl groups are shown and the hydrogen atoms are omitted for clarity. Unlabeled atoms and those labeled with an "A" are related to the atoms with normal labels by the center of symmetry.

structurally characterized as $Fe(CO)_2(\eta^2\text{-MA})(NPP)$ with the NPP ligand N,P coordinated (Figure 5). The analytical and spectroscopic data are fully consistent with this formulation. The coordination about iron can best be described as distorted trigonal bipyramidal with N and C31 in the axial positions (Table 3) while significant back-bonding to the maleic anhydride occurs as evidenced by the lengthening of the C33−C36 distance from 1.303 Å in the free ligand[26] to 1.427(5) Å here (cf. 1.414(14) Å for this distance in $Co(MA)(P(OMe)_3)_3$[27]) and the fact that H33 and H36 are, respectively, 0.49 and 0.61 Å out of the mean plane of the C_4O ring away from the metal.

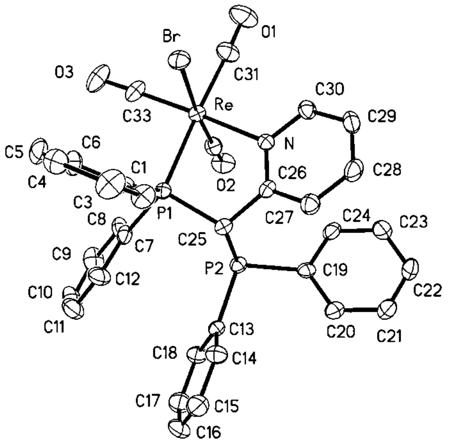

Figure 4. Perspective view of *fac*-Re(CO)$_3$Br(NPP) (**4**). Hydrogen atoms are omitted for clarity.

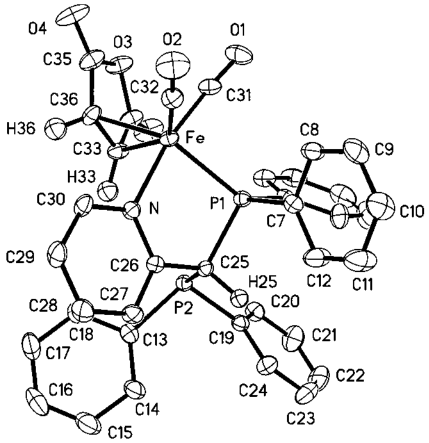

Figure 5. Perspective view of Fe(CO)$_2$(MA)(NPP) (**6**). Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Fe(CO)$_2$((MA)(NPP) (**6**) and Fe(CO)$_3$(NPP) (**7**)

6		**7**	
Fe−C(31)	1.742(4)	Fe−C(2)	1.754(5)
Fe−C(32)	1.782(4)	Fe−C(1)	1.764(6)
Fe−C(36)	2.031(4)	Fe−C(3)	1.772(5)
Fe−N	2.069(3)	Fe−P(2)	2.2077(11)
Fe−C(33)	2.074(4)	Fe−P(1)	2.2212(12)
Fe−P(1)	2.2308(10)		
C(35)−C(36)	1.456(5)		
C(31)−Fe−C(32)	89.58(17)	C(2)−Fe−C(1)	87.5(3)
C(31)−Fe−N	170.28(15)	C(2)−Fe−C(3)	104.9(3)
C(32)−Fe−N	91.47(14)	C(1)−Fe−C(3)	104.4(3)
C(31)−Fe−P(1)	90.14(13)	C(2)−Fe−P(2)	91.06(18)
C(32)−Fe−P(1)	108.68(13)	C(1)−Fe−P(2)	152.7(2)
N−Fe−P(1)	80.37(8)	C(3)−Fe−P(2)	102.26(18)
		C(2)−Fe−P(1)	149.7(2)
		C(1)−Fe−P(1)	94.5(2)
		C(3)−Fe−P(1)	103.83(17)
		P(2)−Fe−P(1)	73.55(4)

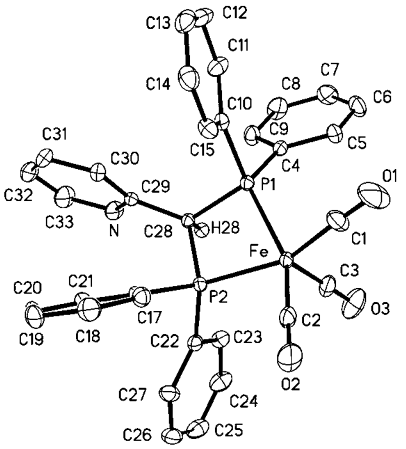

Figure 6. Perspective view of Fe(CO)$_3$(NPP) (**7**). Hydrogen atoms are omitted for clarity.

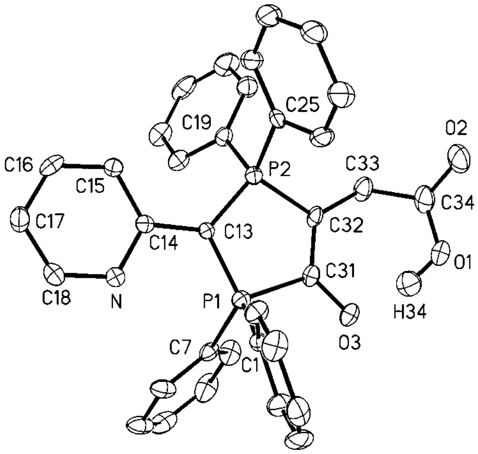

Figure 7. Perspective view of $\overline{\text{Ph}_2\text{PC}(2\text{-C}_5\text{H}_4\text{N})\text{PPh}_2\text{C}(\text{CH}_2\text{CO}_2\text{H})}\text{C}(=\text{O})$ (**5**). Hydrogen atoms attached to carbon are omitted for clarity.

From an X-ray structure determination, complex **7** has the composition Fe(CO)$_3$(NPP) (Figure 6) with P,P coordination of the NPP ligand, a formulation consistent with the spectroscopic data. The single phosphorus resonance is significantly upfield from the position of the coordinated phosphorus in **6** as expected on the basis of the four-membered chelate ring in the present case.[28] The coordination geometry about iron (Table 3) is more distorted than that in **6** and could be described as derived from either a trigonal bipyramid or from a square pyramid. At least part of this distortion stems from the structures of the four-membered chelate ring.

The third product of the reaction of NPP with Fe(CO)$_4$(MA) (and the initial material to separate from the reaction mixture), **5**, analyzes as a 1:1 adduct of NPP with maleic anhydride and can also be prepared in good yield by the direct reaction of these two compounds in the absence of any iron species. Figure 7 presents a perspective view of the molecule in which the central five-membered ring is within 0.02 Å of planarity, the bridgehead carbon of the NPP ligand (C13) has been deprotonated, and the maleic acid moiety has undergone ring-opening and a 1,2-hydrogen shift in its combining with the phosphorus atoms. There are several structural features (Table 4) bearing on a description of the bonding in **5**. The P1−C13 and P2−C13 distances are equivalent and significantly shorter than both the P−C(phenyl) distances here (1.799(3)−1.814(3) Å) and the P−C(bridgehead) distances in **4**, **6**, and **7** (1.857(3)−1.914(7) Å) where the bridgehead carbon retains its proton. The P2−C32 distance, while significantly longer than that to C13, is still noticeably shorter than to the attached phenyl rings while the P1−C31 distance is much longer than either and, in fact, is approaching the length of the normal P−C(bridgehead) distances

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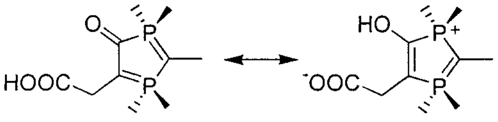
Table 4. Selected Bond Lengths [Å] and Angles [deg] for **5**

P(1)−C(13)	1.718(3)	P(2)−C(19)	1.805(3)
P(1)−C(1)	1.799(3)	P(2)−C(25)	1.814(3)
P(1)−C(7)	1.802(3)	C(31)−O(3)	1.294(4)
P(1)−C(31)	1.836(4)	C(31)−C(32)	1.360(4)
C(13)−C(14)	1.443(4)	C(32)−C(33)	1.508(5)
C(13)−P(2)	1.716(3)	C(34)−O(2)	1.214(5)
P(2)−C(32)	1.761(3)	C(34)−O(1)	1.303(5)
C(13)−P(1)−C(31)	99.87(18)	O(3)−C(31)−P(1)	119.1(3)
C(14)−C(13)−P(2)	127.6(2)	C(32)−C(31)−P(1)	113.1(3)
C(14)−C(13)−P(1)	122.0(3)	C(31)−C(32)−C(33)	123.1(3)
P(2)−C(13)−P(1)	110.33(19)	C(31)−C(32)−P(2)	114.8(3)
C(13)−P(2)−C(32)	101.88(17)	C(33)−C(32)−P(2)	122.0(3)
O(3)−C(31)−C(32)	127.8(3)		

cited above. The C31−O3 distance is only slightly shorter than the C34−O1 distance in the carboxyl group and the refined position of the carboxyl hydrogen (H34) shows it to interact strongly with O3 (O1−H34 = 1.01(4), H34···O3 = 1.54(4), O1···O3 = 2.505(4) Å; ∠ O1−H34−O3 = 159(3)°). The sums of the angles about C13, C31, and C32 are all 360° indicating planarity at each. All these data suggest the bonding can best be described in terms of the tautomeric forms **5a** and **5b**, and the NMR data are consistent with this.



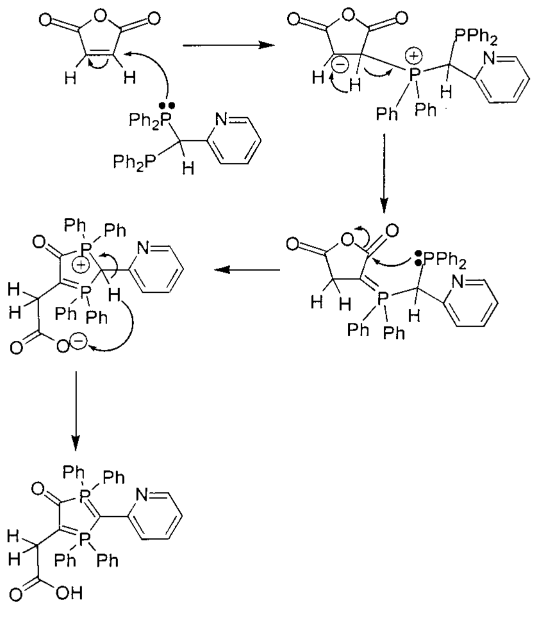
5a **5b**

Although it is not possible to assign the phosphorus chemical shifts with certainty, we suggest that the lower field resonance can be attributed to P1 since this atom is formally a phosphonium cation in **5b**. While ylide formation from the reaction of triphenylphosphine with maleic anhydride has been demonstrated,[29] cleavage of the heterocyclic ring did not occur. We are not aware of instances where diphosphines have been used in this reaction although they are well-known to form cyclic adducts with activated alkynes.[30] We do find that bis(diphenylphosphino)methane (DPPM) rapidly reacts with maleic anhydride to form a product analogous to that formed by triphenylphosphine (i.e., a mono-ylide). It is likely, therefore, that the formation of **5** proceeds initially as for triphenylphosphine and DPPM but that the involvement of the second phosphorus atom is a result of the greater acidity of the methine proton in NPP (also vide infra) as outlined in Scheme 1.

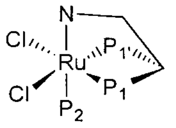
A ready reaction occurs between $PtCl_2(PhCN)_2$ and NPP to form light yellow microcrystals analyzing as $PtCl_2(NPP)\cdot 0.75CH_2Cl_2$ (**8**). The $^{31}P\{^1H\}$ NMR spectrum of **8** consists of a high-field singlet with ^{195}Pt satellites indicative of P,P coordination with consequent formation of a four-membered chelate ring. The deformation band of the pyridyl group has been tentatively located at 1607 cm^{-1} which would indicate coordination of the pyridyl group as well. If so, the complex would have to adopt a distorted square pyramidal geometry to have the phosphorus atoms equivalent unless the molecule were highly fluxional. That such a coordination geometry is possible is indicated by the structure found for **15** (vide infra).

Cycloheptatriene is slowly displaced by NPP from $Cr(CO)_3(\eta^6\text{-}C_7H_8)$ in refluxing acetone to yield orange microcrystals analyzing as $Cr(CO)_3(NPP)\cdot$acetone (**9**). The spectroscopic data are consistent with formulation of **9** as the *fac* isomer with all three donor atoms of the NPP ligand coordinated, and although the shift of the deformation band of the pyridyl moiety is not as large as in the other instances noted earlier, the great propensity for zerovalent Group 6 complexes to be 6-coordinate makes it likely that this formulation is correct.

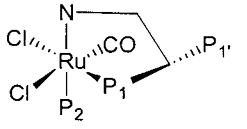
Scheme 1



Two of the three triphenylphosphine ligands in $RuCl_2(PPh_3)_3$ can be replaced by NPP in refluxing dichloromethane to yield fibrous yellow orange needles analyzing as $RuCl_2(PPh_3)(NPP)\cdot 0.1CH_2Cl_2$ (**10**). The chemical shifts and splitting pattern of the phosphorus NMR resonances clearly indicate P,P coordination of the NPP ligand, and while the deformation band of the pyridyl group could not be confidently identified, the general tendency for Ru(II) complexes to be 6-coordinate together with the slow reaction of **10** with CO (vide infra) suggest that the pyridyl group is also coordinated. Treatment of a dichloromethane solution of **10** with CO causes a change in color from orange yellow to bright yellow over a period of ca. 0.5 h, and from this solution yellow crystals analyzing as $RuCl_2(CO)(PPh_3)(NPP)\cdot CH_2Cl_2$ (**11**) could be obtained.



10



11

The ^{31}P NMR spectrum clearly indicates that one phosphorus atom of the NPP ligand is now uncoordinated while that which remains coordinated has shifted downfield from its position in **10** indicating that it is now part of a five-membered rather than a four-membered chelate ring. We conclude that NPP is N,P coordinated in **11** with the small value of $^2J(P_1 - P_2)$ indicating retention of the cis disposition of the two coordinated phosphorus atoms.

In an attempt to extend the chemistry of $Fe(CO)_4(MA)$ to related ruthenium systems, the reaction of NPP with $Ru(CO)_4(NCCH{=}CH_2)$,[31] prepared in situ in dichloromethane/acryloni-

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(29) Hudson, M. A.; Chopard, P. A. *Helv. Chim. Acta* **1963**, *46*, 2178.

(30) Shaw, M. A.; Tebby, J. C.; Ward, R. S.; Williams, D. H. *J. Chem. Soc. C* **1970**, 504.

(31) Edwards, A. J.; Leadbeater, N. E.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1995**, *503*, 15.

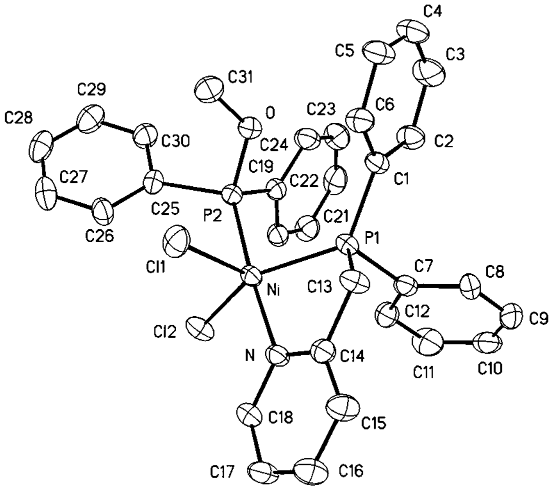


Figure 8. Perspective view of NiCl$_2$(P(OMe)Ph$_2$)(Ph$_2$PCH$_2$py) (**12**). Hydrogen atoms are omitted for clarity.

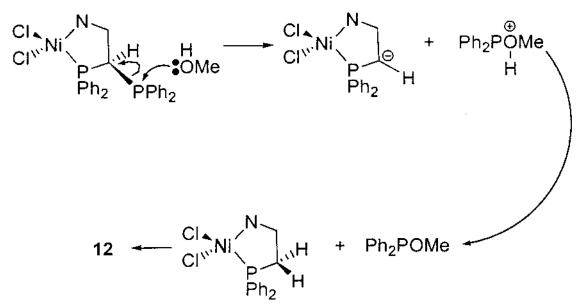
Table 5. Selected Bond Lengths [Å] and Angles [deg] for NiCl$_2$(PPh$_2$(OMe))(Ph$_2$PCH$_2$Py) (**12**) and NiCl$_2$(Ph$_2$P(O)CH$_2$Py)$_2$ (**13**)

12		13	
Ni−N	2.007(5)	Ni−O	2.053(2)
Ni−P(2)	2.1470(18)	Ni−N	2.133(3)
Ni−P(1)	2.1595(18)	Ni−Cl	2.4884(10)
Ni−Cl(2)	2.2712(18)		
Ni−Cl(1)	2.457(2)		
N−Ni−P(2)	175.87(18)	O−Ni−N	89.31(10)
N−Ni−P(1)	81.92(16)	O−Ni−Cl	91.47(7)
P(2)−Ni−P(1)	94.02(7)	N−Ni−Cl	91.13(8)
N−Ni−Cl(2)	95.29(16)		
P(2)−Ni−Cl(2)	87.48(7)		
P(1)−Ni−Cl(2)	142.45(8)		
N−Ni−Cl(1)	89.42(17)		
P(2)−Ni−Cl(1)	92.41(7)		
P(1)−Ni−Cl(1)	106.03(8)		
Cl(2)−Ni−Cl(1)	111.40(8)		

trile solution, was investigated. Addition of the ligand caused the initial pale yellow solution to become orange, and a ^{31}P-$\{^1$H$\}$ NMR spectrum of the reaction solution showed it to contain several phosphine complexes. Attempts to separate the resulting mixture by chromatography or by fractional crystallization were unsuccessful.

We have previously reported on the reaction of NPP with hydrated Ni(II) chloride[32] which appeared to parallel that of the closely related ppn ligand[3] but lacking in both studies was an exploration of the reactivity of NPP toward anhydrous transition metal halides. Little reaction appeared to have taken place after stirring anhydrous NiCl$_2$ with NPP in THF overnight at room temperature and the majority of the NiCl$_2$ appeared not to have dissolved. Sufficient dry methanol was then added to dissolve the solid whereupon the color of the solution darkened considerably and the crystalline product obtained was found from a crystal structure determination to be NiCl$_2$(Ph$_2$P(OMe))(Ph$_2$PCH$_2$py) (**12**). The analytical data are consistent with this formulation, and as seen in Figure 8, the complex contains the modified fragments of the NPP ligand which has undergone cleavage of one P−C bond. The coordination about nickel is distorted trigonal bipyramidal with P2 and N occupying the axial sites. The major distortion (Table 5) is the opening of the P1−Ni−Cl2 angle to 142.45(8)° which can be attributed to steric crowding on this side of the molecule. Thus the hydrogen atom attached to C20 makes a relatively close approach (2.64 Å) to Cl2 and the hydrogen atom attached to C12 is also directed toward this area of the coordination sphere.

Scheme 2



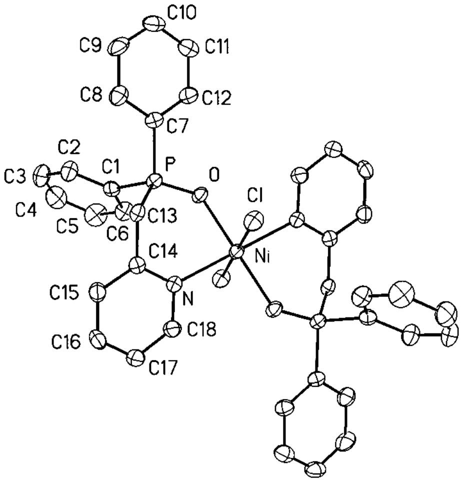


Figure 9. Perspective view of *trans*-NiCl$_2$(Ph$_2$P(O)CH$_2$py)$_2$ (**13**). Hydrogen atoms are omitted for clarity. Unlabeled atoms are related to labeled ones by the center of symmetry.

Inspection of the filtrate from the reaction forming **12** by ^{31}P NMR after the residual nickel-containing material had been removed by precipitation showed NPP to be the only significant phosphorus-containing material to be present. While not conclusive, this is consistent with a process for cleavage of the NPP ligand analogous to that proposed for the cleavage of the mono-oxide of 2-(bis(diphenylphosphino)methyl)-6-methylpyridine.[5] In the present case, coordination of NPP in an N,P fashion should make the uncoordinated phosphorus susceptible to nucleophilic attack by methanol as outlined in Scheme 2.

Solutions of **12** in 1,2-dichloroethane or CD$_2$Cl$_2$ in the presence of air slowly change color from dark brown to lime green with the formation of crystals of the same color. These were shown by a structure determination to be *trans*-NiCl$_2$(Ph$_2$P(O)CH$_2$py)$_2$ (**13**) containing the oxidized 2-(diphenylphosphinomethyl)pyridine ligand (Figure 9). Complex **13** has crystallographically imposed centrosymmetry, and pertinent metrical parameters are presented in Table 5. The process by which **12** converts to **13** is not entirely clear although it has been established that oxygen is a key reactant since under rigorous exclusion of air, solutions of **12** remain dark brown, while if the solution is saturated with oxygen, the bleaching of the solution occurs much more rapidly than if the solution is merely left open to the air.

A rapid reaction occurs between NPP and Pt(C$_2$H$_4$)(PPh$_3$)$_2$ to yield a light yellow, microcrystalline product analyzing as Pt(PPh$_3$)(NPP) (**14**). The ^{31}P$\{^1$H$\}$ NMR spectrum consists of three doublets of doublets of equal intensity and all having ^{195}Pt satellites indicating that the three phosphorus atoms are all

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[32] Mague, J. T.; Hawbaker, S. W. *J. Chem. Crystallogr.* **1997**, *27*, 603.

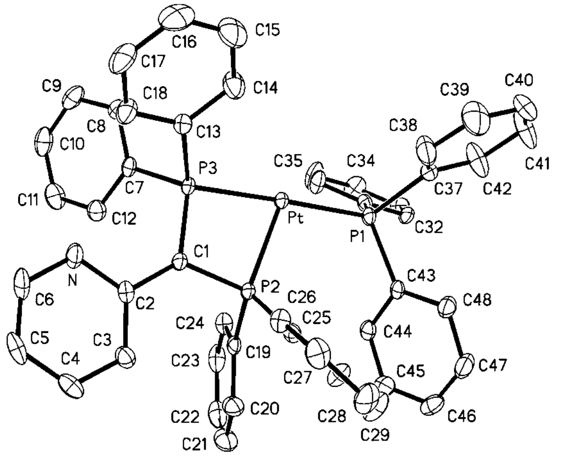

Figure 10. Perspective view of Pt(H)(PPh$_3$)(NPP−H) (**14**). Hydrogen atoms are omitted for clarity.

Table 6. Selected Bond Lengths [Å] and Angles [deg] for Pt(H)(PPh$_3$)(NPP−H) (**14**)

Pt−P(1)	2.2913(12)
Pt−P(3)	2.3019(12)
Pt−P(2)	2.3285(12)
P(2)−C(1)	1.752(5)
P(2)−C(19)	1.822(5)
P(2)−C(25)	1.828(5)
P(3)−C(1)	1.745(4)
P(3)−C(7)	1.827(5)
P(3)−C(13)	1.833(5)
C(1)−C(2)	1.441(7)
P(1)−Pt−P(3)	178.43(4)
P(1)−Pt−P(2)	107.80(4)
P(3)−Pt−P(2)	70.64(4)
C(2)−C(1)−P(3)	129.3(4)
C(2)−C(1)−P(2)	130.5(4)
P(3)−C(1)−P(2)	99.9(2)

coordinated and in different environments. The one large and two small P−P coupling constants further indicates an approximately T-shaped arrangement. The proton NMR spectrum shows no resonance that can be assigned to the methine proton of the NPP ligand; instead there is a doublet of doublets of doublets resonance having ^{195}Pt satellites at −5.93 ppm indicating the presence of a hydride ligand which, from the magnitude of the P−H coupling constants, is cis to two phosphorus atoms and trans to the third. The infrared spectrum shows a weak band at 1994 cm^{-1} which compares well with bands previously assigned to Pt−H stretching vibrations where the hydride is trans to a phosphine ligand.[33] The formulation of **14** as a formally Pt(II) hydride complex of a deprotonated NPP ligand (NPP−H) is confirmed by the X-ray structure determination (Figure 10). This is indicated particularly by the planarity of the Pt, P2, P3, C1 unit to within 0.02 Å and by the C1−P2 and C1−P3 distances (Table 6) which, although longer than the corresponding distances in **5**, are nonetheless still significantly shorter than the P−C(phenyl) distances here and the P−C(bridgehead) distances in those complexes containing intact NPP ligands. This indicates a degree of delocalization of the negative charge formally attached to C1 over the P2−C1−P3 unit. The mean plane of the pyridyl group makes a dihedral angle of only 1.7(2)° with the mean Pt, P2, P3, C1 plane suggesting that there may also be some degree of π interaction between the pyridyl group and this delocalized charge. This is also suggested by the C1−C2 distance of 1.441(7) Å which is marginally shorter than the 1.46 Å distance for a formal single bond between two sp^2 carbon atoms. As noted in the Experimental Section, the hydride ligand could not be located crystallographically though there is no doubt of the approximately square planar coordination about platinum so that the hydride should be positioned trans to P2 as the NMR data indicate. The residual peak seen in that area in difference maps (see Experimental Section) seems best to be explained by the cocrystallization of a small quantity of an analogue of **14** with some other ligand in place of hydride since the position of the peak remained unaltered in a sequence of difference maps calculated with decreasing upper limits on sin θ/λ. We have attempted to determine the source of the hydride ligand by repeating the synthesis of **14** using NPP deuterated at the methine carbon. While the yellow precipitate obtained showed the same three phosphorus resonances as the original sample of **14** and did not show a noticeable band at 1994 cm^{-1} in its infrared spectrum, the proton spectrum still showed the high field resonance attributed to the hydride ligand in **14**. Repeating this experiment in d$_6$ acetone, however, gave the product free of this hydride resonance suggesting that there is solvent assistance (with concomitant H/D scrambling) with the transfer of the methine hydrogen of NPP to the metal. Unfortunately the region of the infrared spectrum where the Pt−D stretch is expected (ca. 1410 cm^{-1})[34] is obscured by ligand absorptions so the formation of the deuteride analogue of **14** is based more on negative rather than positive evidence.

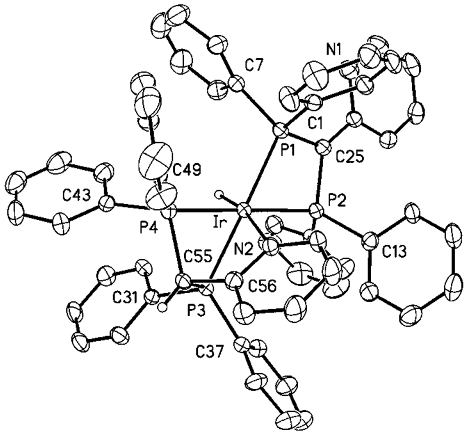

Figure 11. Perspective view of the [Ir(H)(NPP)(NPP−H)]$^+$ cation in (**15**). Hydrogen atoms except for the hydride ligand are omitted for clarity.

The complex [Rh(NPP)$_2$]BF$_4$[35] has been used for the synthesis of heterobimetallic complexes. The iridium analogue has not been reported previously, and in attempts to prepare it from the known [Ir(COD)(NPP)]BF$_4$[15] a yellow product was obtained (**15**) which analyzed satisfactorily for the expected compound but whose ^{31}P{^{1}H} NMR spectrum showed there to be two pairs of nonequivalent phosphorus atoms (this is strictly an AA′XX′ spectrum but evidently one in which $J_{AA'}$ and $J_{XX'}$ are very small so that it appears as a pair of apparent doublets). The proton NMR spectrum revealed the presence of a high-field resonance attributable to a hydride ligand as an apparent septet. Simulation of the hydride resonance showed that this resulted from the fortuitous occurrence of one P−H coupling constant being almost exactly twice the other. The formulation of **15** as a hydride complex containing one deprotonated and one intact NPP ligand is confirmed by the crystal structure determination

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[33] Schwartz, D. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 4014.

[34] Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063.

[35] McNair, R. J.; Nilsson, P. V.; Pignolet, L. H. *Inorg. Chem.* **1985**, *24*, 1935.

Table 7. Selected Bond Lengths [Å] and Angles [deg] for [Ir(H)(NPP)(NPP−H) (**15**)

Ir−H(61)	1.52	P(2)−C(13)	1.830(5)
Ir−N(2)	2.213(4)	P(2)−C(19)	1.831(5)
Ir−P(3)	2.3172(13)	P(3)−C(31)	1.809(5)
Ir−P(1)	2.3313(13)	P(3)−C(37)	1.828(5)
Ir−P(2)	2.3325(13)	P(3)−C(55)	1.874(5)
Ir−P(4)	2.3443(13)	P(4)−C(43)	1.810(5)
P(1)−C(25)	1.753(5)	P(4)−C(49)	1.812(5)
P(1)−C(7)	1.817(5)	P(4)−C(55)	1.876(5)
P(1)−C(1)	1.826(5)	C(25)−C(26)	1.426(7)
P(2)−C(25)	1.751(5)	C(55)−C(56)	1.508(7)

H(61)−Ir−N(2)	169	P(1)−Ir−P(2)	69.24(5)
H(61)−Ir−P(3)	90.5	H(61)−Ir−P(4)	96.2
N(2)−Ir−P(3)	78.92(11)	N(2)−Ir−P(4)	76.60(11)
H(61)−Ir−P(1)	84.7	P(3)−Ir−P(4)	70.62(5)
N(2)−Ir−P(1)	105.92(11)	P(1)−Ir−P(4)	111.14(5)
P(3)−Ir−P(1)	175.07(5)	P(2)−Ir−P(4)	177.94(5)
H(61)−Ir−P(2)	85.9	C(26)−C(25)−P(2)	130.3(4)
N(2)−Ir−P(2)	101.33(11)	C(26)−C(25)−P(1)	131.4(4)
P(3)−Ir−P(2)	109.19(5)	P(2)−C(25)−P(1)	98.3(3)

(Figure 11). In this instance, the hydride ligand was successfully located in low angle difference maps. Also located was the methine hydrogen attached to the bridgehead carbon (C55) of the intact NPP ligand. In this instance there is a direct internal comparison of the phosphorus to bridgehead carbon distances between intact and deprotonated NPP ligands (Table 7) where it is evident that in the latter the distance is over 0.1 Å shorter. As with **14**, the Ir, P1, C25, P2 unit is planar to within 0.1 Å, the pyridyl ring makes a dihedral angle of 11.2° with this plane, and the C25−C26 distance, at 1.426(7) Å, is significantly shorter than that expected for a single bond between two sp^2 carbon atoms. The coordination about iridium is distorted octahedral with the major distortions being the result of the short "bites" of the ligands. On the basis of the ^{31}P chemical shift of δ 9.6 for [Ir(COD)(NPP)]BF$_4$[15] we suggest that the δ 1.9 resonance for **15** be assigned to the phosphorus atoms of the intact NPP ligand while that at δ −51.8 be associated with those of the deprotonated one.

Conclusions

With this work, the ligating behavior of the 2-pyridylbis(diphenylphosphino)methane toward the majority of the metals in Groups 6−12 has been explored. All three possible modes of chelation (N,P, P,P, N,P,P) of NPP have been found in this work. There does not appear to be any strong correlation between the observation of N,P vs P,P coordination and the hardness or softness of the metal center since both Co(II) (moderately hard) and Cd(II) (moderately soft) both show the former mode. With the exception of rhodium,[6,9] iridium,[6,9] and nickel,[32] NPP does not appear to readily promote the formation of dinuclear complexes and those monometallic complexes in which it is only N,P or P,P coordinated have not been found to be useful precursors to heterobimetallic complexes. Neither does there seem to be any pattern to the lability of one arm of the ligand that would lead to its predictable function as a semilabile ligand in catalytic applications. Thus in RuCl$_2$(PPh$_3$)(NPP) (**10**) it is one of the phosphine arms that is displaced on reaction with CO while in the case of *fac*-M(CO)$_3$(NPP) (M = Mo, W)[36] CO displaces the nitrogen arm. As in previous studies, the susceptibility of the ligand to cleavage of a P−C bond has been a complicating factor. Perhaps the most significant result has been the demonstration of the significant acidity of the methine proton of NPP which clearly poses a problem for the use of this ligand in catalytic systems.

Acknowledgment. We thank the Tulane University Chemistry Department and the Tulane College Undergraduate Research Fund for support of this research.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**−**7** and **12**−**15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Mague, J. T.; Johnson, M. P. *Organometallics* **1990**, *9*, 1254.