2-[Bis(diphenylphosphino)methyl]pyridine (PNP) Derivatives of Rhenium Carbonyl. Crystal and Molecular Structure of $Re_2(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^4\text{-}CHPPh_2C_5H_4N)(CO)_7$

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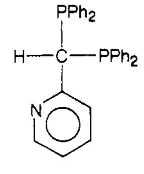
Two new 2-[bis(diphenylphosphino)methyl]pyridine (PNP) complexes of rhenium have been synthesized. $Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$ was synthesized from $Re_2(CO)_8(\mu\text{-H})(\mu\text{-CH}{=}CHC_4H_9)$ and an excess of PNP in CH_2Cl_2 solution. $Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$ was characterized by IR, mass, and ^1H, ^{31}P, and ^{13}C NMR spectroscopies. The structure of $Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$ is based on $Re_2(CO)_{10}$ in which one eq-CO on each Re has been replaced with phosphino groups from the bridging PNP ligand. The pyridyl group is not coordinated. $Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$ thermally decarbonylates in toluene solution to afford $Re_2(\mu\text{-PPh}_2)(\mu\text{-}\eta^1,\eta^4\text{-CHPPh}_2C_5H_4N)(CO)_7$ in high yield. $Re_2(\mu\text{-PPh}_2)(\mu\text{-}\eta^1,\eta^4\text{-CHPPh}_2C_5H_4N)(CO)_7$ was characterized spectroscopically and by a single-crystal X-ray diffraction [$P\bar{1}$, $a = 10.906$ (10) Å, $b = 18.164$ (9) Å, $c = 10.973$ (6) Å, $\alpha = 98.56$ (5)°, $\beta = 119.12$ (6)°, $\gamma = 94.14$ (8)°, $Z = 2$, $D = 1.951$ g cm^{-3}, $R = 0.045$]. The molecular structure was found to consist of two octahedral rhenium centers joined by a μ-PPh$_2$ ligand and a μ-$C_5H_4NCHPPh_2$ (PN) moiety. These two bridges are the fragments that result when the coordinated PNP in $Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$ undergoes P–C bond activation. The PN group chelates in a bidentate manner to one Re and is σ-bonded via the methine C to the other Re. No Re–Re bond exists (4.189 Å).

Introduction

Organotransition-metal complexes containing diphosphine ligands have been extensively studied over recent years. Typically these ligands can coordinate in either a bidentate or bridging fashion. Organometallic complexes of the latter type are of special interest because they feature adjacent metal sites.[1-5] As such these complexes are potentially capable of binding organic substrates to two metal atoms or fragmenting an organic substrate and binding each portion to adjacent metal centers.

We have become interested in preparing bimetallic carbonyl complexes containing a novel diphos ligand, 2-[bis(diphenylphosphino)methyl]pyridine (PNP).



This ligand is relatively new and reports of its chemistry in the inorganic literature are limited.[6-12] Our interest in this specific ligand results from the unique structural features it possesses. The ligand is potentially P,P- or P,N-bidentate or P,P,N-tridentate. It can also bind in a bridging fashion analogous to that of dppm; the pyridine nitrogen may or may not be coordinated to one of the metals. Our efforts are directed toward preparing and studying PNP complexes of fundamental organometallic molecules. Progress has been made in the chemistry of PNP with the binary carbonyl complexes of Cr, W, and Re. We have prepared $Cr(CO)_4(PNP)$ in which the PNP ligand is P,N-coordinated[13] and $W(CO)_4(PNP)$ in which it is P,P-coordinated.[14] Reported here are the synthesis and characterization of two new rhenium complexes of the PNP ligand, $Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$ (**1**) and $Re_2(\mu\text{-PPh}_2)(\mu\text{-}\eta^1,\eta^4\text{-CHPPh}_2C_5H_4N)(CO)_7$ (**2**). X-ray structural characterization of **2** showed that the coordination geometry about each rhenium was distorted octahedral. The PNP ligand from the starting reagent $Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$ has presumably undergone P–C bond cleavage and oxidative addition across the Re–Re bond. The Re–Re bond has been cleaved, and the two rhenium moieties are held together by a bridging phosphido and a (2-pyridyl)(diphenylphosphino)methyl (PN) group. Other examples of P–C bond cleavage in PNP-type ligands are known,[6,12] but this is the first example in which the cleavage products have oxidatively added across a metal–metal bond while forming a metal–carbon σ-bond.

Experimental Section

General Methods. All manipulations were carried out under prepurified nitrogen with the use of standard Schlenk-line procedures. Solvents were purified by standard methods. 1-Hexene (Aldrich) was distilled from CaH_2 prior to use. Rhenium carbonyl was obtained from Pressure Chemical and used without treatment. 2-[Bis(diphenylphosphino)methyl]pyridine was prepared according to the literature method.[9] Liquid chromatography was used to purify the products. Neutral alumina (80–200 mesh) was used as the stationary phase; the mobile phase consisted of a 50:50 hexane/methylene chloride mixture.

Physical Measurements. $^{31}P\{^1H\}$ NMR spectra were recorded at 121.5 MHz and at 25 °C with a Nicolet NT-300 spectrometer.

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Table I. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR Data (δ) for 1 and 2

	$Re_2(CO)_8(PNP)$ (1)	$Re_2(CO)_7(PN)(PPh_2)$ (2)
$^{31}P\{^1H\}$ NMR data	CD_2Cl_2 solvent 21.3	$CDCl_3$ solvent (−20 °C) 70.3 (d, $J_{PP'}$ = 24 Hz, 1 P) −12.8 (d, $J_{PP'}$ = 22 Hz, 1 P)
^{13}C NMR data	$CDCl_3$ solvent	$CDCl_3$ solvent
CO region	201.7 (s, 2 C) 199.6 (s, 2 C) 194.3 (t, J_{PC} = 28 Hz, 2 C) 189.6 (s, 2 C)	196.7, 188.8 196.3, 187.5 195.8, 187.3 192.4, 181.9 192.1
^1H NMR data	CD_2Cl_2 solvent	$CDCl_3$ solvent
phenyl region	7.2–7.5 (m, 20 H)	7.0–7.8 (m, 20 H)
pyridyl region	7.87 (d, $J_{HH'}$ = 4.4 Hz, 1 H) 7.08 (m, 1 H) 6.82 (m, 1 H) 6.47 (d, $J_{HH'}$ = 7.8 Hz, 1 H)	8.76 (d, $J_{HH'}$ = 5.7 Hz, 1 H) 7.74 (m, 1 H) 6.65 (m, 1 H)
PN methine	4.91 (t, J_{PH} = 14.3 Hz, 1 H)	4.45 (dd, J_{PH} = 10.3, 13.0 Hz, 1 H)
CH_2Cl_2		5.30

The chemical shifts are reported in parts per million relative to the external standard 85% H_3PO_4 with positive shifts downfield. ^1H NMR spectra were recorded at 300 MHz by use of the same instrument. $^{13}C\{^1H\}$ NMR spectra were recorded at 125.7 MHz on a Bruker WM-500 at 25 °C. Infrared spectra were recorded in toluene solution and KBr disk with a Perkin-Elmer 467 grating spectrophotometer interfaced to an Apple IIe computer for the purpose of spectral expansion.[15] EI (70 eV) and fast atom bombardment mass spectra (FABMS) were obtained from a Finnigan 4000 and a VG 7070-EHF mass spectrometer, respectively. All *m/e* values are reported relative to Re at 187. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN.

$Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$ (1). $Re_2(CO)_8(\mu\text{-H})(\mu\text{-CH=CHC}_4H_9)$ was prepared from $Re_2(CO)_{10}$ (2.0 g, 3.1 mmol) and hexene (70 mL) by the method of Nubel and Brown[3] and was used without further purification. $Re_2(CO)_8(\mu\text{-H})(\mu\text{-CH=CHC}_4H_9)$ and 1.5 equiv of PNP (2.121 g, 46 mmol) were dissolved in CH_2Cl_2 (100 mL). The mixture was freeze–pump–thaw degassed and then stirred under nitrogen in the dark for approximately 20 h during which time the IR spectrum was monitored for the appearance of bands at 2024, 1976, and 1916 cm^{-1}. The solvent was removed under vacuum leaving an orange solid. Purification by chromatography separated **1** from a similar amount of red-brown uncharacterized material. Recrystallization from CH_2Cl_2/hexane gave air-stable yellow crystals which were spectroscopically characterized to be $Re_2(\eta^2,\eta^2\text{-PNP})(CO)_8$. Yield based on $Re_2(CO)_{10}$: 35% after chromatography/crystallization. Melting point: 197 °C dec. IR (cm^{-1}): ν_{CO} (toluene) 2076, 2024, 1976, 1943, 1916 cm^{-1}; $\nu_{py\text{-}CN}$ (KBr) 1577 cm^{-1}. FAB (DMSO matrix) mass spectrum (*m/e*): [M + H$^+$] 1060 and [M + H$^+$ − *n*CO], *n* = 1–5. NMR data are summarized in Table I. Anal. Calcd for $C_{38}H_{25}NO_8P_2Re_2$: C, 43.14; H, 2.38; N, 1.32. Found: C, 43.27; H, 2.68; N, 1.23.

$Re_2(\mu\text{-PPh}_2)(\mu\text{-}\eta^1,\eta^4\text{-CHPPh}_2C_5H_4N)(CO)_7$ (2). A solution of **1** (0.187 g, 0.177 mmol) in dry toluene (20 mL) was refluxed under a N_2 atmosphere. The CO region of the IR spectrum was monitored throughout the course of the reaction. After 3 days the reaction appeared nearly complete. The solvent was removed under vacuum leaving a light yellow solid. Purification by chromatography and recrystallization from CH_2Cl_2/hexane gave air-stable pale yellow crystals. Yield: 90% after purification. Melting point: 225 °C dec. IR (cm^{-1}): ν_{CO} (toluene) 2086, 2026, 1972, 1914 cm^{-1}; $\nu_{py\text{-}CN}$ (KBr) 1604 cm^{-1}. EI mass spectrum (*m/e*): [M$^+$] 1031 and [M − *n*CO], *n* = 1–5. NMR data are summarized in Table I. Anal. Calcd for $C_{37}H_{25}NO_7P_2Re_2\cdot CH_2Cl_2$: C, 40.94; H, 2.44; N, 1.26. Found C, 41.26; H, 2.65; N, 1.30.

Table II. Summary of Crystal Data and Intensity Collection for 2

Crystal Parameters	
cryst	triclinic
space group	$P\bar{1}$
cell params	
a, Å	10.906 (10)
b, Å	18.164 (9)
c, Å	10.973 (6)
α, deg	98.56 (5)
β, deg	119.12 (6)
γ, deg	94.14 (8)
V, Å^3	1851 (6)
Z	2
d(calcd), g cm^{-3}	1.951
temp, °C	25
abs coeff, cm^{-1}	68.5
max, min, av transmissn factors	1.00, 0.43, 0.81
formula	$C_{37}H_{25}NO_7P_2Re_2\cdot CH_2Cl_2$
fw	1087.72
cryst dimens, mm^3	0.35 × 0.35 × 0.05
Measurement of Intensity Data	
diffractometer	CAD 4
radiation	Mo K$\bar{\alpha}$ (λ = 0.71069 Å), graphite monochromatized
scan type; range (2θ), deg	ω scan; 0–52
no. of unique reflcns measd (quadrant)	7338 (±*h*,±*k*,l)
obsd reflcns^a	6312 [$F_o^2 \geq 1\sigma(F_o^2)$]
refinement by full-matrix least squares	
no. of params	443
R^b	0.045
$R_w{}^b$	0.051
GOF^b	1.37
p^a	0.05

[a] The intensity data were processed as described in: *CAD4 and SDP User's Manual*; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = [K/(\mathrm{NPI})](C - 2B)$, where K = 20.1166 × attenuator factor, NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $[\sigma(I)]^2 = [K/(\mathrm{NPI})^2[C + 4B + (pI)^2]$ where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2[\sigma(I)/I]F_o$. [b] The function minimized was $\sum\omega(|F_o| - |F_c|)^2$, where $\omega = 1/[\sigma(F_o)]^2$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum\omega(|F_o| - |F_c|))^2/(\sum\omega|F_o|^2]^{1/2})$. The error in an observation of unit weight (GOF) is $[\sum\omega(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

X-ray Structure Determination. Collection and Reduction of X-ray Data. A summary of crystal and intensity collection data for **2** is presented in Table II. The crystal of **2** was found to belong to the triclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search, centering, and indexing programs.[16] The space group was verified by successful solution and refinement (vide infra). The unit cell dimensions were determined by least-squares refinement of the angular settings of 25 peaks centered on the diffractometer. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure, and no decay with time was noted. The data were corrected for Lorentz, polarization, and background effects. The effects of absorption were included with use of the empirical absorption program EAC (ψ-scan data).[16]

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom techniques. The metal

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Table III. Positional Parameters and Their Estimated Standard Deviations for the Atoms of 2[a]

atom	x	y	z	B, Å^2
Re1	0.04526 (3)	0.16186 (2)	0.08404 (3)	2.960 (6)
Re2	0.02460 (3)	0.36004 (2)	0.31845 (3)	2.734 (6)
P1	−0.1838 (2)	0.2775 (1)	0.1185 (2)	2.93 (4)
P2	0.1466 (2)	0.2453 (1)	0.3280 (2)	2.78 (4)
C1	−0.0962 (8)	0.0897 (5)	0.0936 (8)	3.9 (2)
O1	−0.1677 (6)	0.0428 (4)	0.0935 (7)	5.2 (2)
C2	0.1821 (9)	0.0953 (5)	0.1592 (9)	4.2 (2)
O2	0.2630 (7)	0.0557 (4)	0.2053 (8)	6.1 (2)
C3	0.1943 (8)	0.2215 (5)	0.0671 (7)	3.9 (2)
O3	0.2814 (6)	0.2497 (5)	0.0554 (6)	5.4 (2)
C4	−0.0354 (9)	0.1078 (5)	−0.1126 (9)	4.4 (2)
O4	−0.0789 (9)	0.0816 (5)	−0.2297 (7)	7.3 (2)
C5	−0.0766 (8)	0.4443 (5)	0.2952 (8)	3.7 (2)
O5	−0.1364 (7)	0.4948 (4)	0.2826 (7)	5.6 (2)
C6	0.2034 (8)	0.4270 (5)	0.4622 (8)	3.7 (2)
O6	0.3026 (7)	0.4660 (4)	0.5483 (7)	5.5 (2)
C7	−0.0138 (8)	0.3448 (5)	0.4667 (8)	3.8 (2)
O7	−0.0376 (6)	0.3376 (5)	0.5548 (5)	5.5 (2)
N	0.0466 (6)	0.3700 (4)	0.1298 (5)	2.9 (1)
C2N	−0.0243 (7)	0.3160 (5)	0.0085 (7)	3.2 (2)
C3N	−0.0152 (9)	0.3248 (5)	−0.1118 (8)	4.0 (2)
C4N	0.0663 (9)	0.3870 (6)	−0.1070 (8)	4.6 (2)
C5N	0.1387 (9)	0.4431 (5)	0.0176 (8)	4.5 (2)
C6N	0.1255 (8)	0.4312 (5)	0.1315 (7)	3.7 (2)
C21	−0.1090 (7)	0.2477 (5)	0.0059 (7)	3.1 (2)

[a] Starred values indicate atoms were refined isotropically. Phenyl group positional parameters are given in the supplementary material. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

atoms were located by Patterson synthesis. Full-matrix least-squares refinement and difference-Fourier calculations were used to locate all remaining non-hydrogen atoms. Hydrogen atom positions were calculated and included in structure factor calculations but were not refined. The crystal of 2 was found to contain CH_2Cl_2 in fractionally occupied positions which were severely disordered and could not be satisfactorily modeled. These were therefore not included in the refinement. The atomic scattering factors were taken from the usual tabulation,[17] and the effects of anomalous dispersion were included in F_c by using Cromer and Ibers' values of $\Delta f'$ and $\Delta f''$.[18] Corrections for extinction were not applied. The final difference-Fourier map did not reveal significant residual electron density. The final positional parameters of the refined atoms appear in Table III, and an ORTEP view of the coordination core is shown in Figure 1. A complete listing of thermal parameters, calculated positions for the H atoms, distances, angles, least-squares planes, and structure factor amplitudes are included as supplementary material.[19]

Results and Discussion

Brown and co-workers have reported that (μ-hydrido)(μ-alkenyl)dirhenium octacarbonyl, prepared by photolysis of $Re_2(CO)_{10}$ in 1-alkene, is an excellent precursor for 1,2-diequatorially substituted dirhenium octacarbonyls.[3,20] The synthesis of 1 was carried out following this general approach. A 50% excess of PNP was stirred with $Re_2(CO)_8(\mu\text{-H})(\mu\text{-CH=CHC}_4\text{H}_9)$ in CH_2Cl_2 solution until the IR band at ν_{CO} = 1916 cm^{-1} had become strong (ca. 20 h). Product workup by column chromatography and fractional crystallization was done to separate 1 from a similar amount of uncharacterized red-brown, less soluble material. Direct cophotolysis of $Re_2(CO)_{10}$ and PNP proved to be an unacceptable synthetic approach due to the instability of PNP under photochemical conditions.

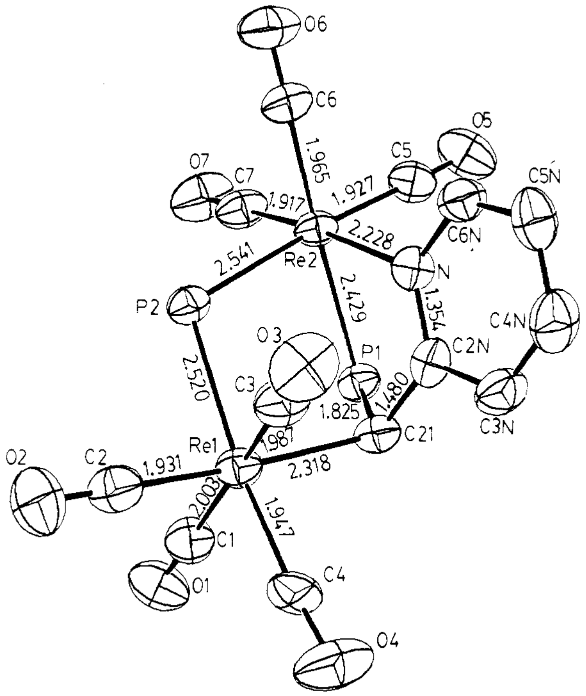
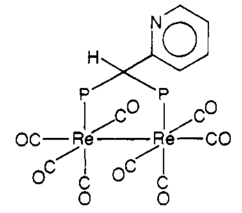


Figure 1. ORTEP drawing of the coordination core of 2 with selected distances. The ellipsoids are drawn with 50% probability boundaries. The phenyl rings have been omitted for clarity.

The physical properties of 1 are summarized above and in Table I. The absorption pattern in the CO stretching region of the IR spectrum indicates that all carbonyl ligands are terminal. The pattern is complex (five to six bands) but similar to that reported for $Re_2(CO)_8$(dppm) and $Re_2(CO)_8(py)_2$.[3] The pyridyl C–N stretching frequency ($\nu_{py\text{-}CN}$ = 1577 cm^{-1}, KBr disk) is indicative of an unbound pyridyl nitrogen atom.[8-12] Mass spectral data show the parent ion peak and peaks for the subsequent loss of several CO ligands. The ^{31}P {^{1}H} NMR spectrum consists of a single resonance at δ = 21.3 ppm indicating that the two phosphorus atoms are equivalent. Further support is given by the methine carbon which exhibits a triplet pattern in the ^{13}C NMR spectrum (δ = 73.1 ppm (J = 18.3 Hz)). The carbonyl region of the ^{13}C NMR spectrum shows four unique peaks of similar area. Singlets at 202, 200, and 190 ppm are assigned to the six ^{13}CO carbons cis to phosphorus. Two peaks are observed for the two pairs of mutually trans ^{13}COs due to the asymmetry introduced by the pyridyl group. The triplet pattern at 195 ppm is part of an AA′X spectrum and is assigned to the ^{13}CO carbon nuclei trans to phosphorus. A similar second-order spectrum is reported for $Re_2(CO)_{10}$(dppm).[2]

On the basis of all of the spectroscopic evidence gathered, we conclude that the structure of 1 features the PNP ligand bridging the two rhenium centers with the phosphorus atoms in equatorial positions.



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Refluxing 1 in toluene gives clean conversion to 2. Overall conversion of 1 to 2 was determined by IR spec-

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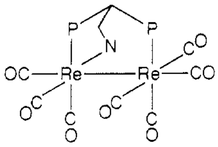
[17] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.4. Cromer, D. T., *Ibid.*, Table 2.3.1.

[18] Cromer, D. T.; Ibers, J. A. In ref 17.

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

[20] Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* 1982, *104*, 4955.

troscopy to be >90%. The product is isolated from unreacted 1 by column chromatography. Crystallization from CH_2Cl_2/hexane affords pale yellow, air-stable crystals of 2. Most of the spectroscopic data for 2 were consistent with the anticipated molecular structure of 2 that featured a bridging diphosphino arrangement as in 1 along with pyridyl N-coordination in place of a cis CO. The pyridyl C–N stretching frequency ($\nu_{py\text{-}CN}$ = 1604 cm^{-1}, KBr disk), indicative of a bound pyridyl nitrogen,[8-12] also supported this tentative structure:



This structural arrangement for PNP is precedented in $[Rh(PNP)(CO)]_2^{2+}$[10] and is a reasonable product that could result from thermal decarbonylation of 1. The $^{31}P\{^1H\}$ NMR spectrum of 2 cast the most uncertainty on this tentative structural assignment. Although two doublets were observed, the chemical shifts (70.3 and −12.8 ppm) were surprising. The resonance at −12.8 ppm is shifted upfield of the free ligand and occurs in a region associated with phosphido ligands.[21] To resolve these questions, a single-crystal X-ray structure determination was done.

The crystal structure of 2 consisted of two well-separated molecules per triclinic unit cell. No unusually close intermolecular contacts were found. The molecular structure of 2 is shown in Figure 1 and as supplementary material.[19] Important intramolecular distances and angles are given in Table IV.

Re1 features a distorted octahedral geometry. The methine carbon of the PN moiety, $C_5H_4NCHPPh_2$, is σ-bonded to Re1 (2.318 (7) Å). A diphenylphosphido bridge joins Re1 and Re2. Four CO ligands complete the coordination sphere for Re1. The most significant distortion from an idealized octahedral geometry for Re1 involves the CO1 ligand. The axis containing CO1 (C1–Re1–C3) is bent to 172.7 (3)°. The P2–Re1–C1 angle is opened to 97.8°. These distortions both involve CO1 and are possibly the result of crystal packing.

Re2 also exhibits a distorted octahedral geometry. The PN moiety, $C_5H_4NCHPPh_2$, along with Re2 form a five-membered ring in which the pyridyl-N and the phosphino group are coordinated as a bidentate chelate. The bite angle (75.6 (2)°) is consistent with similar PN ligands.[12] The Re2–P1 distance (2.429 (2) Å) is within the range reported for phosphino ligands bonded to rhenium in low formal oxidation states.[23]

Table IV. Distances and Angles in the Coordination Core of 2

Distances, Å			
Re1–Re2	4.189 (0)	Re2–C5	1.927 (8)
Re1–P2	2.520 (2)	Re2–C6	1.965 (7)
Re1–C21	2.318 (7)	Re2–C7	1.917 (7)
Re1–C1	2.003 (8)	C5–O5	1.150 (9)
Re1–C2	1.931 (8)	C6–O6	1.123 (9)
Re1–C3	1.987 (8)	C7–O7	1.139 (9)
Re1–C4	1.947 (8)	N–C2N	1.354 (9)
C1–O1	1.113 (10)	C21–C2N	1.480 (10)
C2–O2	1.148 (10)	P1–C21	1.825 (7)
C3–O3	1.118 (9)	P1–C1A	1.835 (7)
C4–O4	1.138 (10)	P1–C1B	1.805 (8)
Re2–P1	2.429 (2)	P2–C1C	1.861 (7)
Re2–P2	2.541 (2)	P2–C1D	1.837 (7)
Re2–N	2.228 (5)		

Angles, deg			
Re1–P2–Re2	111.7 (1)	P2–Re2–C6	92.9 (2)
P2–Re1–C1	97.8 (2)	P2–Re2–C7	94.3 (3)
P2–Re1–C2	91.6 (2)	P2–Re2–N	85.7 (2)
P2–Re1–C3	86.9 (2)	C5–Re2–C6	90.5 (3)
P2–Re1–C4	173.6 (3)	C5–Re2–C7	88.7 (3)
P2–Re1–C21	85.2 (2)	C5–Re2–N	91.0 (3)
C1–Re1–C2	88.6 (3)	C6–Re2–C7	89.4 (3)
C1–Re1–C3	172.5 (3)	C6–Re2–N	96.7 (3)
C1–Re1–C4	86.4 (4)	C7–Re2–N	173.9 (3)
C1–Re1–C21	93.4 (3)	Re2–P1–C21	99.3 (2)
C2–Re1–C3	85.4 (4)	Re1–C1–O1	171.2 (7)
C2–Re1–C4	93.4 (3)	Re1–C2–O2	179.0 (8)
C2–Re1–C21	176.4 (3)	Re1–C3–O3	174.4 (8)
C3–Re1–C4	89.4 (4)	Re1–C4–O4	174.3 (9)
C3–Re1–C21	92.9 (3)	Re2–C5–O5	179.4 (6)
C4–Re1–C21	89.7 (3)	Re2–C6–O6	176.7 (7)
P1–Re2–P2	84.9 (1)	Re2–C7–O7	178.2 (8)
P1–Re2–C5	91.4 (2)	Re2–N–C2N	120.5 (4)
P1–Re2–C6	172.1 (2)	N–C2N–C21	119.1 (6)
P1–Re2–C7	98.3 (2)	Re1–C21–P1	114.7 (3)
P1–Re2–N	75.6 (2)	Re1–C21–C2N	106.3 (4)
P2–Re2–C5	175.5 (2)	P1–C21–C2N	106.9 (5)

Re1 and Re2 are not bonded to each other as is evident from the Re1–Re2 distance (4.189 (0) Å). The Re–Re distance in $Re_2(CO)_{10}$ is 3.041 Å.[22] Re1 and Re2 are joined by a bridging diphenylphosphido ligand. The Re1–P2–Re2 bond angle is 111.72 (6)°. Bonding between Re1 and Re2 is not required to satisfy the 18-electron rule for each metal center, however the μ-PPh_2 ligand must be thought of as contributing two electrons to Re1 while σ-bonded to Re2. The phosphido ligand appears almost symmetrically placed from the crystallographic data. The Re–P distances are very similar: 2.520 (2) and 2.541 (2) Å for Re1–P2 and Re2–P2, respectively. The Re–P2–C_6H_5 bond angles also reflect the nearly symmetric disposition of the μ-PPh_2 ligand. The Re–P2–C (from phenyl) bond angles are 114.5 (3)° and 112.5 (3)° for Re1–P2–C1C and Re2–P2–C1C, respectively. The analogous values for the other phenyl are 107.3 (2)° and 112.3 (3)° for Re1–P2–C1D and Re2–P2–C1D, respectively.

All seven of the CO ligands are terminal as is evident from the Re–C–O bond angles. The largest distortion from linearity occurs with CO1 for which the Re1–C1–O1 angle is 171.2 (7)°. The average bond angle (Re–C–O) for all seven ligands is 176.2°. Five of the CO ligands are trans to non-carbonyl ligands; their average Re–CO bond distance is 1.9374 Å. The shortest Re–CO bond distance occurs for CO7 (1.917 (7) Å) which is trans to the pyridyl group. CO1 and CO3 are the only two mutually trans carbonyl ligands in 2. They exhibit the two longest Re–CO bond distances: 2.003 (8) and 1.987 (8) Å for Re1–C1 and Re1–C3, respectively. The average (1.995 Å) is very close to that found for mutually trans COs in $Re_2(CO)_{10}$ (1.987 Å).[22] CO1 and CO3 also have the shortest C–O bond distances: 1.113 (10) and 1.118 (9) Å, respectively. The other five CO ligands have C–O bond distances that range from 1.123 (9) Å for CO6 to 1.150 (9) Å for CO5 with an average value of 1.1396 Å. These observed bond distances are in accordance with the accepted model for M–CO bonding from competition for dπ electron density among CO ligands.[22]

The physical properties of 2 are summarized above and in Table I. The IR spectrum features an absorption pattern for the CO stretching region that is similar to that

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of 1. A significant difference is noted for the pyridyl ring C–N stretch. The frequency has shifted about 20 cm^{-1} from 1586 cm^{-1} for 1 to 1604 cm^{-1} for **2**. This is consistent with a coordinated pyridyl nitrogen in the latter.[8-12] The mass spectrum exhibits a parent ion peak (m/e = 1029) and peaks due to sequential CO loss. The $^{31}P\{^1H\}$ NMR spectrum consists of two well-separated doublets of equal intensity and with a coupling constant, $J_{PP'}$ = 23 Hz. The chemical shift of the phosphido resonance gives direct evidence regarding the presence or absence of a metal–metal bond.[12,21] Phosphido ligands exhibit resonances upfield from that of the H_3PO_4 standard (85%) in situations where no M–M bond occurs. In cases where M–M bonding does occur, a downfield shift is noted. In the case of **2**, the resonance at $\delta = -12.8$ ppm confirms the absence of a Re–Re bond. The resonance at $\delta = 70.3$ ppm is assigned to the PN phosphorus. This large downfield shift is indicative of a five-membered chelate ring.[24] The ^1H NMR spectrum of **2** provides further evidence for the nonequivalency of the two phosphorus nuclei. The methine proton at 4.45 ppm exhibits a doublet of doublets (J_{PH} = 10.3 Hz and $J_{P'H}$ = 13.0 Hz). **2** exhibits a complicated ^{13}C NMR spectrum. Each of the seven carbonyls is unique. Three of these are trans to phosphorus and so are expected to exhibit strong coupling. Nine of the ten theoretical resonances for the COs are observed in the 180–200 ppm region. Coupling to P is evident for at least one of the ^{13}CO carbons. The lack of symmetry produces a complicated aromatic region with significant overlapping of resonances even with the use of a 125-MHz magnetic field spectrometer. Thus a complete assignment of this spectral region is not possible. The spectrum is supplied as supplementary material.[19]

The conversion of **1** to **2** occurs under vigorous conditions. The reaction occurs with decarbonylation either in refluxing toluene or by photolysis. The reaction can be thought of formally as the intramolecular oxidative addition of a coordinated PNP ligand with concomitant cleavage of the Re–Re bond. Two new σ-bonds to rhenium (Re1–C21 and Re2–P2) are formed. The PNP ligand is known to be susceptible to P–C bond activation at elevated temperatures[7,12] as are tertiary phosphines in general.[25] The closest analogue to the structure of **2** is found in the heterobimetallic species, $[RhPt(\mu\text{-}PPh_2)(\mu\text{-}PNP)(PN)(PPh_3)]^{2+}$ reported by McNair and Pignolet.[12] In this cation a phosphido ligand bridges the heterobimetallic metal centers, and a PN bidentate ligand is coordinated to Rh. Both the PN chelate and the phosphido-bridging ligand result from the cleavage of a PNP ligand analogous to **2**.

Attempts to convert **2** back to **1** by stirring under 3 atm of CO in toluene at 25 °C for a period of 20 h were unsuccessful.

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Registry No. 1, 117469-79-1; 2, 117469-81-5; PNP, 60398-55-2; $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}CH{=}CHC_4H_9)$, 82621-40-7.

Supplementary Material Available: The ^{13}C spectrum of 2 and tables of positional parameters for phenyl group carbons, general temperature factor expressions, calculated positional parameters for the hydrogen atoms, least-squares molecular planes, and torsional angles for 2 (9 pages); a listing of observed and calculated structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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