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Bimetallic Reactivity. Synthesis of Bimetallic Complexes Containing a Bis(phosphino)pyrazole Ligand

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The ligand PNNHP has been prepared. It is a planar quadridentate ligand consisting of a central pyrazole unit with symmetrically disposed methylenediphenylphosphine arms, and its geometry provides for two metals to reside within cooperative distance but does not allow for metal–metal bond formation. Two types of planar bimetallic complexes have been isolated and characterized: those with anionic bridging groups (X) of the composition $[M_2(PNNP)(X)L_2]$ (M = Pd(II), X = Cl, L = Cl; M = Rh(I), X = Cl and PPh_2, L = CO; M = Ir(I), X = PPh_2, L = CO) and those without bridging atoms of the composition $[M_2(PNNP)L_4]^+$ (M = Pd(II), 2L = π-allyl; M = Rh(I) and Ir(I), 2L = diene and L = CO) have been identified.

It is commonly assumed that organometallic compounds that incorporate more than one reactive proximal metal site might provide a class of catalytic species for which distinctive reactivity patterns would result from cooperative electronic and/or steric effects.[1] Thus, one could conceive of different types of oxidative-addition–reductive-elimination patterns and the stabilization of unusual oxidation states and of ligand-bonding modes that are not possible in monometallic complexes. By the use of bimetallic complexes, an extensive variety of bridging hydrocarbon fragments have been incorporated by involving both of the metals.[2] One of the recurring problems in defining the reactivities of these bridging organic moieties is the tendency of many of these systems to fragment into monometallic units so that, at a mechanistic level, the reactions are those associated with monometallic species. In order to overcome this problem, suitable chemically inert ligand systems that allow the integrity of the multinuclear framework to be retained but still provide the necessary coordination sites for reaction require construction. Some of the ligand systems currently in use to accommodate two metal centers are phosphido bridges,[3] linked cyclopentadienyl ligands,[4] diisocyanides,[5] bridging phosphorus ylides,[6] bis(pyrazole) systems,[7] and a large family of complexes derived from bis(diphenylphosphino)methane, the so-called "A-frames".[8]

In nearly all of these systems, the geometry and flexibility of the bridging ligand are such as to allow for metal–metal bond formation and many of their more interesting reactivity patterns tend to be dominated by the making and breaking of the metal–metal bonds. The significance of metal–metal bond formation in controlling the reactivities of these systems seems to us to be an important issue. We therefore entertained the construction of a binucleating ligand that was capable of coordinating two metals within cooperative proximity but at a distance insufficient for metal–metal bond formation in order to address the effect of metal–metal bond formation on reactivity. The ligand chosen is PNNP (Figure 1).

This paper describes the synthesis of this ligand and a variety of its homobimetallic complexes. The following paper describes a study of the reactivity patterns of some of these complexes.

1. Ligand Synthesis. The binucleating ligand PNNP was prepared by the methods outlined in Figure 2. Reaction of acetylacetone with hydrazine gives 2,4-dimethylpyrazole which is readily oxidized with potassium permanganate to the corresponding diacid and is isolated as the monopotassium salt. In order to facilitate the $LiAlH_4$ reduction, the ether-insoluble salt was converted to its soluble dimethyl ester. The diol that is produced from the reduction is tenaciously bound to the aluminum and required extraction with carbonated methanol to remove it from the alumina cake. The dichloride salt is then readily obtained. We found that the PNNP ligand is most efficiently produced by low-temperature reaction of excess $LiPPh_2$ with the dichlorohydrochloride despite the potential problems that could arise as a result of deprotonation of the pyrazole ring. The ligand was isolated from the reaction mixture as its nickel perchlorate salt, $[Ni_2(PNNP)_2](ClO_4)_2$. This dinickel complex is readily purified by crystallization from acetonitrile, giving large yellow-brown crystals of $[Ni_2(PNNP)_2](ClO_4)_2 \cdot 2CH_3CN$ in which the acetonitrile molecules are probably coordinated to the nickel atoms.

The ligand is readily freed from the nickel by reaction with cyanide ions, but the free ligand is very air sensitive and it crystallises with difficulty. We have therefore found it convenient to store the ligand as its nickel complex and to free it as required.

2. Metal-Transfer Synthesis. We have used two methods for the preparation of bimetallic PNNP complexes, either by metal transfer or by diirect reaction. The direct-transfer method exchanges the ligand from the $[Ni_2(PNNP)_2](ClO_4)_2 \cdot 2CH_3CN$ complex to the appropriate metal complex. The success of this method depends on the stability of the product and requires the use of polar solvents. Figure 3 outlines a number of these metal-transfer reactions. The product of the rhodium reaction, **3**, exhibits one IR stretch in the carbonyl region (1992 cm^{-1}), one signal in the ^{31}P NMR spectrum (a doublet due to ^{103}Rh coupling), and ligand reasonances in the ^1H NMR spectrum consistent with the highly symmetrical structure shown. The analytical and spectroscopic data for the palladium complexes **1** and **2** are also consistent with the structures shown in Figure 3; the π-allyl groups of **2** are fluxional at 25 °C. All three complexes are very stable and the μ-chloro groups of **1** and **3** appear to add exceptional stability to these complexes. The chloro ligands are tenaciously

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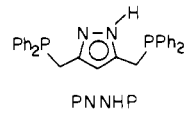

PNNHP

Figure 1. Structure of the binucleating PNNHP ligand.

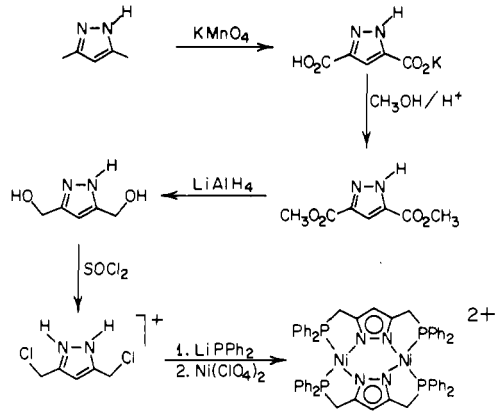

Figure 2. Outline of the synthesis of the nickel complex of the PNNP ligand.

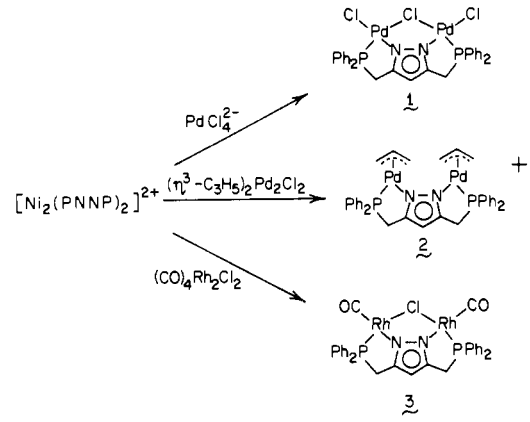

Figure 3. Synthesis of complexes **1**–**3** by transmetalation from the nickel complex.

held in the bridging positions, and all attempts at removing them lead either to no reaction or to incomplete reaction even in the presence of added ligand. Thus, the reaction of **3** with either Ag^+ or Hg^{2+} salts leads to incomplete removal of the μ-chloro group, and in the case of Ag^+ it appeared that the silver ions were partly incorporated in the complex. The terminal chloro ligands of **1** are readily substituted by anionic ligands, but the carbonyl ligands of **3** are inert to thermal substitution. Since the μ-chloro groups occupy the sites where bimetallic cooperativity might occur, we sought to prepare complexes without these very stable halogen bridges. The palladium complex **2** presented one such possibility, but we were unable to remove both π-allyl groups with either CF_3CO_2H or CF_3SO_3H without, at the same time, decomposing the complex. We therefore turned to the bis(diene) complexes of rhodium(I) and iridium(I) that could not be prepared by metal transfer but rather required the use of the free ligand for reaction.

3. Synthesis of Bimetallic Diene Complexes. The ligand, PNNHP, is readily removed from its nickel complex by reaction with cyanide ions in benzene/water mixtures. After removal of the aqueous layer, the ligand is contained in the benzene layer. Addition of this solution to a solution of $[M(diene)_2]BF_4$ (M = Rh, diene = norbornadiene (NBD) or 1,5-cyclooctadiene (COD); M = Ir, diene = COD) followed by addition of base (NEt_3) results in a dramatic color change (purple (Ir) or red (Rh) to yellow). By this method, the three diene complexes **4**–**6** were prepared as yellow-orange crystalline solids (Figure 4). Spectroscopically (^1H and ^{31}P NMR) these three complexes display features in accord with the symmetrical structures illustrated.

The coordinated diene ligands of these complexes can be completely displaced by carbon monoxide at ambient pressures to produce the yellow tetracarbonyl cations **7** and **8** that were isolated as crystalline solids. The presence of two strong, equally intense bands in the terminal carbonyl region of the IR spectra of these complexes indicates the presence of cis-disposed carbonyl ligands on each metal. The stability of these two complexes differs significantly. The rhodium complex, **7**, is stable in solution only under an atmosphere of carbon monoxide. In the absence of CO, dissolution of **7** results in CO evolution and the formation of a red solution from which a gummy red solid may be isolated and which contains coordinated CO (2018, 2001 cm^{-1}). Treatment of a THF suspension of this material with CO results in the complete regeneration of **7**. The exact nature of this red, carbon monoxide deficient complex has not been determined, but it is probable that it results from the release of the two inner carbon monoxide ligands that are trans to the phosphorus ligand and, as molecular models indicate, suffer significant steric interactions. These vacated sites are probably weakly coordinated by the BF_4^- counterion[9] (Figure 5). The analogous iridium complex, **8**, is very much less prone to loss of carbon monoxide. When it is dissolved, no gas evolution occurs and no spectroscopic changes are observed although solutions of **8** slowly redden over several hours. The inner carbon monoxide ligands of the rhodium species **7** are readily replaced by anionic bridging ligands. Thus, **3** is also prepared by the addition of Cl^- ions to **7**. The analogous iridium complex, **8**, undergoes similar reactions but much less readily. Attempts at replacing the inner carbon monoxide ligands with trimethylphosphine led to displacement of the PNNP ligand.

In order to increase the nucleophilicity of the metals, we have prepared the two diphenylphosphido bridging species **9** and **10**. These were prepared by the addition of $LiPPh_2$ to THF suspensions of **7** or **8** at low temperature. The ^{31}P NMR spectrum for either **9** or **10** displayed signals for the μ-PPh_2 phosphorus atom consistent with the absence of a metal–metal bond.[10] Unlike the analogous chloro-bridged complex **3**, which exhibited spectroscopic parameters indicating a high degree of symmetry, the phosphido-bridged analogoues display spectroscopic characteristics consistent with distorted structures. Thus, two closely spaced IR bands are observed in the carbonyl region, and the ^1H and ^{31}P NMR spectra of either **9** or **10** display second-order effects not expected in totally symmetric structures. The origin of this asymmetry probably resides in the nature of the phosphido bridge. It is known that in apparently symmetrical complexes of the type $L_nM(\mu\text{-}PR_2)ML_n$ the two bond lengths to the bridge are significantly different in the solid state.[10,11] This may be the origin of the apparent spectroscopic asymmetry observed for **9** and **10**.

4. Discussion. The present series of bimetallic complexes appear to meet the criteria for which they are designed, namely to form rigid bimetallic complexes in which the metals are within cooperative distance but are sufficiently separated so as not to form metal–metal bonds. The pyrazole unit alone, which was once thought sufficient to prevent metal–metal bond formation, has recently been shown capable of doing so in certain cases.[7] The incorporation of the phosphine "arms" in the PNNP ligand appears to prevent the two metals from attaining metal–metal bond distances. Molecular models suggest that the intra-metal distance in a PNNP bimetallic complex is slightly flexible but is within the range of 3.5–4.3 Å. These circumstances appear to play an important role in the reactivity patterns of these complexes, which in many respects are distinct from those observed in the A-frames and, to a lesser degree, are different from those observed with analogous pyrazole bimetallic systems.

There are, however, a number of features of the present system that may pose difficulties in attempts to exploit the cooperative reactivity. As we have noted, the mono PNNP bimetallic complexes have an exceedingly strong tendency to accept bridging ligands at the inner coordination sites. Whereas these bridging

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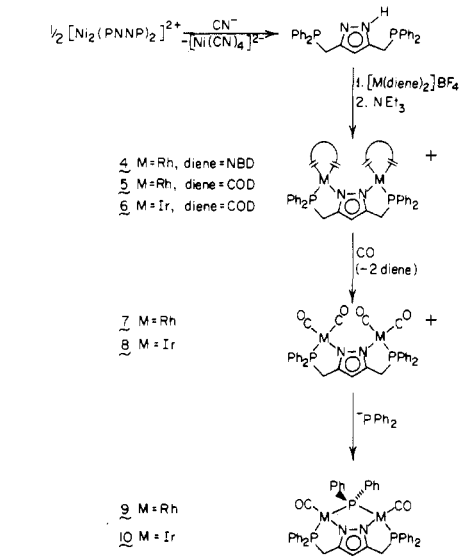

Figure 4. Synthesis of rhodium(I) and iridium(I) complexes from the freed PNNHP ligand.

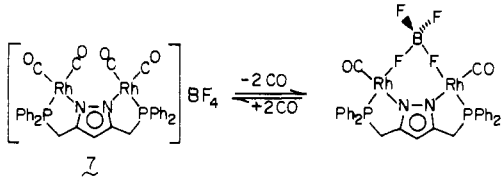

Figure 5. Proposed equilibrium of CO in complex 7.

ligands engender remarkable stability to the complexes, they also lock up the proximal sites. Moreover, for the PNNP system, the inner coordination sites are trans to the phosphorus ligands and hence (nonbridging) ligands with similar trans effects as phosphorus will prefer not to coordinate in these coordination positions. Thus, we have been unsuccessful in replacing the labile carbonyl ligands of **7** with, among others, alkenes, disubstituted alkynes, and trimethylphosphine. Finally, the pyrazole ligand, although providing the necessary structural dimensions and rigidity, is somewhat deactivating to metals that require electron richness for their reactivities. Despite these difficulties, the complexes described here do display interesting reaction patterns that can be contrasted with mononuclear analogues and with different bimetallic systems. These are described in the following paper.

Experimental Section

All reactions using rhodium(I) or iridium(I) compounds were performed under N_2 or Ar by using standard Schlenk techniques. Solid samples of these complexes were stored at 5 °C although most of them appear to be air-stable in the solid state. Solvents were dried over CaH_2 (CH_2Cl_2), Na/benzophenone (THF), or $LiAlH_4$ (ether). All other solvents were thoroughly degassed prior to use. ^1H NMR spectra were obtained on Varian T-60 or XL-200 spectrometers. Chemical shifts are reported on $CDCl_3$ solutions relative to Me_4Si unless stated otherwise. ^{31}P NMR spectra were recorded on Bruker WP-80, Varian XL-200, or Bruker WH-400 spectrometers operating at 32.3, 80.96, and 161.92 MHz, respectively, in CH_2Cl_2 solutions with a coaxial 4-mm sealed glass insert containing $C_6D_6/P(OMe)_3$ (lock/reference). Chemical shifts are reported relative to 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer and were obtained from solid samples (Nujol mull).

Ligand Synthesis. Monopotassium Pyrazole-3,5-dicarboxylate. A solution of 3,5-dimethylpyrazole (96 g, 1.0 mol) in H_2O (3840 mL) in a flask equipped with a mechanical stirrer and a condensor was heated to 80 °C, and a steady stream of CO_2(g) was passed through the solution (the CO_2 provides a buffered medium). To this hot solution was added, in portions, solid $KMnO_4$ (672 g, 4.2 mol) at a rate sufficient to maintain an internal temperature of 90–95 °C. The solution was then held at this temperature for an additional 2 h. The solution was then allowed to cool, and the CO_2 delivery tube was removed. The precipitate (MnO_2) was filtered and was washed with H_2O. The aqueous filtrate was evaporated under reduced pressure to ~1 L, and then acetic acid (175 mL, 17 M) was added slowly with stirring whereupon a white precipitate formed. After stirring overnight, the precipitate was filtered, washed with H_2O (4×), ethanol (4×), and ether, and dried to give a white solid, 140 g (72%).

Dimethyl Pyrazole-3,5-dicarboxylate. A suspension of monopotassium pyrazole-3,5-dicarboxylate (80 g, 0.13 mol) in methanol (800 mL) was treated with HCl(g) until the solution boiled. The solution was allowed to cool to room temperature, and then the HCl treatment was repeated. After stirring overnight, the precipitate (KCl) was filtered and washed with methanol. The combined filtrate and washings were evaporated under reduced pressure, and the residue was dissolved in methanol and reevaporated (4×). The residue was then slurried in hexane to obtain the crude product that was isolated. This solid was dissolved in hot benzene (~700 mL), and Na_2SO_4 was added. The solution was filtered, and upon addition of hexane to the filtrate, white needles were obtained; 65 g (86%). ^1H NMR: δ 3.92 (s, 6 H), 7.22 (s, 1 H), 10.08 (br s, 1 H).

3,5-Bis(hydroxymethyl)pyrazole Hydrochloride. A suspension of $LiAlH_4$ (15.10 g, 0.40 mol) in dry ether (1.0 L) under N_2 was prepared. Finely ground dimethyl pyrazole-3,5-dicarboxylate (18.8 g, 0.10 mol) was placed in a paper thimble of a Soxhlet apparatus that was then fitted to the flask. The ether was refluxed for 24 h with a recycle time of 10–15 min. Then, H_2O (50 mL) was added dropwise to the cooled suspension over 45 min. The ether was removed under reduced pressure, and the resulting white cake was suspended in methanol (1.0 L), treated with CO_2(g) for 10 min, and then refluxed for 6 h. The solid was filtered, and the filtrate was evaporated to give an oily residue (~12 g). Water in this residue was removed azeotropically with ethanol. The residue was redissolved in ethanol and filtered, and the filtrate was evaporated. The product (as the hydrochloride salt) was obtained as white needles by dissolution of this residue in ethanolic HCl (40 mL) by the addition of ether; 12 g (73%). ^1H NMR (Me_2SO-d_6): δ 4.53 (s, 4 H), 6.40 (s, 1 H), 9.6 (br s, 4 H). Anal. Calcd for $C_5H_9ClN_2O_2$: C, 36.49; H, 5.51; Cl, 21.54; N, 17.02. Found: C, 36.75; H, 5.75; Cl, 21.88; N, 16.79.

3,5-Bis(chloromethyl)pyrazole Hydrochloride. A mixture of 3,5-bis(hydroxymethyl)pyrazole hydrochloride (13.2 g, 0.08 mol) in neat $SOCl_2$ (100 mL, distilled from $P(OPh)_3$) was placed in a preheated 95 °C oil bath and was refluxed for 0.5 h. The excess $SOCl_2$ was removed by distillation under reduced pressure. The residue was dissolved in ethanol (150 mL) and filtered, and ether was added to produce white plates, 14.8 g (92%). Anal. Calcd for $C_5H_7Cl_3N_2$: C, 29.81; H, 3.50; Cl, 52.79; N, 13.90. Found: C, 29.63; H, 3.45; Cl, 52.24; N, 13.90.

$[Ni_2(PNNP)_2](ClO_4)_2 \cdot 2CH_3CN$. To a solution of PPh_3 (36.41 g, 0.139 mol) in dry THF (300 mL) under N_2 was added finely cut lithium metal (2.12 g, 0.305 mol). The resulting red solution was stirred at room temperature for 2 h and was cooled to −75 °C, and solid 3,5-bis(chloromethyl)pyrazole hydrochloride (7 g, 0.035 mol) was added over 10 min. The mixture was stirred at −75 °C for an additional 10 min and then at 0 °C for 1 h. The cooling bath was removed, and ethanol (15 mL) was added. Acetic acid (17.5 mL, 0.305 mol) was added with ice cooling, followed by a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (15.86 g, 0.0434 mol) in ethanol (50 mL). The mixture, now containing a yellow precipitate, was stirred for 20 min and filtered, and the precipitate was washed with ethanol (3×), 95% ethanol (3×), and ether (3×) and was air-dried. Recrystallization was carried out by dissolution in boiling CH_3CN (~200 mL), filtration, and gradual addition of ether to afford yellow gold prisms, 12.8 g (55%). ^1H NMR (CD_3CN): δ 2.07 (s, 6 H), 3.67 (apparent t, J = 8 Hz, 4 H), 6.20 (s, 1 H), 6.7–7.8 (m, 20 H). Anal. Calcd for $C_{58}H_{50}Cl_2N_4O_8P_4Ni_2 \cdot 2CH_3CN$: C, 56.19; H, 4.26; Cl, 5.35; N, 6.34; O, 9.66; P, 9.35. Found: C, 55.81; H, 4.35; Cl, 5.38; N, 6.42; O, 9.50; P, 9.31.

Metal Complexes. Although the preparations of the $[M(diene)_2]^+$ precursors have been previously reported, the following modifications result in significant improvements.

$[Rh(NBD)_2]BF_4$. To an ice-cooled suspension of $[Rh(C_2H_4)_2Cl]_2$[12] (1.5 g, 3.86 mmol) in CH_2Cl_2 (45 mL) was added a solution of NBD (2.0 mL, 19.3 mmol) in CH_2Cl_2 (15 mL). When the gas evolution had ceased (~30 min); solid $AgBF_4$ (2.25 g, 11.6 mmol) was added all at once. The cooling was removed, and the solution was stirred for 45 min. The deep red solution, containing a white precipitate, was filtered by cannula through Celite, THF (10 mL) was added, and the volume was reduced on a rotary evaporator at 25 °C to ~5 mL to obtain deep red needles that were filtered, washed with THF (2 × 5 mL) and ether, and dried to give 2.9 g (100%).

$[Rh(COD)_2]BF_4$. To a solution of $[Rh(COD)Cl]_2$[13] (1.47 g, 2.98

(12) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

(13) Prepared by refluxing a solution of $RhCl_3 \cdot 3H_2O$ (1.93 g, 7.3 mmol), H_2O (3 mL), ethanol (35 mL), and COD (6 mL, 48 mmol) overnight. From the cooled solution was obtained the crude product which was recrystallized (CH_2Cl_2/hexane) to give 1.5 g (82%).

mmol) in CH_2Cl_2 (20 mL) was added COD (1.1 mL, 8.97 mmol) followed by a solution of $AgBF_4$ (1.33 g, 6.83 mmol) in acetone (10 mL). This resulted in the immediate formation of a deep red solution, containing a white precipitate, which was stirred for 20 min and then was filtered through Celite. To the filtrate was added THF (20 mL), and the volume was reduced on a rotary evaporator at 25 °C to 10 mL. The deep red crystals so obtained were filtered, washed with THF (2 × 5 mL) and ether, and air-dried; 2.35 g (97%).

$[Ir(COD)_2]BF_4$. This complex was prepared exactly as described above from $[Ir(COD)Cl]_2$,[14] COD, and $AgBF_4$. The yield was 93%.

$[Rh_2(\mu\text{-}Cl)(CO)_2PNNP]$ (3). A mixture of $[Rh(CO)_2Cl]_2$[15] (1.0 g, 2.57 mmol) and $[Ni_2(PNNP)_2](ClO_4)_2\cdot 2CH_3CN$ (1.94 g, 1.46 mmol) was dissolved in CH_3CN (60 mL). Methanol (60 mL) was added, and the resulting golden brown solution was refluxed for 1 h. During this time the solution became green with concomitant formation of a lemon yellow precipitate. The reaction mixture was cooled to 0 °C, and the precipitate was filtered in air, washed with methanol, ethanol, and ether, and dried to yield 1.8 g (92%). The product may be recrystallized from benzene/hexane. IR: 1992 cm^{-1}. ^1H NMR: δ 3.78 (d, J = 11 Hz, 4 H), 5.88 (s, 1 H), 7.3–8.0 (m, 20 H). ^{31}P NMR (C_6D_6, 32.3 MHz): δ 56.30 (d, J = 184 Hz). Anal. Calcd for $C_{29}H_{25}ClN_2O_2P_2Rh_2$: C, 48.93; H, 3.29; Cl, 4.66; N, 3.68; P, 8.15. Found: C, 48.33; H, 3.43; Cl, 4.97; N, 3.71; P, 8.39.

Liberation of PNNHP. A mixture of finely ground $[Ni_2(PNNP)_2](ClO_4)_2\cdot 2CH_3CN$ (0.63 g, 0.474 mmol), NaCN (2.32 g, 47.3 mmol), benzene (25 mL), and H_2O (25 mL) was vigorously stirred and refluxed until all the solids had dissolved (30–60 min). The mixture was cooled, and the aqueous layer was removed by syringe. The organic layer was thoroughly washed with H_2O (5 × 10 mL), removing each wash by syringe, and was dried (Na_2SO_4). The benzene solution of PNNHP was then ready for further use. ^1H NMR (C_6H_6): δ 3.38 (br s, 4 H), 5.88 (br s, 1 H), 11.12 (br s, 1 H).

$[Rh_2(NBD)_2PNNP]BF_4$ (4). A benzene solution of PNNHP was prepared as described above from $[Ni_2(PNNP)_2](ClO_4)_2\cdot 2CH_3CN$ (1.0 g, 0.75 mmol), NaCN (3.7 g, 75 mmol), benzene (35 mL), and H_2O (35 mL). The resulting clear colorless benzene solution of the ligand was filtered from the drying agent (through Celite) into a solution of $[Rh(NBD)_2]BF_4$ (1.0 g, 2.72 mmol) in CH_2Cl_2 (30 mL). To the resulting red solution was added NEt_3 (0.19 mL, 1.36 mmol) which rapidly turned the solution yellow. Removal of the solvents under reduced pressure afforded an orange oil that was dissolved in hot methanol, filtered through Celite, and concentrated to ~7 mL (at 60 °C). Slow cooling to −15 °C gave yellow-orange crystals that were filtered, washed with a small amount of cold methanol and ether, and dried, 0.79 g (62%). ^1H NMR (CD_3CN): δ 1.5 (br s, 2 H), 3.81 (d, J = 11 Hz, 4 H), 4.0 (m, 2 H), 4.9 (m, 4 H), 6.02 (s, 2 H), 7.2–7.6 (m, 20 H). ^{31}P NMR (32.3 MHz): δ 40.32 (d, J = 169 Hz). Anal. Calcd for $C_{43}H_{41}N_2P_2Rh_2BF_4$: C, 54.92; H, 4.39; N, 2.98; P, 6.59. Found: C, 54.74; H, 4.45; N, 3.04; P, 6.84.

$[Rh_2(COD)_2PNNP]BF_4\cdot 2CH_3OH$ (5). This compound was prepared by the method just described using $[Rh(COD)_2]BF_4$. The yield was 64%. ^1H NMR: δ 1.4–3.6 (m, 16 H), 3.43 (s, 6 H), 3.8 (m, 4 H), 4.5 (m, 4 H), 6.13 (s, 1 H), 6.6 (m, 4 H), 7.0–8.0 (m, 20 H). Anal. Calcd for $C_{45}H_{53}N_2P_2Rh_2BF_4\cdot 2CH_3OH$: C, 54.46; H, 5.54; F, 7.33; N, 2.70; P, 5.98. Found: C, 54.42; H, 5.24; F, 7.74; N, 2.86; P, 6.19.

$[Ir_2(COD)_2PNNP]BF_4\cdot CH_3OH$ (6). This complex was prepared by the method described above using $[Ir(COD)_2]BF_4$ in 75% yield. ^1H NMR: δ 1.0–3.0 (m, 16 H), 3.38 (s, 3 H), 3.6–4.6 (m, 10 H), 5.95 (br t, J = 6 Hz, 2 H), 6.28 (s, 1 H), 7.1–8.0 (m, 20 H). ^{31}P NMR (32.3 MHz): δ 38.52 (s). Anal. Calcd for $C_{45}H_{49}N_2P_2Ir_2BF_4\cdot CH_3OH$: C, 46.70; H, 4.52; N, 2.37; P, 5.24. Found: 46.42; H, 4.39; N, 2.26; P, 5.50.

$[Rh_2(CO)_4PNNP]BF_4\cdot 0.25CH_2Cl_2$ (7). This compound may be prepared from either **2** or **3** by the following procedure. A solution of **2** or **3** (1.7 mmol) in CH_2Cl_2 (5 mL) was treated with CO(g), and the atmosphere of CO was maintained throughout the preparation. Within 15 min the solution became yellow, and the addition of hexane (80 mL in 5-mL portions) caused a yellow precipitate to form. The precipitate was allowed to settle, and the supernatant liquor was removed by syringe. The precipitate was recrystallized from CH_2Cl_2/hexane to afford yellow crystals of the product, 1.51 g (100%). IR: 2105, 2050 cm^{-1}. ^1H NMR: δ 3.90 (d, J = 12 Hz, 4 H), 5.23 (s, 0.5 H), 6.53 (s, 1 H), 7.5–7.9 (m, 20 H). ^{31}P NMR (32.3 MHz, under CO): δ 47.79 (d, J = 127 Hz). Anal. Calcd for $C_{33}H_{25}N_2O_4P_2Rh_2BF_4\cdot 0.25CH_2Cl_2$: C, 44.90; H, 2.89; Cl, 1.99; F, 8.54; N, 3.15; P, 6.96. Found: C, 44.61; H, 2.89; Cl, 2.6; F, 8.09; N, 3.12; P, 6.28.

$[Ir_2(CO)_4PNNP]BF_4\cdot 0.25CH_2Cl_2$ (8). This complex was prepared exactly as described above for the analogous rhodium compound (100%). IR: 2065, 2006 cm^{-1}. ^1H NMR: δ 3.99 (d, J = 11 Hz, 4 H), 5.23 (s, 0.5 H), 6.70 (s, 1 H), 7.4–8.0 (m, 20 H). ^{31}P NMR (32.3 MHz): δ 41.16 (s). Anal. Calcd for $C_{33}H_{25}N_2O_4P_2Ir_2BF_4\cdot 0.25CH_2Cl_2$: C, 37.40; H, 2.41; N, 2.62. Found: C, 37.28; H, 2.12; N, 2.61.

$[Rh_2(\mu\text{-}PPh_2)(CO)_2PNNP]$ (9). A: From $[Rh_2(NBD)_2PNNP]BF_4$. A stock solution of $LiPPh_2$ (15 mL) was prepared from $PHPh_2$ (0.60 mL, 3.42 mmol) in THF (12.25 mL) by the addition of BuLi (2.14 mL, 3.42 mmol). A suspension of $[Rh_2(NBD)_2PNNP]BF_4$ (0.77 g, 0.82 mmol) in THF (20 mL) was treated with CO(g) until all of the solid had dissolved (~20 min). To the resulting yellow solution was added $LiPPh_2$ (3.8 mL of the stock solution, 0.87 mmol) at room temperature, resulting in an immediate color change from yellow to red followed by the formation of a yellow precipitate within 5–10 min. The mixture was stirred for 1 h, and then the solvent was removed under reduced pressure. The residue was treated with methanol (10 mL), stirred for 15 min, filtered in air, washed with methanol followed by pentane, and dried. Recrystallization from CH_2Cl_2 (60 mL)/ether (175 mL) gave yellow needles, 0.65 g (87%). IR: 1956, 1943 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 3.85 (d, J = 10 Hz, 4 H), 5.93 (s, 1 H), 7.0–8.3 (m, 30 H). ^{31}P NMR (161.92 MHz): δ 7.48 (tt, J = 233, 106 Hz, 1 P), 36.88 (dd, J = 233, 123 Hz, 2 P). Anal. Calcd for $C_{43}H_{35}N_2O_2P_3Rh_2$: C, 56.72; H, 3.87; N, 3.08; P, 10.21. Found: C, 56.54; H, 3.83; N, 3.08; P, 10.70.

B: From $[Rh_2(COD)_2PNNP]BF_4\cdot 2CH_3OH$. The following modification was required in order to remove the methanol solvate. $[Rh_2(COD)_2PNNP]BF_4\cdot 2CH_3OH$ was dissolved in THF (10 mL/g) and stirred for 10 min, and the solvent was removed under reduced pressure. The residue was resuspended in THF, and the procedure described above was followed.

C: From $[Rh_2(CO)_4PNNP]BF_4\cdot 0.25CH_2Cl_2$. The procedure described in A was followed except that the initial CO treatment was not required.

$[Ir_2(\mu\text{-}PPh_2)(CO)_2PNNP]$ (10). The procedure described immediately above was followed (80% yield). IR: 1946, 1926 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.02 (d, J = 8 Hz, 4 H), 6.05 (s, 1 H), 6.6–8.2 (m, 30 H). ^{31}P NMR (CD_2Cl_2, 32.3 MHz): δ −2.86 (dd, J = 250, 208 Hz), 37.46 (d, J = 208 Hz), 37.63 (d, J = 250 Hz). Anal. Calcd for $C_{43}H_{35}N_2O_2P_3Ir_2$: C, 47.42; H, 3.24; N, 2.57; P, 8.53. Found: C, 47.67; H, 3.54; N, 2.36; P, 8.29.

$[Pd_2(\mu\text{-}Cl)Cl_2PNNP]$ (1). To a hot solution of $PdCl_2$ (1.36 g, 7.7 mmol) in Me_2SO (30 mL) was added solid LiCl (0.5 g, 12 mmol) followed by solid, finely ground $[Ni_2(PNNP)_2](ClO_4)_2\cdot 2CH_3CN$ (2.54 g, 1.92 mmol). The mixture was heated and stirred at 150 °C for 15 min. Then, water (~100 mL) was added slowly to the green solution to precipitate the product which, after recrystallization from hot Me_2SO/water formed as fine orange crystals, 2.6 g (86%). ^1H NMR (Me_2SO-d_6): δ 4.1 (d, J = 14 Hz, 4 H), 6.1 (s, 1 H), 7.3–8.0 (m, 20 H). Anal. Calcd for $C_{29}H_{25}Cl_3N_2P_2Pd_2$: C, 44.51; H, 3.22; Cl, 13.59; N, 3.58; P, 7.92. Found: C, 44.27; H, 3.02; Cl, 13.60; N, 3.48; P, 7.63.

$[Pd_2(\eta^3\text{-}C_3H_5)_2PNNP]ClO_4$ (2). A mixture of $[(\eta^3\text{-}C_3H_5)PdCl]_2$[16] (0.5 g, 1.37 mmol) and $[Ni_2(PNNP)_2](ClO_4)_2\cdot 2CH_3CN$ (0.91 g, 0.684 mmol) in CH_3CN (40 mL) and CH_3OH (40 mL) was refluxed for 3 h. The resulting light green solution was allowed to cool, and the volume was reduced to 5–10 mL. To this residue was added CH_3OH (20 mL) followed by $LiClO_4\cdot 3H_2O$ (0.35 g, 2.2 mmol). Slow addition of H_2O (5 mL) precipitated an off-white solid which was collected, washed with H_2O, ethanol, and ether, and dried. Recrystallization from acetone/ether yielded off-white needles of the product, 0.76 g (65%). ^1H NMR: δ 2.67 (m, 2 H), 3.4–4.2 (m, 8 H), 4.83 (apparent t, J = 6 Hz, 2 H), 5.8 (br m, 2 H), 6.3 (s, 1 H), 7.3–7.9 (br s, 20 H). Anal. Calcd for $C_{35}H_{35}N_2P_2Pd_2ClO_4$: C, 49.00; H, 4.11; N, 3.27; O, 7.46; P, 7.22. Found: C, 48.84; H, 4.10; N, 3.53; O, 6.98; P, 7.23.

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Registry No. **1**, 96616-74-9; **2**, 96616-76-1; **3**, 96532-16-0; **4**, 96532-18-2; **5**, 96616-78-3; **6**, 96532-20-6; **7**, 96633-00-0; **8**, 96616-80-7; **9**, 96616-81-8; **10**, 96532-22-8; $[Ni_2(PNNP)_2](ClO_4)_2$, 96633-02-2; $[Rh(C_2H_4)_2Cl]_2$, 12122-73-5; $[Rh(NBD)_2]BF_4$, 36620-11-8; $[Rh(COD)_2]BF_4$, 35138-22-8; $[Rh(COD)Cl]_2$, 12092-47-6; $[Ir(COD)_2]BF_4$, 35138-23-9; $[Ir(COD)Cl]_2$, 12112-67-3; $[Rh(CO)_2Cl]_2$, 14523-22-9; $[(\eta^3\text{-}C_3H_5)PdCl]_2$, 12012-95-2; PNNHP, 96616-85-2; CO_2, 124-38-9; monopotassium pyrazole-3,5-dicarboxylate, 96616-83-0; 3,5-dimethylpyrazole, 67-51-6; dimethyl pyrazole-3,5-dicarboxylate, 4077-76-3; 3,5-bis(hydroxymethyl)pyrazole hydrochloride, 96616-84-1; 3,5-bis(chloromethyl)pyrazole hydrochloride, 96616-82-9.

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