

2 apparently results when some molecules crystallize with the carbonyl and chloro ligands having exchanged coordination sites. This can be achieved by simply rotating the molecule 180° about a vector bisecting the Rh-Rh bond and the O(1)-N(3)-O(2) angle. A model consisting of a half Cl and a half CO at each site fits the data as well as the one with the CO totally contained in one site and the Cl in the other site. Because of this disorder the C-O and the Rh(1)-Cl(2) distances cannot be determined accurately.

Concluding Remarks. We have further demonstrated that electrochemical oxidation of dinuclear rhodium(I) complexes in the presence of coordinating ligands can lead to novel rhodium(II) dimers. An increase in the oxidation state from Rh(I) to Rh(II) is generally accompanied by an increase in coordination number. In the present case it is somewhat interesting that though Cl⁻ is generally considered to be a better coordinating ligand for transition metals than NO₃⁻, the dinuclear Rh(I) species adds a Cl⁻ and a NO₃⁻ instead of two Cl⁻ ions. It is also interesting to note that, even in the absence of an external source of Cl⁻, oxidation of **1** in the CH₂Cl₂/TBAN medium still affords compound **2**. Either the starting material or some other rhodium-containing species serves as the source of the additional chloride found in **2**. This is apparently the reason for the lower yield of **2** under these conditions. The solvent, CH₂Cl₂, is not the source of Cl⁻ since the same results are obtained with the medium (CH₃)₂CO/TBAN.

It is possible that the addition of the bridging NO₃⁻, instead of a bridging Cl⁻ for instance, may result from the ability of the bridging nitrate to accommodate the twist angle (see Figure 1) imposed by the Ph₂Ppy ligands while still allowing each rhodium to have an electron count of 18. Studies that probe the relationship between geometric constraints and the relative coordination abilities of nitrate and other donors are being conducted.

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Registry No. **1**, 75361-61-4; **2**, 103438-59-1; TBAN, 1941-27-1; TBAC, 1112-67-0; TBAH, 3109-63-5; Rh, 7440-16-6.

Supplementary Material Available: Tables II, III, and V, giving complete bond distances and angles, hydrogen atom coordinates, and anisotropic temperature factors (5 pages); Table VI, giving observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Chemical and Structural Characterization of W(CO)₅OPPh₂NPPPh₃. A Novel Complex Containing a Phosphine Oxide Ligand Derived from the Bis(triphenylphosphine)nitrogen(1+) Cation

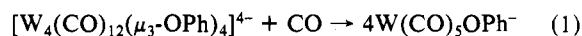
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There is wide-spread advance of the intermediacy of low-valent metal-alkoxides²⁻⁷ and -alkoxycarbonyl⁸⁻¹⁵ species in homoge-

neous-catalyzed reactions. An illustrative and pertinent example to our research efforts is the methanol carbonylation to methyl formate process employing group 6 or 8 metal carbonyl catalysts.^{16,17} Nevertheless, there are few reports of isolated and well-characterized alkoxide derivatives of zerovalent group 6 metals, and all of these are polynuclear.¹⁸⁻²⁰ One of these species is an anionic chromium tetramer recently reported by McNeese and co-workers.²⁰ The alkoxide derivative was obtained from the reaction of chromium hexacarbonyl and excess hydroxide ion in refluxing methanol. This tetraanion has a cubane-like structure comprised of four [Cr(CO)₃(OCH₃)]⁻ monomers, where the Cr₄O₄ core is a distorted cube with chromium and methoxide oxygen atoms occupying alternate corners.²¹

Preliminary results from our laboratories demonstrate that these species react reversibly with carbon monoxide in THF to provide the mononuclear derivatives, with results being unequivocal for the process described in eq 1.²² The species W(CO)₅[OPh][PPN] has previously been reported to be formed from the reaction of W(CO)₅THF with [PPN][OPh].²³



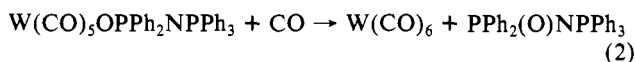
Our interest in fully characterizing low-valent group 6 methoxy- and carbonylmethoxy species as possible intermediates in methanol carbonylation processes prompted us to attempt the preparations of an anhydrous, aprotic solvent soluble salt of the methoxide ion. For this purpose the PPN⁺ (bis(triphenylphosphine)nitrogen(1+)) cation is widely used in organometallic chemistry. Furthermore, it customarily affords stabilization, both in solution²⁴ and in the solid state,²⁵ to reactive transition-metal carbonyl anions. In

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general, it is possible to prepare a large variety of PPN^+ salts by the metathesis reaction of the readily obtainable $[\text{PPN}][\text{Cl}]$ with alkali-metal salts (MX) in water where the resulting $[\text{PPN}][\text{X}]$ is usually insoluble.²⁶

In an attempt to prepare the $[\text{PPN}][\text{OMe}]$ salt with excess NaOCH_3 in methanol we have isolated a novel ligand, $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$, which presumably results from nucleophilic attack at the phosphorus atom by methoxide or hydroxide.²⁷ In this communication we wish to describe the synthesis of this ligand and its $\text{W}(\text{CO})_5$ derivative, along with spectroscopic data and X-ray structural analysis of the latter species. Kinetic measurements of the ligand displacement reaction (eq 2) have been



carried out in an effort to assess the bonding capabilities of the $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$ ligand relative to other phosphine oxides, e.g., Ph_3PO and Me_3PO .

Experimental Section

All manipulations were performed under a nitrogen atmosphere on a double-manifold Schlenk line or in an argon-filled glovebox. Phosphine oxides (Me_3PO , Strem and Ph_3PO , Aldrich) were used as received. NaOCH_3 was obtained from Aldrich and was opened and stored in the glovebox. Tetrahydrofuran and hexane were dried over sodium/benzophenone, diethyl ether was distilled from LiAlH_4 , and acetone was dried with NaI and distilled under nitrogen. Methanol was dried over magnesium methoxide. Infrared spectra were collected on an IBM FT/85 spectrometer. ^{31}P and ^{13}C NMR spectra were measured on a Varian XL-200 instrument.

Synthesis of the Ligand $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$. A 0.50-g sample of NaOCH_3 (ca. 8.9 mmol) was loaded into a 50-mL Schlenk flask in the glovebox. $[\text{PPN}][\text{Cl}]$ (1.10 g, 1.90 mmol) was added to the flask outside of the drybox under a stream of nitrogen. Reactions employing smaller quantities of NaOMe (e.g., 1:1 mole ratio of $[\text{PPN}][\text{Cl}]$ and NaOCH_3) resulted in a low yield of product. The flask was degassed and backfilled with nitrogen, and the solids were dissolved in 20 mL of dry MeOH. It is not possible to use smaller quantities of solvent initially due to the solubility of the reactants. The reaction mixture was refluxed for 4 h and then allowed to cool to ambient temperature under nitrogen. The solvent was removed under vacuum at 30–40 °C, leaving behind a pinkish residue, which was redissolved in 15 mL of MeOH and filtered through Celite to provide a clear colorless solution. The volume of filtrate was reduced to ca. 6 mL, and 40 mL of Et_2O was added to provide a white precipitate. The product was isolated and dried in vacuo with a yield of ca. 49% (mp 227–229 °C). IR (Nujol): 1171 cm^{-1} due to P–O stretching motion. ^{31}P NMR (CH_3OD): 16.07 (d, $J_{\text{PP}} = 3.7$ Hz), 18.7 ppm (d, $J_{\text{PP}} = 3.7$ Hz). A small ^{31}P signal at 34.6 ppm was assigned to Ph_3PO impurity. Anal. Calcd: C, 75.47; H, 5.40; P, 13.17. Found: C, 75.13; H, 5.50; P, 13.12.

Synthesis of $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPH}_3$. A solution of $\text{W}(\text{CO})_5\text{THF}$, prepared photochemically from 0.080 g (0.23 mmol) of $\text{W}(\text{CO})_6$ in 20 mL of THF, was transferred via cannula to a 50 mL Schlenk flask containing 0.18 g (0.37 mmol) of ligand ($\text{OPPh}_2\text{NPPH}_3$). The yellow mixture was stirred for 35 min and filtered through Celite. Infrared spectroscopy revealed a near-quantitative yield of tungsten pentacarbonyl product. The volume of bright yellow filtrate was reduced to ca. 2 mL. Upon the addition of 20 mL of hexane, allowing the solution to stand below 0 °C overnight, yellow crystals were formed in 30% yield. IR (THF) $\nu(\text{CO})$: 2065.6 w, 1974.0 w, br, 1918.1 vs, 1866.0 m cm^{-1} . IR (Nujol): 1125 s, 1118 m, 1087 s cm^{-1} . ^{31}P NMR (THF): 15.1 (s), 25.3 ppm ($s, J_{\text{PW}} \approx 27$ Hz). Anal. Calcd: C, 52.46; H, 3.14; P, 7.75. Found: C, 52.42; H, 3.40; P, 8.06.

Synthesis of $\text{W}(\text{CO})_5\text{OPR}_2$ (R = Me or Ph). A solution of $\text{W}(\text{CO})_5\text{THF}$, prepared photochemically from $\text{W}(\text{CO})_6$ in THF, was added via cannula to a degassed flask containing phosphine oxide dissolved in THF. The ratio of $\text{W}(\text{CO})_5\text{THF}$ to phosphine oxide was ca. 1:2.5. The resulting solid product was isolated by solvent removal under vacuum. $\text{W}(\text{CO})_5\text{OPPh}_2$: IR (THF) $\nu(\text{CO})$ 2069.5 w, 1974.1 w, 1924.9 s, 1875.7 m; IR (Nujol) 1146 cm^{-1} ; ^{31}P NMR (THF) 43.6 ppm; ^{13}C NMR (THF) 199.4 ($J_{\text{CW}} = 130.8$ Hz), 201.5 ppm. $\text{W}(\text{CO})_5\text{OPMe}_2$: IR (THF) $\nu(\text{CO})$ 2069.5 w, 1973.1 w, 1919.1 s, 1873.7 m; ^{31}P NMR (THF) 65.8 ppm; ^{13}C NMR (THF) 199.0 ($J_{\text{CW}} = 131.0$ Hz), 201.5 ppm.

Table I. Crystallographic Summary

A. Crystal Parameters			
formula	$\text{WC}_{35}\text{H}_{25}\text{NO}_6\text{P}_2$	$V, \text{\AA}^3$	1622.8 (6)
cryst syst	triclinic	Z	2
space group	$P\bar{1}$	μ, cm^{-1}	39.1
$a, \text{\AA}$	11.248 (2)	color	yellow
$b, \text{\AA}$	12.434 (3)	size, mm	$0.32 \times 0.33 \times 0.36$
$c, \text{\AA}$	13.353 (3)	temp, K	298
α, deg	75.07 (2)	$D(\text{calcd}), \text{g cm}^{-3}$	1.64
β, deg	80.84 (2)	$F(000)$	888
γ, deg	63.85 (2)		
B. Data Collection			
diffractometer	Nicolet R3	scan speed, deg min^{-1}	4–20
radiation	Mo $K\alpha$ ($\lambda = 0.71073 \text{\AA}$)		
monochromator	graphite	no. of reflns colld	5981
2θ limits, deg	$4 \leq 2\theta \leq 50$	no. of unique reflns	5713
data colld	$\pm h, \pm k, +l$	$R(\text{merge}), \%$	2.53
std reflns	3 stds/197 reflns	no. of unique reflns	5099
	(<1% variation)	with $F_0 \geq 4\sigma(F_0)$	
C. Refinement			
$R_F, \%$	2.94	Δ/σ , last cycle	0.100
$R_{wF}, \%$	3.13	highest peak, $e \text{\AA}^{-3}$	0.79 (1.00 \AA w)
GOF	1.034		
slope, norm prob	0.919	data/parameter	14.7

Kinetic Measurements. The respective tungsten pentacarbonyl complexes were dissolved in THF or methanol (concentration ~ 0.02 M) in a Schlenk flask filled with carbon monoxide. Samples were withdrawn with a syringe, and the reaction progress was monitored by the disappearance of the strongest $\nu(\text{CO})$ band in the infrared spectrum. Reactions were found to be first order in the metal complex.

X-ray Structural Determination

Diffraction quality crystals of $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPH}_3$ were obtained by recrystallization from acetone/ Et_2O and were affixed to a fine glass fiber with a heavy coating of epoxy cement to provide a barrier to the atmosphere. Table I provides the crystal parameters, and the data collection and refinement data. A total of reflections ($23^\circ \leq 2\theta \leq 29^\circ$), which included Friedel pairs to check optical and diffractometer alignment, were used to determine the cell constants from the least-squares fit of the angular settings. A search for higher than triclinic symmetry was negative. The centrosymmetric space group $P\bar{1}$ was selected and proved correct by the smooth and chemically reasonable refinement of the structure.

Intensity data, collected by a Wyckoff scan procedure, were corrected for L_p effects and for absorption (empirical, 4-scan, seven reflections, 10° increments, six-parameter ellipsoid, min/max transmission = 0.395/0.752).

A sharpened Patterson synthesis provided the W atom position, and the remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. The final cycles of refinement included anisotropic temperature factors for all non-hydrogen atoms, isotropic idealized hydrogen atom contributions ($d(\text{C-H}) = 0.96 \text{\AA}$), and phenyl rings constrained to rigid, planar hexagons ($d(\text{C-C}) = 1.395 \text{\AA}$).

All computer programs are contained in the SHELXTL (version 4.1) program library (Nicolet Corp., Madison, WI). Atomic coordinates are given in Table II, and selected bond distances and angles are given in Table III. Additional crystallographic data, including anisotropic temperature factors, hydrogen atom coordinates, and observed vs. calculated structure factors, have been deposited as supplementary material.

Results and Discussion

The novel phosphine oxide ligand $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$ has been synthesized from the reaction of sodium methoxide and $[\text{PPN}][\text{Cl}]$ in methanol. Upon completion of 4 h of refluxing $[\text{PPN}][\text{Cl}]$ and an excess of NaOMe under nitrogen in dry methanol, there is only a small quantity (3.5% conversion) of $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$ produced as indicated by two doublets in the ^{31}P NMR spectrum at 15.8 and 18.3 ppm ($J = 3.7$ Hz). At this stage the reaction solution revealed by ^{31}P NMR spectroscopy primarily the presence of starting cation PPN^+ (singlet at 22.9 ppm, 88%), with a small quantity of Ph_3PO (singlet at 33.9 ppm, 5.3%) and a trace of an unidentified phosphorus containing material with a signal at 123.9 ppm. The $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_2$ product is formed only after the reaction solution is concentrated as a result of solvent removal under reduced pressure at 30 °C. The ^{31}P NMR spectrum of the re-

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Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^6$)

atom	x	y	z	U_{iso}^a
W	-16.7 (2)	2759.4 (2)	1814.7 (1)	37 (1)
P(1)	2904 (1)	774 (1)	3128 (1)	31 (1)
P(2)	4639 (1)	-1767 (1)	2911 (1)	33 (1)
N(1)	3650 (3)	-678 (3)	3439 (3)	37 (1)
O(1)	348 (6)	4826 (4)	2556 (4)	93 (3)
O(2)	-2738 (4)	4752 (4)	1020 (4)	89 (2)
O(3)	-1646 (4)	2313 (4)	3915 (3)	74 (2)
O(4)	-659 (4)	914 (4)	987 (4)	73 (2)
O(5)	962 (5)	3688 (4)	-465 (3)	96 (3)
O(6)	1932 (3)	1264 (3)	2289 (2)	38 (1)
C(1)	268 (5)	4048 (5)	2301 (4)	54 (2)
C(2)	-1720 (5)	4017 (5)	1329 (4)	59 (2)
C(3)	-988 (5)	2424 (5)	3189 (4)	48 (2)
C(4)	-398 (4)	1549 (4)	1294 (4)	45 (2)
C(5)	698 (5)	3296 (5)	363 (4)	57 (2)
C(11)	5042 (3)	1230 (3)	3353 (2)	60 (3)
C(12)	5971 (3)	1716 (3)	2992 (2)	79 (4)
C(13)	5911 (3)	2438 (3)	1994 (2)	90 (4)
C(14)	4921 (3)	2673 (3)	1356 (2)	77 (4)
C(15)	3991 (3)	2187 (3)	1716 (2)	54 (3)
C(16)	4051 (3)	1465 (3)	2715 (2)	39 (2)
C(21)	1827 (3)	2382 (3)	4480 (2)	49 (2)
C(22)	1008 (3)	2812 (3)	5322 (2)	62 (3)
C(23)	405 (3)	2110 (3)	5987 (2)	64 (3)
C(24)	621 (3)	978 (3)	5810 (2)	66 (3)
C(25)	1440 (3)	548 (3)	4969 (2)	52 (2)
C(26)	2043 (3)	1251 (3)	4304 (2)	37 (2)
C(31)	2473 (3)	-1583 (2)	2027 (3)	48 (2)
C(32)	1821 (3)	-2001 (2)	1520 (3)	61 (2)
C(33)	2495 (3)	-3128 (2)	1227 (3)	65 (3)
C(34)	3823 (3)	-3839 (2)	1441 (3)	66 (3)
C(35)	4475 (3)	-3422 (2)	1949 (3)	56 (2)
C(36)	3800 (3)	-2294 (2)	2241 (3)	37 (2)
C(41)	4894 (3)	-3167 (3)	4893 (2)	55 (2)
C(42)	5537 (3)	-4159 (3)	5684 (2)	79 (3)
C(43)	6803 (3)	-5030 (3)	5489 (2)	71 (3)
C(44)	7427 (3)	-4909 (3)	4504 (2)	63 (3)
C(45)	6784 (3)	-3918 (3)	3713 (2)	52 (2)
C(46)	5518 (3)	-3047 (3)	3908 (2)	39 (2)
C(51)	5861 (3)	-1293 (3)	952 (2)	47 (2)
C(52)	6745 (3)	-897 (3)	290 (2)	55 (2)
C(53)	7642 (3)	-654 (3)	700 (2)	55 (2)
C(54)	7655 (3)	-808 (3)	1771 (2)	53 (2)
C(55)	6772 (3)	-1204 (3)	2433 (2)	47 (2)
C(56)	5875 (3)	-1447 (3)	2023 (2)	36 (2)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Angles for $W(\text{CO})_5\text{OPPh}_2\text{NPPh}_3$

(a) Bond Distances (\AA)			
W-C(1)	2.037 (7)	C(1)-O(1)	1.146 (9)
W-C(2)	1.946 (5)	C(2)-O(2)	1.165 (6)
W-C(3)	2.028 (5)	C(3)-O(3)	1.140 (7)
W-C(4)	2.034 (7)	C(4)-O(4)	1.135 (9)
W-C(5)	2.040 (5)	C(5)-O(5)	1.138 (7)
W-O(6)	2.220 (2)	P(1)-O(6)	1.510 (3)
(b) Bond Angles (deg)			
C(1)-W-C(2)	88.6 (3)	C(4)-W-C(5)	89.9 (2)
C(1)-W-C(3)	89.9 (2)	C(4)-W-O(6)	88.6 (2)
C(1)-W-C(4)	176.8 (2)	C(5)-W-O(6)	93.4 (2)
C(1)-W-C(5)	89.6 (2)	W-C(1)-O(1)	175.6 (5)
C(1)-W-O(6)	94.6 (2)	W-C(2)-O(2)	178.2 (6)
C(2)-W-C(3)	86.8 (2)	W-C(3)-O(3)	173.3 (4)
C(2)-W-C(4)	88.1 (2)	W-C(4)-O(4)	177.0 (4)
C(2)-W-C(5)	84.8 (2)	W-C(5)-O(5)	172.7 (4)
C(2)-W-O(6)	176.3 (2)	W-O(6)-P(1)	141.8 (2)
C(3)-W-C(4)	90.2 (2)	O(6)-P(1)-N(1)	115.4 (2)
C(3)-W-C(5)	171.6 (2)	P(1)-N(1)-P(2)	138.0 (2)
C(3)-W-O(6)	95.0 (1)		

action solution revealed 81% of the starting PPN^+ cation was converted to the $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$ product along with 15% Ph_3PO .

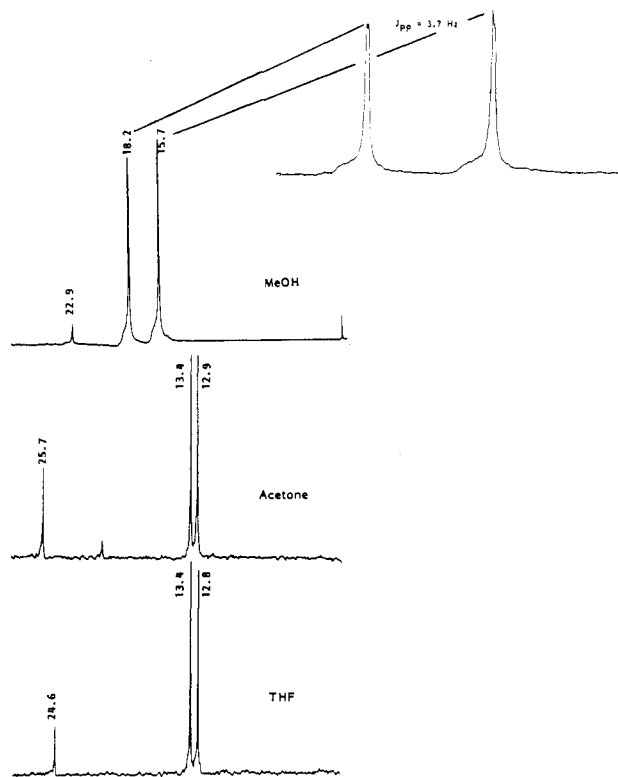


Figure 1. ^{31}P NMR spectra of $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$ in various solvents. Downfield signal is due to unreacted PPN^+ cation.

The $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$ product was isolated by filtration of the methanol solution through Celite followed by precipitation with diethyl ether to afford off-white amorphous material in yields of ca. 50%. The ^{31}P NMR spectrum of the product is strongly affected by the solvent, and only in methanol is the P-P coupling observed with a J value of 3.7 Hz. Figure 1 illustrates the ^{31}P NMR spectra of $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$ in the solvents acetone, THF, and methanol.

$\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$ was found to react with a THF solution of $W(\text{CO})_5\text{THF}$ to afford a species that was isolated as a yellow crystalline solid upon solution concentration and addition of hexane. Chemical analysis indicated this species to be a one-to-one adduct of tungsten pentacarbonyl and $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$, i.e. $W(\text{CO})_5\text{OPPh}_2\text{NPPh}_3$. This complex exhibited ^{31}P NMR resonances at 15.1 and 25.3 ppm. The latter resonance was assigned to the phosphorus atom containing the oxide grouping, $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$, since it was shifted the most upon complexation and showed satellites resulting from W-P coupling ($J_{\text{PW}} = 27$ Hz).

Additional evidence for W-O bonding is readily seen in the infrared spectrum of this derivative, where the band assigned to the P-O stretching vibration is shifted from 1171 cm^{-1} in the free ligand to 1125 cm^{-1} upon complexation to $[W(\text{CO})_5]$. This observation is consistent with similar shifts noted for phosphine oxides, e.g., the corresponding band at 1190 cm^{-1} in Ph_3PO shifts to 1146 cm^{-1} in the $W(\text{CO})_5\text{OPPh}_3$ complex. Shifts in the $\nu(\text{PO})$ vibration in the range of $38\text{--}70\text{ cm}^{-1}$ have been previously observed in cationic complexes of Cd, Zn, Co, Cu, Ni, Mn, and Fe and were attributed to a lowering of the P-O bond order as a result of complex formation.²⁸ Comparison of the infrared bands assigned principally to P-O stretching modes in the free ligands Ph_3PO (1190 cm^{-1}) and $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$ (1171 cm^{-1}) suggests a lower P-O bond order in the latter species (vide infra).²⁹

The pentacarbonyl tungsten complex crystallized in the triclinic $P\bar{1}$ space group. The molecule is shown in Figure 2, where the

(28) (a) Cotton, F. A.; Barnes, R. D.; Bannister, E. J. *Chem. Soc.* **1960**, 2199. (b) Goodgame, D. M. L.; Cotton, F. A. *J. Chem. Soc.* **1961**, 2298, 3735.

(29) For example, the O-P bond in a Ph_3PO -neodymium(III) complex has a bond distance of 1.49 \AA : Leipoldt, J. G.; Bok, L. D. C.; Laubscher, A. E.; Basson, S. S. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2477.

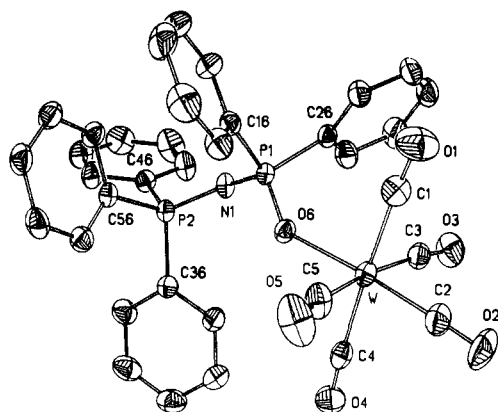
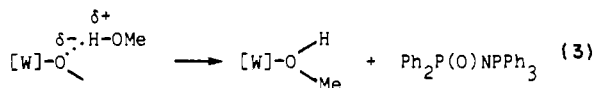


Figure 2. Molecular structure and labeling diagram for $W(CO)_5OPPh_2NPPH_3$.

atom-numbering scheme is also provided. The arrangement of the ligands around the central tungsten atom closely defines a regular octahedron. Table III contains a listing of important bond distances and bond angles. The average $W-CO_{eq}$ bond length is 2.035 (6) Å while that of $W-CO_{ax}$ is 0.090 Å shorter (1.946 (5) Å). Thus, this PPN⁺-derived phosphine oxide ligand displays a significant trans effect, much like that of anionic oxygen donor ligands.³⁰ The $W-O(6)$ bond distance of 2.220 (2) Å is quite similar to those observed in $W(CO)_5O_2CR^-$ ($R = H, CH_3$) species (see Table IV).

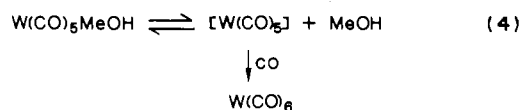
Indicative of some steric repulsion between the $Ph_2P(O)NPPH_3$ ligand and the equatorial carbonyl ligands, the $O(6)-W-C(1)$, $O(6)-W-C(3)$, and $O(6)-W-C(5)$ angles are all greater than 90° (i.e., 94.6 (2), 95.0 (1), and 93.4 (3)°, respectively). This small steric interaction is exhibited as well by the disposition of one of the phenyl rings about the phosphorus atom bearing the oxygen donor, where the $N(1)-P(1)-C(26)$ angle of 105.5 (2)° is much smaller than that typically observed (111.5°). Other structural features common to the PPN⁺ cation and its derived oxide $Ph_2P(O)NPPH_3$ are not greatly different. For example, the two phosphorus-nitrogen bonds are almost equal and average 1.582 Å and the $P(1)-N-P(2)$ angle is 138°, parameters that are well within the range of those reported for the bis(triphenylphosphine)nitrogen(1+) cation.^{25,31}

The $W(CO)_5OP(Ph)_2NPPH_3$ complex, upon dissolution in methanol, instantaneously undergoes $Ph_2P(O)NPPH_3$ ligand substitution at ambient temperature with concomitant formation of the methanol adduct $W(CO)_5MeOH$ (see Figure 3). This process presumably occurs via a hydrogen-bonded intermediate similar to that identified for $W(CO)_5SR^-$ ($R = H, Ph$) complexes in protic solvents (eq 3). The $W(CO)_5MeOH$ species has infrared



absorption bands in the $\nu(CO)$ region at 2074 w, 1932 vs, and 1888 $m\text{ cm}^{-1}$ in methanol, which are identical with those noted upon photolysis of $W(CO)_6$ in methanol.³² The shift to higher $\nu(CO)$ values is consistent with the replacement of $Ph_2P(O)NPPH_3$ with a poorer donor ligand MeOH.

In the presence of carbon monoxide, displacement of methanol from the metal's coordination sphere is a facile process (eq 4).



(30) (a) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudarkoski, R. *Inorg. Chem.* **1982**, *21*, 1656. (b) Darensbourg, D. J.; Pala, M. J. *Am. Chem. Soc.* **1985**, *107*, 5687.

(31) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685.

(32) Darensbourg, D. J.; Ovalles, C., unpublished observations.

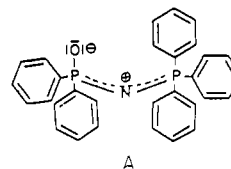
The rate of the substitution reaction is dependent on the CO concentration at moderate CO pressures (Table V); e.g., an increase in the total pressure from 14 to 110 psi (ca. an 8-fold increase in CO concentration) resulted in an 8-fold increase in the reaction rate. An attenuation of this $[CO]$ dependence is expected with further increases in the pressure of carbon monoxide.³³

As noted in Table V, when the ligand substitution reaction (eq 2) is carried out in aprotic solvents, where solvent assistance as indicated in eq 3 is absent, the rate of $Ph_2P(O)NPPH_3$ replacement by carbon monoxide is much slower. Whereas $Ph_2P(O)NPPH_3$ displacement occurs upon dissolution in methanol, this process takes place with $t_{1/2} = 44$ h under 1 atm of CO in tetrahydrofuran. Consistent with the fact that THF is readily displaced by CO in $W(CO)_5THF$, no buildup of this potential intermediate is expected nor observed during the substitution reaction of $W(CO)_5OPPh_2NPPH_3$ in tetrahydrofuran. Hence, the dissociative loss of the $Ph_2P(O)NPPH_3$ ligand from the tungsten center in $W(CO)_5OPPh_2NPPH_3$ is much slower than the dissociation of the neutral O-bonded ligands, THF or MeOH.

In an effort to more accurately assess comparative ligand lability in $[W]-O$ complexes, processes directly related to $[W]-O$ bond strengths, we have examined the rates of unique ligand dissociation in the phosphine oxide complexes, $W(CO)_5OPR_3$ ($R = Me, Ph$). Triphenylphosphine oxide dissociation in $W(CO)_5OPPh_3$ in THF is significantly faster than the comparable process involving $Ph_2P(O)NPPH_3$, the rate of $[W]-OPPh_3$ dissociation being 1 order of magnitude faster than that for $[W]-OPPh_2NPPH_3$. Furthermore, the effect of changing solvents to methanol, where the $W(CO)_5MeOH$ complex is an intermediate, is less dramatic for these more labile OPR_3 ligands. The slightly faster rates noted for methanol replacement in $W(CO)_5MeOH$ derived from OPR_3 ($R = Me$ and Ph) as compared with that derived from $Ph_2P(O)NPPH_3$ suggest that the latter ligand competes more effectively with CO for the open coordination site on the metal center as compared with the OPR_3 ligands.

Concluding Remarks

The purpose for initiating the work described herein was to determine the feasibility of synthesizing $[PPN][OMe]$ for use as a source of aprotic solvent soluble methoxide ion in organometallic synthesis and homogeneous catalysis. Although this was not accomplished, an interesting reaction between NaOMe and $[PPN][Cl]$ was noted, providing the novel $Ph_2P(O)NPPH_3$ ligand. A comparison of structural features common to PPN⁺ and $Ph_2P(O)NPPH_3$ reveals a great deal of similarity between the two species. Hence, the $Ph_2P(O)NPPH_3$ derivative should be viewed as a zwitterion with the negative component of the zwitterion being centered on the oxygen atom (A).



Spectral properties ($\nu(CO)$ and ^{13}C NMR) in solution of the tungsten pentacarbonyl complex containing $Ph_2P(O)NPPH_3$ are supportive of this conclusion. That is, comparison of spectral data for $[W(CO)_5]$ bound to neutral and anionic O-donor ligands is indicative of more anionic character assignable to the oxygen atom in the $Ph_2P(O)NPPH_3$ ligand as compared with that in R_3PO . More importantly, quantitative data for the dissociative loss of the R_3PO ligands from $[W(CO)_5]$ (a direct measure of the $W-O$ bond strength), reveal these processes to be much more facile than the analogous processes involving $Ph_2P(O)NPPH_3$ or anionic ligands such as acetate or formate. Finally, it is evident from this report that the PPN⁺ cation cannot always be considered an

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Table IV. Comparative W-C and W-O Bond Distances (Å) in W(CO)₅ Derivatives

substituent	W-C _{eq}	W-C _{ax}	Δ	ref
O ₂ CH ⁻	2.037 (13)	1.911 (15)	0.126	<i>b</i>
O ₂ CCH ₃ ⁻	2.038 (18)	1.951 (6)	0.087	<i>c</i>
Ph ₂ P(O)NPPh ₃	2.035 (6)	1.946 (5)	0.089	<i>d</i>

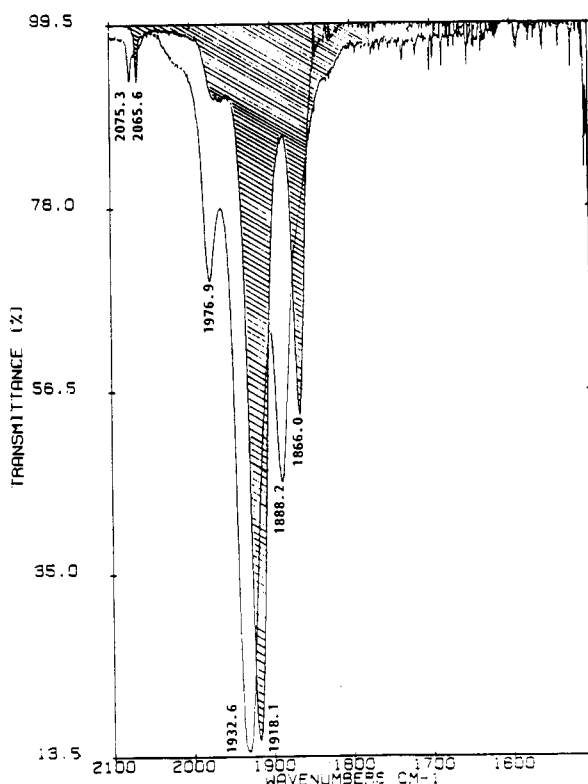
^aThis value represents the average of the four W-C_{eq} distances.

^bDarensbourg, D. J.; Pala, M. *J. Am. Chem. Soc.* **1985**, *107*, 5687.

^cCotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudarski, R. *Inorg. Chem.* **1982**, *21*, 1656. ^dThis work.

Table V. Rate Constants for Phosphine Oxide Displacement at Ambient Temperature

compd	solvent	CO pressure, psi	10 ³ k _{obsd} , min ⁻¹
W(CO) ₅ OP(Ph ₂)NPPh ₃	THF	14	0.26
	MeOH	14	1.76
	MeOH	110	14
W(CO) ₅ OPPh ₃	THF	14	2.49
	MeOH	14	4.88
W(CO) ₅ OPMe ₃	MeOH	14	3.26

**Figure 3.** Infrared spectra in $\nu(\text{CO})$ region of $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPh}_3$: (a) in THF (shaded); (b) in MeOH.

innocent ion, especially in the presence of good nucleophiles.

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Registry No. $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPh}_3$, 99618-35-6; $\text{W}(\text{CO})_5\text{THF}$, 36477-75-5; $\text{W}(\text{CO})_5\text{OPMe}_3$, 103620-60-6; $\text{W}(\text{CO})_5\text{OPPh}_3$, 103620-61-7; $\text{Ph}_2\text{P}(\text{O})\text{NPPh}_3$, 2156-69-6; NaOCH_3 , 124-41-4; $[\text{PPN}][\text{Cl}]$, 21050-13-5; CO, 630-08-0.

Supplementary Material Available: Additional crystallographic data including complete tables of bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (5 pages); a listing of observed vs. calculated structure factors (30 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

Studies of the Synthesis and Thermolysis of Tris[tris(amino)phosphine]molybdenum Tricarbonyls: Synthesis of *fac*-[(*i*-PrNH)₃P]₃Mo(CO)₃

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We recently reported synthesis of the diphosphazane complex *cis*-PhN[P(NHPh)₂]₂Mo(CO)₄ by PhNH₂ elimination from the complex [(PhNH)₃P]₂Mo(CO)₄ in a metal-templated phosphorus-nitrogen bond condensation reaction.² In order to pursue this reaction type further, we undertook studies of the synthesis and thermolysis of selected tris[tris(amino)phosphine]molybdenum tricarbonyl complexes to determine if, in reactions analogous to those above, new metal-coordinated triphosphazanes might be obtained. The results of these studies are described below.

Experimental Section

Apparatus and Materials. All operations were carried out in N₂-flushed glovebags and standard vacuum line equipment.³ Infrared, ¹H NMR (90.0 MHz), and mass spectra were obtained with Beckman IR 4250, Varian EM390, and Varian MAT CH5 spectrometers, respectively. ³¹P NMR spectra were obtained on JEOL PFT-100 (40.5 MHz) and FX-90Q (36.4 MHz) spectrometers. ¹H and ³¹P NMR chemical shifts were measured relative to internal Me₄Si and H₃PO₄, respectively; shifts downfield from the standard are given + δ values. Single-crystal X-ray data were collected at ambient temperature with a Syntex PI automated diffractometer (Mo K α radiation, graphite monochromator).

fac-(PCl₃)₃Mo(CO)₃,⁴ *fac*-(PhPCl₂)₃Mo(CO)₃,⁴ (mes)Mo(CO)₃ (mes = mesitylene),⁵ and PhP(NHPh)₂⁶ were prepared and purified as described previously. Aniline (Mallinckrodt), Et₃N (Eastman Chemicals), and *i*-PrNH₂ (Matheson Coleman and Bell) were distilled from CaH₂. Benzene and toluene were distilled from Na/Pb alloy. CH₂Cl₂ and CHCl₃ were distilled from P₄O₁₀.

Reactions of *fac*-(PCl₃)₃Mo(CO)₃. (A) With *i*-PrNH₂. *i*-PrNH₂ (75 mmol) in toluene (30 mL) was added slowly to (PCl₃)₃Mo(CO)₃ (4.0 mmol) in 150 mL of toluene at 25 °C. After 8 h, *i*-PrNH₂Cl was filtered and the clear filtrate was passed through a 2-cm alumina column. The solution showed major and minor ³¹P NMR resonances at δ 109.5 [(*i*-PrNH)₃P]₃Mo(CO)₃ (**1**) and δ 110.7 (*i*-PrN[P(NH-*i*-Pr)₂Mo(CO)₄] (**2**),² respectively. Evaporation of the solution and recrystallization of the solid from toluene yielded pure **1** (85% yield, based on Mo in reactant; mp 133–135 °C). Anal. Calcd for C₃₀H₇₂N₉P₃O₃Mo: C, 45.17; H, 9.03, N, 15.81; P, 11.67. Found: C, 43.38; H, 9.15; N, 15.16; P, 11.51. ¹H NMR (CDCl₃): δ 3.15–3.90 (m, area 9, CH), 1.10–1.55 (s, area 54, CH₃), 0.90 (m, area 9, NH). ³¹P NMR (C₆D₆): δ 109.5 (s). MS: parent and seven most intense envelopes at *m/e* (relative intensity) 685 (0.2, M⁺), 392 (7.8), 333 (6.2), 177 (5.1), 147 (17.5), 88 (13.9), 44 (100), 42 (64.8). IR (Nujol): characteristic absorptions at 3410 (w), 3370 (m), 1918 (s), 1815 (vs), 1166 (m), 1134 (s), 868 (m), and 791 cm⁻¹.

Under conditions identical with those above, except that reaction was allowed to proceed for 65 h at 25 °C, after recrystallization from benzene pure *i*-PrN[P(NH-*i*-Pr)₂Mo(CO)₄] (**2**); 57% yield, based on Mo in reactant; mp 116–118 °C) was obtained. Anal. Calcd for C₁₉H₃₉N₉P₃MoO₄: C, 40.79; H, 7.03; N, 12.52; P, 11.07. Found: C, 41.00; H, 7.14; N, 12.63; P, 11.11. ¹H NMR (CDCl₃): δ 3.50 (broad m, area 5, CH), 1.68 (d, area 4, *J* = 7.3 Hz, NH), 1.35 (d, area 6, *J* = 6.9 Hz, CH₃), 1.20 (d of d, area 24, *J* = 6.0 Hz, CH₃). ³¹P NMR (C₆D₆): δ 110.7 (s). MS: parent and six most intense envelopes at *m/e*

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