rapid purging with N_2 while warming to ~40 °C. The purple suspension was cooled to -30 °C, and the dark red solids were collected by filtration and dried under vacuum. The crude yield was 0.076 g. The predominant product (~40% of the solid) is $[RuH(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4]$, as determined by comparison of ^{31}P and ^1H NMR spectra with those of a pure sample, which was prepared by method B. Additional products, including a ruthenium hydride complex (δ -12.6 (t, J = 20.7 Hz)), were detected via NMR spectroscopy.

Method B. A suspension of $RuClH(CO)(PCy_3)_2$ (0.160 g) and S_2CPCy_3 (0.0784 g in 35 mL of absolute ethanol) was stirred for 20 min. The purple solution was filtered, and 0.30 g $NaBPh_4$ was added to the filtrate. The purple suspension was cooled to -20 °C, and the purple solid was collected by filtration, washed with ethanol, and dried under vacuum. The yield was 0.177 g (59%). Anal. Calcd for $C_{80}H_{120}BOP_3RuS_2$: C, 70.31; H, 8.85; P, 6.80; S, 4.70. Found: C, 70.57; H, 9.02: P, 6.49; S, 4.55.

$[RuH(CO)(S_2CPEt_3)(PCy_3)_2][BPh_4]$ (2). A suspension of $RuClH(CO)(PCy_3)_2$ (0.135 g) and S_2CPEt_3 (0.054 g in 20 mL of anhydrous methanol) was stirred for 5 min. Carbon disulfide (2.0 mL) was then added to the suspension, and the clear purple solution was stirred for 5 min. Addition of 0.20 g of $NaBPh_4$ gave a purple precipitate which was collected by filtration, washed with cold methanol, and dried under vacuum. The yield was 0.188 g (84%). Anal. Calcd for $C_{68}H_{102}BOP_3RuS_2$: C, 67.81; H, 8.54; P, 7.71; S, 5.32. Found: C, 67.69; H, 8.37; P, 7.45: S, 5.50.

$[RuCl(CO)(S_2CPCy_3)_2(PCy_3)_2][BPh_4]$ (3). A suspension of $RuCl_2(CO)(PCy_3)_2$ (0.080 g) and S_2CPCy_3 (0.24 g in 40 mL of deoxygenated methanol) was stirred for 0.5 h under nitrogen at 40 °C. The purple solution was cooled to 20 °C and filtered. Addition of 0.40 g of $NaBPh_4$ to the filtrate gave a red-brown solid. The solid was recrystallized three times from chloroform-methanol to give a dark red solid which analyzed as $[RuCl(CO)(S_2CPCy_3)(PCy_3)_2][BPh_4]\cdot CHCl_3$. The yield was 0.065 g (40%). Anal. Calcd for $C_{81}H_{120}BCl_4OP_3RuS_2$: C, 63.98; H, 7.95; Cl, 9.33; P, 6.11; S, 4.22. Found: C, 63.10; H, 8.07; Cl, 8.27; P, 6.59; S, 4.21.

$RuClH(CO)_2(PCy_3)_2$. Method A. Carbonyl sulfide was bubbled through a solution of $RuClH(CO)(PCy_3)_2$ (0.102 g in 10 mL of deoxygenated toluene) until the color faded from yellow to colorless. The solvent was removed under vacuum, and the white solid which remained was recrystallized from $CHCl_3$-MeOH to give the complex as white crystals. The yield was 0.069 g (60%). The complex was identified by comparison of ^1H NMR and IR spectra with those of an authentic sample.[13] The complex has previously been assigned a stereochemistry with trans PCy_3 ligands and cis CO ligands.[13] See Table I for spectral data.

Method B. Carbonyl sulfide (~10 g) was condensed into a liquid-nitrogen-cooled pressure reactor which contained 0.054 g of $RuClH(CO)(PCy_3)_2$, 0.10 g of PCy_3, and 8 mL of deoxygenated methanol. The vessel was allowed to warm to room temperature (*Caution*! 12 atm). The metal complex dissolved to give an orange solution which faded to colorless and precipitated a white solid. The carbonyl sulfide was distilled off, and the white solid was collected by filtration and dried under vacuum. The complex was identified by comparison of ^1H NMR and IR spectra with those of an authentic sample.

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Registry No. **1**, 80697-67-2; **2**, 80697-69-4; **3**, 80697-71-8; $RuClH(CO)(PCy_3)_2$, 40935-25-9; $RuClH(CO)_2(PCy_3)_2$, 55100-76-0; $RuCl_2(CO)(PCy_3)_2$, 52524-94-4; CS_2, 75-15-0.

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Stabilization of RN=NN=PR$_3$. Preparation and Structural Characterization of Stable Tetraarylphosphazide Complexes Containing Molybdenum and Tungsten

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The reaction of aromatic azides ($R'N_3$) with $MBr_2(CO)_3(PPh_3)_2$ (M = Mo, W; Ph = C_6H_5; tol = p-$CH_3C_6H_4$) in dry methylene chloride at 20 °C affords $MBr_2(CO)_3(R'N_3PPh_3)$, N_2, and $R'N{=}PPh_3$ (R' = Ph, tol). The phosphazide complexes exhibit remarkable stability with respect to N_2 loss. In contrast to the Mo(II) and W(II) complexes, $ReCl_3(CH_3CN)(PPh_3)_2$ and $ReCl_3(PPh_2Me)_3$ yield $ReCl_4(PR_3)_2$ upon treatment with the same aryl azides. Triclinic needles of $WBr_2(CO)_3(tolN_3PPh_3)$ were grown from chloroform-ether and crystallized in space group C_i^1-$P\bar{1}$ with $Z = 2$, $a = 13.715$ (6) Å, $b = 9.904$ (5) Å, $c = 10.397$ (5) Å, $\alpha = 100.98$ (2)°, $\beta = 83.11$ (2)°, and $\gamma = 85.80$ (1)°. An X-ray diffraction study at -145 (5) °C showed the complex to be monomeric and seven-coordinate. The tolyl azide had inserted into the W-P bond, forming a phosphazide ligand ($tolN_3PPh_3$) which is bound to W in a chelating fashion through the α and γ nitrogen atoms; the N_3W metallacycle is nearly planar. Salient metrical parameters of the structure include the following: W-N(1) = 2.163 (4) Å, W-N(3) = 2.220 (5) Å, N(1)-N(2) = 1.279 (6) Å, N(2)-N(3) = 1.364 (6) Å, N(3)-P = 1.672 (5) Å, N(1)-C(41) = 1.423 (7) Å; N(1)-W-N(3) = 56.7 (2)°, W-N(1)-N(2) = 102.4 (3)°, W-N(3)-N(2) = 96.8 (3)°, N(1)-N(2)-N(3) = 103.8 (4)°. The full-matrix, least-squares refinement converged to $R(F) = 0.028$ and $R_w(F) = 0.037$ for 4066 unique data with $F_o^2 > 3\sigma(F_o^2)$.

Introduction

The reaction of tertiary phosphines with organic azides is known to proceed via a reactive intermediate, $R'NNNPR_3$, which decomposes in a bimolecular process to dinitrogen and the corresponding phosphoranimine[1] (eq 1 and 2). These

$$R'N_3 + PR_3 \xrightarrow[\text{temp}]{\text{low}} R'N{=}NN{=}PR_3 \tag{1}$$

$$2R'N_3PR_3 \xrightarrow[\text{temp}]{\text{room}} 2R'N{=}PR_3 + 2N_2 \tag{2}$$

intermediates, which were originally named "phosphazides" by Staudinger,[2] are only rarely stable under ambient conditions; when $R = R' = C_6H_5$, the phosphazide decomposes rapidly at temperatures above -20 °C. Certain phosphazides

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[2] Staudinger, H.; Hauser, E. *Helv. Chim. Acta* **1921**, *4*, 861. Though unsystematic, the phosphazide nomenclature is easy to use and descriptive in its own right. Chemical Abstracts Service names $RNNNPR_3$ as a derivative of phosphoranylidenetriazene.

0020-1669/82/1321-2064$01.25/0

can be isolated in special cases where R′ is stongly electron withdrawing, where R is strongly electron donating, or where R and R′ are sterically bulky.[3]

Owing to the instability of free phosphazides toward N_2 loss, there has been little known about the coordination of phosphazides to transition metals. The only published report dealing with stable phosphazide complexes describes the action of furoyl azide, $N_3C(O)C_4H_3O$, on $CoBr_2(P(C_6H_{11})_3)_2$ at 0 °C to give $CoBr_2((C_6H_{11})_3PN_3C(O)C_4H_3O)$.[4] This green cobalt phosphazide complex is moderately stable in the solid state but decomposes in solution at room temperature to give the blue cobalt phosphoranimine complex, $CoBr_2((C_6H_{11})_3P\text{-}NC(O)C_4H_3O)$ and dinitrogen. We now report that the reaction of aryl azides with $MBr_2(CO)_3(PPh_3)_2$ (M = Mo, W) under ambient conditions yields remarkably stable compounds, $MBr_2(CO)_3(R'N_3PPh_3)$. In order to elucidate the binding mode of the phosphazide ligand to the metal, we also undertook a structural study at low temperature of $WBr_2(CO)_3(p\text{-}CH_3C_6H_4N_3PPh_3)$. The structural results and detailed synthetic procedures are contained herein; a preliminary account of this work has appeared.[5]

Experimental Section

All reactions were carried out with standard Schlenk techniques under a dry-nitrogen atmosphere. Solvents were carefully dried and degassed prior to use. Infrared spectra were recorded in Nujol and Fluorolube S-30 mulls with a Perkin-Elmer Model 283 infrared spectrophotometer and calibrated with a polystyrene film. NMR spectra (^1H, ^{31}P) were measured in CD_2Cl_2 with a Varian Associates XL-100 spectrometer; internal tetramethylsilane and external 85% H_3PO_4 were used as references. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Gas-evolution measurements were carried out with standard Toepler vacuum-line methods, and the gases were analyzed by high-resolution mass spectroscopy (AEI, MS-9 instrument). Labeled $Na^{15}NO_2$ (99% ^{15}N) was obtained from Stohler Isotope Chemicals, Rutherford, NJ. Unless noted otherwise, phenyl and tolyl azides were prepared from the respective diazonium salts and NaN_3 in water. The pure azides were obtained as pale yellow liquids by vacuum distillation. They were diluted with alkane solvents to make 2 M solutions that were indefinitely stable when stored below 0 °C in the dark. The presence of small amounts of residual water in the azide solutions had a deleterious effect on the yields of the phosphazide products. $WBr_2(CO)_2(PPh_3)_2$ and $[MoBr_2(CO)_4]_2$ were prepared according to the published procedures.[6]

Dibromotricarbonylbis(triphenylphosphine)tungsten(II). This compound was prepared by a modification of the literature method.[6] Tungsten hexacarbonyl (10.0 g) was suspended in 100 mL of dry CH_2Cl_2 and rapidly stirred in a nitrogen atmosphere at −78 °C (dry ice–acetone bath). Dropwise addition of a bromine solution (4.8 g in 20 mL of dry CH_2Cl_2) over a period of about 5 min resulted in evolution of carbon monoxide. The mixture was stirred at −78 °C for 10 min and then allowed to slowly warm to 0 °C over a period of 15 min after the cold bath was removed. The reaction solution was filtered into another filtered, stirring solution of 30 g of PPh_3 in 100 mL of dry CH_2Cl_2. The mixture was stirred for 30 min at room temperature to complete the formation of the yellow product. Absolute ethanol (200 mL) was added, and then the volume of the mixture was reduced by about half with use of a rotary evaporator. The temperature of the mixture was maintained at 25–30 °C during the solvent stripping in order to prevent decarbonylation of the yellow product to form the deep violet dicarbonyl. The mixture was cooled to −20 °C to ensure complete crystallization and then filtered. The solid was washed with absolute MeOH, absolute EtOH, and finally pentane to yield 24.6 g (91%) of a bright yellow, microcrystalline powder. **Dibromotricarbonylbis(triphenylphosphine)molybdenum(II)** was prepared analogously in 86% yield as yellow microcrystals. The molybdenum complex loses CO more easily than the tungsten analogue; thus, just prior to filtration, CO gas was bubbled through the mixture to convert any dicarbonyl to the tricarbonyl.

Dibromotricarbonyl(*N*-(*p*-tolyltriphenylphosphoranylidene)triazene)tungsten(II). To a stirred solution of 3.05 g of $WBr_2(CO)_3(PPh_3)_2$ in 90 mL of CH_2Cl_2 was added 2.8 equiv of $tolN_3$ (4.5 mL of a freshly prepared 2.0 M solution in cyclopentane). After 20 min of stirring at 20 °C, the solution was filtered and the solvent was removed under vacuum. The oily residue was redissolved in 10 mL of CH_2Cl_2 to form a viscous liquid which gave crystals of the complex upon careful dropwise addition of Et_2O. The product was washed with warm absolute ethanol and then ether to remove any residual phosphoranimine, yielding 2.10 g (81%) of pure $WBr_2(CO)_3(tolN_3PPh_3)$ as yellow-orange crystals: IR ν(CO) = 2037, 1948, 1892 cm^{-1}; ^1H NMR δ 2.38 (s, 3 H), 7.23 (AA′BB′ q, 4 H), 7.8 (m, 15 H); $^{31}P\{^1H\}$ NMR (−80 °C) δ 42.70 (s with W satellites, $^2J_{PW}$ = 17.0 Hz); $^{31}P\{^1H\}$ NMR (30 °C) δ 42.03 (br s, 14 Hz (fwhm)); gas evolution 1.1 equiv of N_2/W and 0.05 equiv of CO/W after 20 min. Anal. Calcd for $C_{28}H_{22}N_3Br_2O_3PW$: C, 40.86; H, 2.69; N, 5.10. Found: C, 40.56; H, 2.65; N, 4.86.

Dibromotricarbonyl(*N*-(tetraphenylphosphoranylidene)triazene)tungsten(II). This compound was prepared analogously to the foregoing compound except that a 2.0 M solution of phenyl azide was used. The reaction of 3.25 g of $WBr_2(CO)_3(PPh_3)_2$ produced 1.07 g (42% yield) of yellow-orange crystals: IR ν(CO) = 2038, 1955, 1909 cm^{-1}; ^1H NMR δ 7.7 (m, 20 H); $^{31}P\{^1H\}$ NMR (−60 °C) δ 43.21 (s with W satellites, $^2J_{PW}$ = 16.2 Hz; $^{31}P\{^1H\}$ NMR (30 °C) 42.20 (br s, 16 Hz (fwhm)). Anal. Calcd for $C_{27}H_{20}N_3Br_2O_3PW$: C, 40.08; H, 2.49; N, 5.19. Found: C, 39.54; H, 2.66; N, 4.62.

Dibromotricarbonyl(*N*-(*p*-tolyltriphenylphosphoranylidene)triazene)molybdenum(II). (a) The compound was prepared analogously to the tungsten analogue except that 2.76 g of $MoBr_2(CO)_3(PPh_3)_2$ was used. The reaction produced 0.63 g (27% yield) of yellow crystals.

(b) A solution of 0.45 g of PPh_3 in 40 mL of dry CH_2Cl_2 was frozen and placed under an inert atmosphere. To this was added 2 mmol of $tolN_3$ (1.2 equiv), and the mixture was warmed to −40 °C and stirred at this temperature for 15 min. The ^{31}P NMR spectrum at −40 °C of an aliquot of this solution showed only very small amounts of tolN=PPh$_3$ and free PPh$_3$; a large, somewhat broadened singlet at δ 20.28 was assigned to the free phosphazide, $tolN_3PPh_3$. When the sample was warmed to −10 °C, the tolN=PPh$_3$ signal increased in intensity, and at 0 °C it was the only observed phosphorus-containing compound. To the bulk phosphazide solution was added 0.50 g of $[MoBr_2(CO)_4]_2$. The temperature of the stirring solution was maintained at −40 °C for 30 min and then gradually raised to 0 °C over a period of 30 min. The solvent was removed under vacuum and the residue redissolved in 5 mL of CH_2Cl_2. Et_2O was carefully added dropwise to precipitate 0.20 g (20% yield) of yellow crystals: IR ν(CO) = 2045, 1968, 1911 cm^{-1}; ^1H NMR δ 2.38 (s, 3 H), 7.27 (AA′BB′ q, 4 H), 7.7 (m, 15 H); $^{31}P\{^1H\}$ NMR (30 °C) δ 41.77 (s, 2 Hz (fwhm)). Anal. Calcd for $C_{28}H_{22}N_3Br_2O_3PMo$: C, 45.74; H, 3.02; N, 5.72. Found: C, 45.46; H, 3.26; N, 5.58.

Displacement Reactions with tolN=PPh$_3$. Pure tolN=PPh$_3$ was prepared by allowing $tolN_3$ (slight excess) and PPh$_3$ to react in a minimum of Et_2O. After 30 min of stirring at 20 °C, crystals of tolN=PPh$_3$ precipitated from the ether and were washed with cold Et_2O.

(a) To a solution of 0.20 g of $WBr_2(CO)_3(PPh_3)_2$ in 10 mL of CH_2Cl_2 was added 1.95 equiv (0.15 g) of tolN=PPh$_3$. The mixture was stirred for 2 h at ambient temperature during which time the solution darkened in color and became homogeneous. The $^{31}P\{^1H\}$ NMR spectrum of an aliquot of this solution showed two equally intense signals at δ 4.80 (free PPh$_3$) and 32.52, in addition to several minor (<5% of the total P) signals. The IR spectrum (CH_2Cl_2 solution) of this mixture showed two carbonyl bands at 1930 and 1845 cm^{-1}, consistent with a dicarbonyl complex. Upon stepwise addition of more tolN=PPh$_3$, the signal at δ 32.52 broadened and shifted toward the chemical shift value of free tolN=PPh$_3$ (δ 1.17).

(b) The procedure of section a was repeated with 0.20 g of $WBr_2(CO)_2(PPh_3)_2$ and 0.95 equiv of tolN=PPh$_3$. The solution darkened in color almost immediately, and the ^{31}P spectrum of 1 aliquot showed two signals at δ 41.76 (2 P, J_{PW} = 159 Hz) and 22.86 (1 P). Upon addition of another 1.0 equiv of tolNPPh$_3$ these signals disappeared in favor of signals at δ 4.80 (free PPh$_3$) and 32.52. The

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[7] Bowden, J. A.; Colton, R. *Aust. J. Chem.* **1968**, *21*, 2657.

latter was shown to be in equilibrium with free tolN=PPh$_3$ upon addition of more phosphoranimine. The solution IR spectrum of the final solution was identical with that found in (a) above.

(c) To 15 mL of CH_2Cl_2 were added 0.30 g of $WBr_2(CO)_3(tolN_3PPh_3)$ and 0.13 g of tolN=PPh$_3$ (0.95 equiv), and the solution was stirred for 3 h at ambient temperature. The $^{31}P\{^1H\}$ NMR spectrum of this solution showed a strong single resonance at δ 32.52. Neither starting material was present. The solution IR spectrum was identical with that recorded for section a above.

Reaction of tolN$_3$ with WBr$_2$(CO)$_2$(PPh$_3$)$_2$. To 10 mL of CH_2Cl_2 were added 0.20 g of $WBr_2(CO)_2(PPh_3)_2$ and 2.5 equiv of tolN$_3$. An immediate reaction with gas evolution was observed, and the solution was stirred at 20 °C for 30 min. The $^{31}P\{^1H\}$ NMR spectrum of an aliquot of this solution showed a sharp, single resonance at δ 32.52. The solution IR spectrum showed two carbonyl bands at 1930 and 1845 cm^{-1}. A brown solid was isolated (0.15 g), which approximately analyzed for $WBr_2(CO)_2(tolN{=}PPh_3)_2$. Anal. Calcd for $C_{52}H_{44}N_2Br_2O_2P_2W$: C, 55.05; H, 3.91; N, 2.47. Found: C, 54.41; H, 4.01; N, 2.87.

Preparation of WBr$_2$(CO)$_3$(tolNN^{15}NPPh$_3$). In a 50-mL flask were placed 1.00 g of recrystallized *p*-tolylhydrazine hydrochloride, 7 mL of distilled water, 3 mL of diethyl ether, and 2 mL of 12 M HCl. The flask was immersed in a cold bath, and its contents were cooled to −10 °C. A cooled solution of 0.45 g of Na^{15}NO$_2$ in 5 mL of distilled water was added in a dropwise manner to the above mixture. The temperature of the reaction mixture was maintained between −5 and +5 °C. The mixture was then allowed to warm to room temperature, and the azide was extracted with two 10-mL portions of diethyl ether, which were combined and dried over anhydrous $CaCl_2$. The ether was completely removed under vacuum, yielding 0.52 g (62%) of a yellow viscous oil which was sufficiently pure to use without further purification. Under these reaction conditions, no appreciable amount of tolN^{15}NN was formed.[8]

To the tolNN^{15}N prepared above was added 1.24 g of $WBr_2(CO)_3(PPh_3)_2$ in 60 mL of dry CH_2Cl_2. The reaction was carried out as described for the unlabeled complex, giving 0.56 g (52%) of pure yellow-orange crystals (tol^{14}N=PPh$_3$ (NMR) and $^{15}N{\equiv}^{14}N$ (mass spectroscopy) were identified as byproducts): IR ν(CO) = 2037, 1948, 1892 cm^{-1} (see discussion for bands associated with phosphazide ligand); ^{1}H NMR: identical with that of unlabeled compound; $^{31}P\{^1H\}$ NMR: (−80 °C) δ 42.73 (sharp d with W satellites, $^1J_{PN}$ = 24.4 Hz, $^2J_{WP}$ = 17 Hz); $^{31}P\{^1H\}$ NMR (30 °C) δ 42.05, br d, $^1J_{PN}$ = 24 Hz, fwhm = 14 Hz.

Reaction of WBr$_2$(CO)$_3$(tolN$_3$PPh$_3$) with Ph$_2$PCH$_2$CH$_2$PPh$_2$. To 20 mL of CH_2Cl_2 were added 0.57 g (0.7 mmol) of $WBr_2(CO)_3(tolN_3PPh_3)$ and 0.75 g (1.9 mmol) of 1,2-bis(diphenylphosphino)ethane (diphos). The mixture was stirred at ambient temperature for 1 h and the solvent removed under vacuum. To the resulting residue was added 25 mL of toluene, and the mixture was refluxed for 1 h, precipitating a yellow product which was filtered and washed with hexane to yield 0.55 g (66%) of [WBr(CO)$_2$(diphos)$_2$][Br]: ν(CO) = 1933 and 1847 cm^{-1}. The product was identical with an authentic sample prepared from $WBr_2(CO)_3(PPh_3)_2$.

Reaction of WBr$_2$(CO)$_3$(tolN$_3$PPh$_3$) with PPh$_3$ and NaS$_2$CN(CH$_2$)$_4$. To a 50-mL flask were added 10 mL of CH_2Cl_2, 10 mL of CH_3OH, 0.15 g (0.2 mmol) of $WBr_2(CO)_3(tolN_3PPh_3)$, 0.20 g (0.8 mmol) of PPh$_3$, and 0.20 g (1.2 mmol) of $NaS_2CH(CH_2)_4$. This mixture was refluxed under N$_2$ with stirring for 10 min; then the contents were filtered and washed with H$_2$O and CH$_3$OH to yield 0.11 g (81%) of red-orange crystals of $W(CO)_2(PPh_3)(S_2CN(CH_2)_4)_2$: ν(CO) = 1920, 1831 cm^{-1}; ν(CN) = 1488 cm^{-1}. This product was identical with an authentic sample prepared by other means.[9]

Table I. Summary of Crystallographic Data

compd	$WBr_2(CO)_3(p\text{-}CH_3C_6H_4N_3P(C_6H_5)_3)$
formula	$Br_2C_{28}H_{22}N_3O_3PW$
formula wt	823
a, Å	13.715 (6)
b, Å	9.904 (5)
c, Å	10.397 (5)
α, deg	100.98 (2)
β, deg	83.11 (2)
γ, deg	85.80 (1)
V, Å^3	1361
Z	2
space group	C_i^1-$P\overline{1}$
cryst size, mm	(a) 0.28 × 0.10 × 0.08 (b) 0.18 × 0.11 × 0.08
V, mm^3	(a) 2.2×10^{-3} (b) 1.6×10^{-3}
crystal shape	triclinic needle with {100}, {110}, and {001} faces
radiation	Mo Kα, λ = 0.710 69 Å, monochromatized with highly oriented graphite
density, g/cm^3	2.008 (calcd), 2.00 (2) (exptl) obsd at 25 °C
temp, °C	−145 (5)
μ, cm^{-1}	73.32
range of transmission factors	0.38–0.59
aperature, mm	2.5 wide × 3.5 high
takeoff angle, deg	2.0
scan speed, deg/min	2.0
scan range, deg	1.00 below Kα_1 to 1.20 above Kα_2
bkgd counting, s	15
2θ limits, deg	3.0–50.0
no. of variables	217
unique data with $I_o > 3\sigma(I_o)$	4066
error in obsn of unit weight	1.12 electrons
$R(F)$	0.028
$R_w(F)$	0.037

Reaction of PhN$_3$ and ReCl$_3$(PPh$_2$Me)$_3$. To a solution of $ReCl_3(PPh_2Me)_3$ (0.25 g, 0.28 mmol) in 10 mL of CHCl$_3$ was added 1.1 mmol of PhN$_3$. The solution was refluxed for 30 min, and the volume was then reduced to about 2 mL under reduced pressure. Absolute ethanol (15 mL) was added and caused the product to precipitate as violet crystals. The product was filtered, washed with ethanol and hexane, and dried under vacuum to yield 0.15 g (74%) of $ReCl_4(PPh_2Me)_2$, which was identical with an authentic sample. When the reaction was conducted in 10 mL of refluxing benzene, the yield was 0.10 g. When the reaction was carried out with 1.1 mmol of tolN$_3$, the yield was 0.15 g. When the reaction was conducted in 10 mL of CHCl$_3$ at 25 °C for 5 h, the yield was 0.14 g. When the reaction was carried out in 10 mL of benzene at 25 °C for 12 h, the yield was 0.08 g.

Reaction of PhN$_3$ and ReCl$_3$(CH$_3$CN)(PPh$_3$)$_2$. Phenyl azide (1.2 mmol) was added to a solution of 0.25 g of $ReCl_3(CH_3CN)(PPh_3)_2$ (0.33 mmol) in 10 mL of CHCl$_3$. The mixture was refluxed for 30 min and then handled as the same reaction above (with use of $ReCl_3(PPh_2Me)_3$), yielding 0.21 g (85%) of the brown Re(IV) product, $ReCl_4(PPh_3)_2$. When the reaction was carried out in 10 mL of refluxing benzene, the yield was 0.12 g.

Crystal Preparation. Crystals were grown by slow vapor diffusion of diethyl ether into a chloroform solution of the phosphazide complex $WBr_2(CO)_3(tolN_3PPh_3)$. The complex crystallized as beautiful, solvent-free orange needles with well-formed faces. An experimental density was obtained by suspending crystals of the complex in a mixture of liquids of the same density; this experimental density measured at 25 °C agreed well with the calculated value (see Table I). A suitably sized data crystal was selected and mounted on a glass fiber with silicone grease and placed in a nitrogen cold stream on the diffractometer. ω scans showed well-shaped, acceptably narrow peaks.

X-ray data collection was accomplished with a locally constructed diffractometer consisting of a Picker goniostat interfaced with a Texas Instruments TI980B computer. The attached low-temperature device has been described.[10] During data processing, 60 low-angle, high-intensity data were irretrievably lost. Consequently, these data were recollected with a new crystal that had about two-thirds the volume of the original data crystal. Treatment of these 60 data is described below.

Crystallographic Data. The crystal of the phosphazide complex was mounted on the diffractometer, and no symmetry could be identified. A careful search of all diffraction peaks in the region 4.0° < 2θ < 8.0° indicated the absence of any symmetry or extinction pattern. A primitive, reduced triclinic unit cell was chosen. The space

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(8) Clusius, K.; Schwarzenback, K. *Helv. Chim. Acta* **1959**, *42*, 739. Clusius, K.; Weisser, H. R. *Ibid.* **1952**, *35*, 1548.

(9) Chen, G. Y.; Yelton, R. O.; McDonald, J. W. *Inorg. Chim. Acta* **1977**, *22*, 249.

(10) Huffman, Ph.D. Dissertation, Indiana University, Bloomington, IN, 1974, p 10.

Table II. Final Positional and Thermal Parameters for $WBr_2(CO)_3(tolN_3PPh_3)$

Atom	X[a]	Y	Z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	0.19811(17)	0.10942(2)	0.16876(2)	21.65(14)	36.8(3)	26.2(2)	-2.20(12)	-3.66(12)	9.60(17)
Br(1)	0.32336(5)	-0.04316(6)	0.26334(6)	35.2(4)	60.4(7)	43.1(6)	6.4(4)	-9.9(4)	16.1(5)
Br(2)	0.33304(5)	0.07576(6)	-0.04231(6)	35.0(4)	69.9(7)	38.5(6)	2.6(4)	5.3(4)	16.3(5)
P	0.33393(11)	0.39167(15)	0.33770(14)	21.0(8)	46.9(16)	31.4(13)	-4.0(8)	-5.5(8)	9.6(12)
N(1)	0.1723(3)	0.2951(4)	0.0921(4)	22. (3)	41. (5)	28. (4)	-8. (3)	-5. (3)	4. (4)
N(2)	0.2218(4)	0.3801(5)	0.1598(5)	28. (3)	50. (5)	36. (5)	-2. (3)	-7. (3)	18. (4)
N(3)	0.2542(3)	0.3091(5)	0.2493(4)	25. (3)	46. (5)	32. (5)	-2. (3)	-4. (3)	12. (4)
C(1)	0.0558(4)	0.1086(5)	0.1560(5)	20. (3)	39. (6)	44. (6)	0. (3)	-15. (3)	5. (5)
O(1)	-0.0245(3)	0.1045(5)	0.1513(4)	34. (3)	72. (5)	69. (5)	-3. (3)	-5. (3)	12. (4)
C(2)	0.1822(4)	-0.0828(6)	0.0722(6)	28. (3)	40. (7)	47. (6)	2. (4)	-4. (4)	6. (5)
O(2)	0.1756(3)	-0.1911(5)	0.0194(4)	47. (3)	57. (5)	74. (5)	-5. (3)	-15. (3)	3. (4)
C(3)	0.1291(4)	0.1212(6)	0.3515(6)	31. (3)	47. (6)	40. (6)	-6. (4)	-8. (4)	3. (5)
O(3)	0.0876(3)	0.1236(5)	0.4531(4)	42. (3)	89. (6)	38. (4)	-6. (3)	8. (3)	14. (4)
C(41)	0.1330(4)	0.3397(6)	-0.0150(5)	19. (3)	47. (6)	35. (5)	2. (3)	-2. (3)	13. (5)
C(42)	0.1347(4)	0.4784(6)	-0.0285(6)	26. (3)	47. (6)	48. (6)	-8. (4)	-5. (4)	17. (5)
C(43)	0.1002(4)	-0.4810(6)	-0.1388(6)	22. (3)	60. (7)	50. (6)	3. (4)	-6. (3)	21. (5)
C(44)	0.0630(4)	0.4223(6)	-0.2328(5)	20. (3)	80. (7)	29. (5)	6. (4)	-2. (3)	18. (5)
C(45)	0.0592(4)	0.2855(6)	-0.2146(5)	25. (3)	71. (7)	31. (5)	-5. (4)	-7. (3)	6. (5)
C(46)	0.0956(4)	0.2458(6)	-0.1067(5)	26. (3)	45. (6)	34. (5)	-2. (3)	-3. (3)	12. (5)
C(4)	0.0273(5)	0.4693(7)	-0.3502(6)	36. (4)	80. (8)	42. (6)	1. (4)	-11. (4)	21. (5)

Group	Xc[c]	Yc	Zc	δ	ε	η
Ph-1	0.2403(2)	0.6843(3)	0.5120(3)	0.968(5)	2.166(2)	-2.002(5)
Ph-2	0.39452(18)	0.2118(2)	0.5419(2)	1.663(2)	-2.870(2)	-0.834(2)
Ph-3	0.52489(19)	0.4252(3)	0.1468(2)	-3.062(2)	2.769(2)	0.565(3)

[a] Estimated standard deviations of the least significant figure are given in parenthesis in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients multiplied by 10^4. [c] *Xc*, *Yc*, and *Zc* are the fractional coordinates of the rigid-group centers; the angles δ, ϵ, and η (radians) have been previously defined: Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* 1965, *4*, 793.

group was assumed to be centrosymmetric, C_i^1–$P\bar{1}$, and verified by successful refinement of the structure and location of all 38 nonhydrogen atoms and all 22 hydrogen atoms. On the basis of a least-squares analysis of the angular positions of 12 strong, machine-centered reflections in diverse regions of reciprocal space ($20° < 2\theta < 30°$), accurate unit cell dimensions were established. See Table I for pertinent crystal information and details of data collection. Background counts were measured at both ends of the θ–2θ scan with both the crystal and counter stationary. The intensities of three standard reflections were measured periodically and remained constant during the entire data acquisition. The intensity data were corrected for background effects and for Lorentz polarization effects. An absorption correction was performed with use of Gaussian integration.[11]

A least-squares refinement of 12 reflections of the second data crystal yielded cell parameters agreeing within experimental error with those from the original crystal. Under the same operating conditions, a total of 600 data were collected with this crystal. The data were corrected for background and Lorentz polarization effects, and an absorption correction was applied. Data common to both crystals were used to compute by hand a scaling factor for the second data set. The 60 data unique to the second data set were properly scaled and merged with the original data to form a data shell complete out to 50° in 2θ. Only reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in least-squares calculations. The values of $\sigma(F_o)$ were estimated with a value of 0.05 for p.[12]

Structure Refinement. The structure was solved with a Patterson synthesis to locate the metal atom. Solving the Patterson map was initially complicated because the W–W ($2X$, $2Y$, $2Z$) vector was the fifth most intense peak. Subsequent difference Fourier syntheses aided in locating all the remaining, nonhydrogen atoms. The structure was refined with full-matrix, least-squares techniques.[13] During the refinements, the quantity minimized was $Q = \sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes and where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were taken from the usual sources,[14] and the anomalous dispersion terms for W, Br, and P were included in F_c. The three phenyl rings attached to the P atom were refined isotropically as three rigid planar groups with intragroup parameters of C–C–C = 120.0° and C–C = 1.390 Å. All other nonhydrogen atoms were refined anisotropically. The tolyl hydrogen atoms were clearly located in difference Fourier syntheses. Although the 19 aromatic hydrogen atoms were clearly visible in difference Fourier syntheses, these atoms were placed in idealized positions and isotropic thermal parameters were chosen to be 1.0 Å^2 larger than the isotropic equivalents of the respective carbon atoms to which the H atoms are bound. The C–H distance was chosen to be 0.95 Å. Neither the positional nor thermal parameters of the hydrogen atoms were varied during refinement.

Table IV. Thermal and Derived Positional Parameters for Group Atoms in $WBr_2(CO)_3(tolN_3PPh_3)$

atom[a]	x	y	z	B[b]
C(11)	0.2795 (3)	0.5568 (3)	0.4355 (3)	1.91 (10)
C(12)	0.3009 (3)	0.5958 (4)	0.5639 (4)	2.33 (11)
C(13)	0.2616 (3)	0.7233 (4)	0.6404 (3)	3.07 (13)
C(14)	0.2010 (3)	0.8118 (3)	0.5885 (4)	2.99 (13)
C(15)	0.1796 (3)	0.7728 (4)	0.4601 (4)	2.94 (12)
C(16)	0.2189 (3)	0.6453 (4)	0.3836 (3)	2.35 (11)
C(21)	0.3679 (2)	0.2874 (4)	0.4496 (3)	1.76 (10)
C(22)	0.4664 (2)	0.2423 (4)	0.4485 (3)	1.93 (10)
C(23)	0.4931 (2)	0.1667 (4)	0.5408 (4)	2.19 (11)
C(24)	0.4212 (3)	0.1362 (4)	0.6342 (3)	2.36 (11)
C(25)	0.3226 (2)	0.1813 (4)	0.6352 (3)	2.27 (11)
C(26)	0.2960 (2)	0.2569 (4)	0.5430 (4)	1.92 (10)
C(31)	0.4401 (2)	0.4139 (4)	0.2303 (3)	1.75 (10)
C(32)	0.4760 (3)	0.5419 (3)	0.2326 (4)	2.15 (10)
C(33)	0.5608 (3)	0.5532 (3)	0.1492 (4)	2.74 (12)
C(34)	0.6097 (3)	0.4365 (4)	0.0633 (4)	2.69 (12)
C(35)	0.5738 (3)	0.3085 (3)	0.0610 (4)	2.51 (11)
C(36)	0.4890 (3)	0.2972 (3)	0.1444 (4)	1.97 (10)

[a] C(x1) is attached to P, and the atoms in the ring are sequentially numbered around the ring. [b] The units are Å^2.

This model, consisting of 20 anisotropic nonhydrogen atoms, 18 isotropic group atoms and 22 isotropic unrefined hydrogen atoms converged to $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.028$ and $R_w(F) = (Q/\sum wF_o^2)^{1/2} = 0.037$ for the 4066 unique data. The largest parameter shift during the final least-squares refinement was less than 10% of its error. A statistical analysis of the trends of Q as a function of observed structure amplitudes, diffractometer setting angles, and Miller indices showed nothing unusual and indicated that the weighting scheme was adequate. A careful check of F_o and F_c in the final refined model showed that no extinction correction was necessary. A final difference Fourier synthesis showed no significant residual electron density, with the exception of one W residual (1.2 e/Å^3) and residuals

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(11) Cahen, D.; Ibers, J. A. *J. Appl. Crystallogr.* **1972**, *5*, 298.

(12) Haymore, B. L.; Maatta, E. A.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1979**, *101*, 2063.

(13) In addition to the various local programs for the CDC-6600 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Johnson's ORTEP thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program, and the Northwestern full-matrix, least-squares program NUCLS which, in its nongroup form, closely resembles the Busing and Levy ORFLS program.

(14) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

near the centers of the rigid phenyl groups (about 1.0 e/Å^3). Of the reflections with $F_o^2 < 3\sigma(F_o^2)$, none had $F_c^2 > 5\sigma(F_o^2)$.

A careful examination of F_o and F_c for the 60 recollected data showed that our scaling scheme was adequate. The final positional and thermal parameters of the refined atoms appear in Table II, and the root-mean-square amplitudes of vibration are given in Table III.[15] Table IV contains final positional and thermal parameters for the refined group atoms, while Table V lists the positional and thermal parameters for the unrefined hydrogen atoms.[15] A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.[15]

Results and Discussion

Synthesis. Aromatic azides, $R'N_3$ (R' = phenyl, *p*-tolyl), react rapidly with $MBr_2(CO)_3(PPh_3)_2$ (M = Mo, W) at room temperature (~20 °C) to form yellow-orange products, $MBr_2(CO)_3(R'N_3PPh_3)$, which can be isolated in reasonably good yields (30–81%). When M = W and R = tol, careful gas evolution studies in the presence of excess azide showed that 1.1 equiv of N_2 and 0.05 equiv of CO were produced/equiv of starting complex after 20 min; N_2 and CO continued to be produced at much slower rates after the initial reaction. Other systems produced more N_2 and less phosphazide complex. Phosphorus NMR spectra of the reaction media (CH_2Cl_2 solutions) showed that what at first seemed to be a simple reaction (eq 3) was far more complicated owing to several side reactions.

$$MBr_2(CO)_3(PPh_3)_2 + 2R'N_3 \xrightarrow{\text{fast}} MBr_2(CO)_3(R'N_3PPh_3) + R'N{=}PPh_3 + N_2 \quad (3)$$

$$MBr_2(CO)_3(R'N_3PPh_3) + R'N{=}PPh_3 \xrightarrow{\text{slow}} MBr_2(CO)_2(R'NPPh_3)_2 + N_2 + CO \quad (4)$$

Although small quantities of $R'N{=}PPh_3$ could be isolated from the supernatant reaction solution, its ^{31}P resonance could not be observed in the reaction solution. Addition of pure $R'NPPh_3$ to the reaction solution after 20 min showed that the phosphoranimine was in dynamic equilibrium and undergoing fast exchange on the NMR time scale with a byproduct in the reaction solution. Reaction 5 carried out in the absence of azide showed this byproduct to be a phosphoranimine complex, $WBr_2(CO)_2(R'NPPh_3)_2$, which underwent fast exchange with free phosphoranimine; the equilibrium in eq 5 lies to the right.

$$WBr_2(CO)_3(PPh_3)_2 + 2R'NPPh_3 \rightleftarrows WBr_2(CO)_2(R'NPPh_3)_2 + 2PPh_3 + CO \quad (5)$$

Although we had some difficulty isolating the analytically pure phosoranimine product, solution infrared studies and ^{31}P NMR titration showed that one CO and two phosphine ligands were replaced by two phosphoranimine ligands. We found no evidence of a monophosphine monophosphoranimine intermediate. Once formed, $WBr_2(CO)_2(R'NPPh_3)_2$ is soluble in methylene chloride, but after it was crystallized from solution, it would not readily redissolve in any ordinary solvent. Thus, reactions 1, 2, and 5 constitute an alternate pathway for the consumption of starting materials when the organic azide is present in excess quantities. If reactions 2 and 5 were not sufficiently slow and reaction 3 sufficiently fast under the reaction conditions, little phosphazide complex would have been isolated. We also discovered that the yield of the phosphazide complex increased with reaction time, reached a maximum after 10–30 min, and then decreased with longer times. After 3–4 h, little of the phosphazide complex remained in the reaction solution, yet an equally concentrated solution of the pure phosphazide complex underwent no observable decomposition during this same time period. Not only does free $R'NPPh_3$, produced in reaction 3, react with the starting material, $MBr_2(CO)_3(PPh_3)_2$, but it also reacts somewhat more slowly with the phosphazide complex, $MBr_2(CO)_3(R'N_3PPh_3)$ (eq 4); once formed, the phosphazide product must be removed from solution. Thus, by adjusting the initial azide concentration (50–100 mM), the initial metal to azide ratio (1:2–1:3), the reaction temperature (10–20 °C), and reaction time (15–30 min), reasonable yields of the phosphazide complex were obtainable. It should be noted that when reaction 3 was carried out with $p\text{-}CH_3C_6H_4{}^{14}N^{14}N^{15}N$, $^{15}N{\equiv}{}^{14}N$ and $tol^{14}N{=}PPh_3$ were the only observed byproducts.

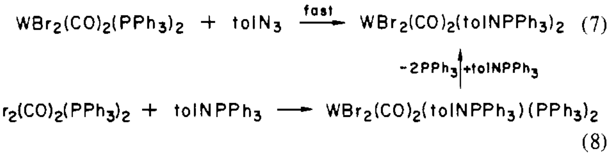
The molybdenum phosphazide complex was also prepared directly from $[MoBr_2(CO)_4]_2$ and free phosphazide (eq 6) at low temperature.

$$tolN_3PPh_3 + MoBr_2(CO)_4 \xrightarrow{-40\ °C} MoBr_2(CO)_3(tolN_3PPh_3) + CO \quad (6)$$

At −40 °C, the reactant phosphazide solution contained a little free $tolN_3$ but no detectable PPh_3 or $tolNPPh_3$. Although the isolated yield was only 20%, ^{31}P NMR spectra showed that the in situ yield at room temperature before workup was 60–65% on the basis of Mo. Although reaction 6 sheds little light on the mechanism of reaction 3, it does show that phosphazide complexes can be prepared directly from free phosphazide. Owing to the difficulty in preparing $[WBr_2(CO)_4]_2$, the analogous tungsten reaction was not attempted.

The phosphazide complexes seem to be indefinitely stable in the solid state and are stable in solution, too; after 2 h of refluxing in benzene, $WBr_2(CO)_3(tolN_3PPh_3)$ was recovered unchanged in quantitative yields. However, after several days at ambient temperature (25–30 °C) under ambient light (fluorescent) conditions, CD_2Cl_2 solutions of $WBr_2(CO)_3(tol^{14}N^{14}N^{15}NPPh_3)$ partially (30–70%) decomposed. A new doublet with tungsten satellites appeared in the $^{31}P\{^1H\}$ NMR spectrum at δ 40.5 with $^1J_{PN} = 21$ Hz and $^2J_{WP} = 17$ Hz. Unlike the ^{31}P NMR spectrum of $WBr_2(CO)_3(tol^{14}N^{14}N^{15}NPPh_3)$, that of the decomposition product was sharp at all temperatures at which it was measured (+30 to −80 °C). The spectroscopic data suggest that the decomposition product is the dicarbonyl, $WBr_2(CO)_2(tolN_3PPh_3)$; however, efforts to thermally or photolytically decarbonylate the tricarbonyl failed to yield a pure, isolable product which was free from $WBr_2(CO)_3(tolN_3PPh_3)$ and $WBr_2(CO)_2(tolNPPh_3)_2$. Free phosphoranimine rapidly converted the $WBr_2(CO)_2(tolN_3PPh_3)$ to $WBr_2(CO)_2(tolNPPh_3)_2$ on mixing at room temperature.

The reactions of $tolN_3$ and $tolNPPh_3$ with $WBr_2(CO)_2(PPh_3)_2$ were also explored. Efforts to produce a dicarbonyl–phosphazide complex failed (see eq 7 and 8); only a phosphoranimine complex was obtained.



$$\begin{tikzcd}
WBr_2(CO)_2(PPh_3)_2 + tolN_3 \arrow[r, "\text{fast}"] & WBr_2(CO)_2(tolNPPh_3)_2 & (7) \\
WBr_2(CO)_2(PPh_3)_2 + tolNPPh_3 \arrow[r] & WBr_2(CO)_2(tolNPPh_3)(PPh_3)_2 \arrow[u, "-2PPh_3", "+tolNPPh_3"'] & (8)
\end{tikzcd}$$

In fact, $WBr_2(CO)_2(PPh_3)_2$ completely reacted on mixing with 0.95 equiv of $tolNPPh_3$ to give a spectroscopically detectable intermediate, $WBr_2(CO)_2(tolNPPh_3)(PPh_3)_2$, which further reacted with $tolNPPh_3$ to form $WBr_2(CO)_2(tolNPPh_3)_2$; this secondary reaction is slow with a deficiency of phosphoranimine and rapid with an excess of phosphoranimine. In the presence of excess $tolNPPh_3$, $WBr_2(CO)_2(tolNPPh_3)_2$ is formed considerably faster from $WBr_2(CO)_2(PPh_3)_2$ than from the tricarbonyl–phosphine complex. If any phosphazide complex was formed in eq 7, we could not find any spectroscopic evidence for it when the reaction was carried out at 25 °C.

At first, we thought that $MBr_2(CO)_3(R'N_3PPh_3)$ would act as a good starting material for preparing other $MBr_2(CO)_3L_2$

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[15] Supplementary material.

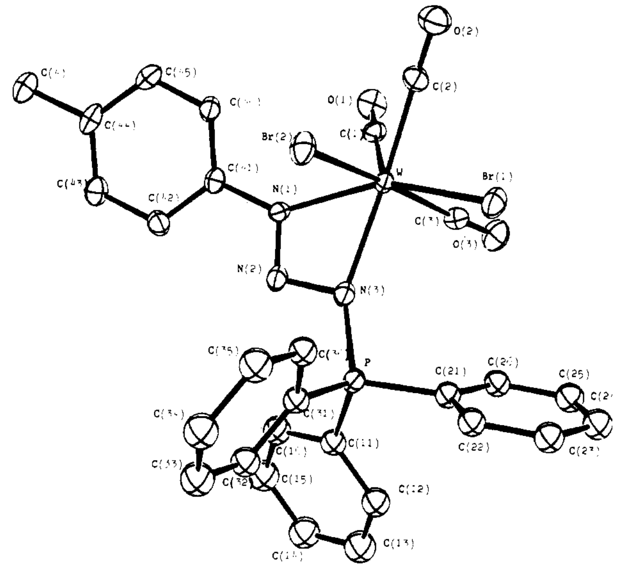

Figure 1. Drawing of a molecule of $WBr_2(CO)_3(p\text{-}CH_3C_6H_4N_3PPh_3)$. The hydrogen atoms have been omitted. Vibrational ellipsoids are drawn at the 50% probability level.

complexes. However, the phosphazide ligand was not easily removed under mild conditions. Carbon monoxide would not displace the phosphazide. Dithiocarbamate salts reacted rapidly with the phosphazide complexes, but no pure product could be isolated. Large excesses of triphenylphosphine quantitatively displaced the phosphazide at 35 °C, but the isolated yields were not particularly good. However, diphos or a mixture of PPh_3 and $NaS_2CN(CH_2)_4$ cleanly displaced the phosphazide ligand with the production of N_2 and $tolNPPh_3$.

$$WBr_2(CO)_3(tolN_3PPh_3) \xrightarrow{\text{diphos}} [WBr(CO)_2(diphos)_2][Br] \tag{9}$$

$$WBr_2(CO)_3(tolN_3PPh_3) \xrightarrow[NaS_2CN(CH_2)_4]{PPh_3} W(CO)_2(PPh_3)(S_2CN(CH_2)_4)_2 \tag{10}$$

In an effort to make other phosphazide complexes, aryl azides were allowed to react with rhenium(III) phosphine complexes, $ReCl_3(CH_3CN)(PPh_3)_2$ and $ReCl_3(PPh_2Me)_3$. In refluxing benzene, 50% yields of $ReCl_4(PPh_3)_2$ and $ReCl_4(PPh_2Me)_2$ were obtained; no other metal-containing products could be isolated. In refluxing chloroform, higher yields were obtained probably because the solvent acted as a chlorine source. $tolNPPh_2Me$ was identified as a byproduct of the $tolN_3$–$ReCl_3(PPh_2Me)_3$ reaction. Only oxidation of Re(III) to Re(IV) was observed and no nitrene(NR′), phosphoranimine, or phosphazide complexes could be isolated. We had expected to find $ReCl_3(NR')(PR_3)_2$ among the products of these reactions, but none was found except in one case when the Re(III) starting material was contaminated with $ReOCl_3(PR_3)_2$.[16] Although both are d^4 compounds, Re(III) complexes behaved quite differently from W(II) complexes toward aryl azides. Conversely, we found no indication of monomeric or dimeric W(III) or Mo(III) complexes in the reaction described earlier.

Description of Structure. The structure of $WBr_2(CO)_3(tolN_3PPh_3)$ consists of discrete monomeric molecules in the unit cell. There are no significant inter- or intramolecular nonbonded contacts (calculated with C–H = 1.08 Å). A perspective view of the complex together with the labeling scheme is shown in Figure 1. The complex is seven-coordinate with the phosphazide ligand bound in a chelating fashion to W at the α- and γ-N atoms. The three carbonyl ligands are linear with averaged parameters of W–C = 2.00 Å, C–O = 1.12 Å, and W–C–O = 178° (see Tables VI and VII) and are arranged in a quasi-facial fashion with respect to each other. The two bromine atoms are also mutually cis with W–Br(1)

Table VI. Selected Bond Distances (A) in $WBr_2(CO)_3(tolN_3PPh_3)$

W–C(1)	1.983 (6)	2.001[a]	C(41)–C(42)	1.409 (8)	1.398[a]
W–C(2)	2.018 (6)		C(42)–C(43)	1.407 (8)	
W–C(3)	2.001 (6)		C(43)–C(44)	1.403 (8)	
W–Br(1)	2.599 (1)	2.620[a]	C(44)–C(45)	1.407 (8)	
W–Br(2)	2.641 (1)		C(45)–C(46)	1.391 (8)	
W–N(1)	2.163 (4)		C(46)–C(41)	1.374 (8)	
W–N(3)	2.220 (5)		P–C(11)	1.808 (3)	1.788[a]
P–N(3)	1.672 (5)		P–C(21)	1.776 (4)	
N(1)–N(2)	1.279 (6)		P–C(31)	1.780 (4)	
N(2)–N(3)	1.364 (6)		N(1)–C(41)	1.423 (7)	
C(1)–O(1)	1.112 (7)	1.123[a]	C(4)–C(44)	1.508 (8)	
C(2)–O(2)	1.124 (7)				
C(3)–O(3)	1.133 (7)				

[a] Average value.

Table VII. Selected Bond Angles and Interplanar Angles (Deg) in $WBr_2(CO)_3(tolN_3PPh_3)$

W–C(1)–O(1)	177.5 (5)	177.6[a]
W–C(2)–O(2)	177.9 (5)	
W–C(3)–O(3)	177.3 (5)	
Br(1)–W–Br(2)	86.34 (4)	
C(1)–W–C(2)	74.6 (2)	
C(1)–W–C(3)	72.6 (2)	
C(2)–W–C(3)	104.4 (2)	
C(1)–W–Br(1)	133.5 (2)	
C(1)–W–Br(2)	122.2 (2)	
C(2)–W–Br(1)	77.7 (2)	
C(2)–W–Br(2)	77.6 (2)	
C(3)–W–Br(1)	79.2 (2)	
C(3)–W–Br(2)	164.4 (2)	
N(1)–W–Br(1)	146.62 (12)	
N(1)–W–Br(2)	76.23 (12)	
N(1)–W–C(1)	79.5 (2)	
N(1)–W–C(2)	124.4 (2)	
N(1)–W–C(3)	113.4 (2)	
N(3)–W–Br(1)	95.71 (12)	
N(3)–W–Br(2)	89.88 (12)	
N(3)–W–C(1)	117.9 (2)	
N(3)–W–C(2)	166.1 (2)	
N(3)–W–C(3)	86.1 (2)	
N(1)–W–N(3)	56.7 (2)	
W–N(1)–N(2)	102.4 (3)	
W–N(1)–C(41)	140.4 (4)	
N(1)–N(2)–N(3)	103.8 (4)	
C(41)–C(42)–C(43)	119.3 (5)	120.0[a]
C(42)–C(43)–C(44)	120.0 (5)	
C(43)–C(44)–C(45)	119.4 (5)	
C(44)–C(45)–C(46)	120.0 (5)	
C(45)–C(46)–C(41)	120.8 (5)	
C(46)–C(41)–C(42)	120.4 (5)	
C(46)–C(41)–N(1)	119.5 (5)	119.8[a]
C(42)–C(41)–N(1)	120.1 (5)	
W–N(3)–P	147.7 (3)	
C(43)–C(44)–C(4)	118.6 (5)	120.3[a]
C(45)–C(44)–C(4)	122.0 (5)	
N(2)–N(1)–C(41)	116.3 (4)	
N(2)–N(3)–P	112.9 (4)	
N(2)–N(3)–W	96.8 (3)	
N(3)–P–C(11)	112.3 (2)	109.7[a]
N(3)–P–C(21)	107.3 (2)	
N(3)–P–C(31)	109.6 (2)	
C(11)–P–C(21)	107.2 (2)	109.2[a]
C(11)–P–C(31)	110.3 (2)	
C(21)–P–C(31)	110.0 (2)	
N(2)–N(1)–C(41) N(1)–C(41)–C(42)	−10.7 (7)	
N(2)–C(1)–C(41) N(1)–C(41)–C(46)	167.8 (5)	

[a] Average value.

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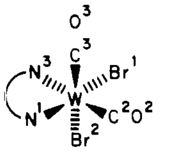
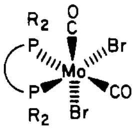
= 2.599 (1) Å and W–Br(2) = 2.641 (1) Å. The W–C distances are typical of those found in other $MX_2(CO)_3L_2$ complexes[17–19] (M = Mo, W; X = Cl, Br; L = AsR_3, PR_3), but the W–Br distances in the phosphazide complex are distinctly shorter than the average 2.66-Å distance found in phosphine and arsine complexes.

The three strong carbonyl stretching bands observed in the infrared spectra of $MBr_2(CO)_3(R'N_3PPh_3)$ occur at frequencies about 12 cm^{-1} higher in energy than do the corresponding stretching frequencies in the parent $MBr_2(CO)_3(PPh_3)_2$. This undoubtedly reflects the decreased σ-donating capability of the N-donor chelate in comparison to two tertiary phosphine ligands. The relative positions and intensities of the three carbonyl absorption bands in the phosphazide products are quite similar to those in the respective starting material, $MBr_2(CO)_3(PPh_3)_2$; they were so similar in fact that at first we thought there had been no reaction with the organic azides after measuring the infrared spectra of the reaction solutions. The similarity of the infrared spectra in the carbonyl region suggested to us that $MBr_2(CO)_3(PPh_3)_2$ and $MBr_2(CO)_3(R'N_3PPh_3)$ possessed similar stereochemistries despite the presence of the chelate in the phosphazide complexes.

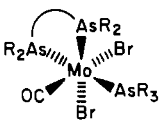
The coordination geometry at the metal in $WBr_2(CO)_3(tolN_3PPh_3)$ is distorted owing to the nitrogen chelate, but the geometry is best described as a capped octahedron as shown in A. The four structures A–D show the coordination spheres of seven-coordinate complexes as viewed down the capping carbonyl ligand which is omitted from each figure. The geometry of the phosphazide complex is remarkably similar to that of $MoBr_2(CO)_3(Ph_2PCH_2CH_2PPh_2)$,[17] which is shown in B. The geometry of $MoBr_2(CO)_2(Ph_2AsCH_2AsPh_2)_2$[18] is shown in C; one of the diarsine ligands is monodentate. Structure D represents the geometry of $MoCl_2(CO)_3(PEt_3)_2$,[19] $WBr_2(CO)_3(Ph_2AsCH_2AsPh_2)_2$[18] (both diarsine ligands are monodentate), and most likely the geometry of the starting materials $MBr_2(CO)_3(PPh_3)_2$ used in the present syntheses. The absence of a trans ligand causes the capping carbonyl to have the shortest bonding distance (W–C(1) = 1.983 (6) Å); the same is true for $MoBr_2(CO)_3(Ph_2PCH_2CH_2PPh_2)$. As expected, cis angles between C(3), C(2), and N(1) are larger than 104°, and the cis angles between Br(1), Br(2), and N(3) are distinctly less. The small bite angle of the phosphazide chelate maintains the N(3)–W–Br(1) and N(3)–W–Br(2) angles near 96° and 90°, respectively; without the chelate, these two angles would drop below 90°. Two of the three trans angles (C(3)–W–Br(2), C(2)–W–N(3)) are near the expected value (~165°), but N(1)–W–Br(1) at 147° is smaller due to the small bite angle in the chelate. The longer W–Br(2) distance at 2.641 (1) Å (W–Br(1) = 2.599 (1) Å) is probably the result of the trans influence of the carbonyl ligand (C(3)–O(3)). Furthermore, the marginally longer noncapping metal–carbonyl distance (W–C(2) = 2.018 (6) Å) is associated with the shorter metal–ligand distance in the trans position. Other idealized geometries were considered. The present phosphazide complex is definitely not pentagonal bipyramidal. The square-capped trigonal prism and 4:3 geometry are not very different from the capped octahedron, but the latter description is the best.



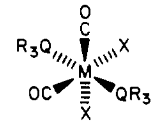
A



B



C



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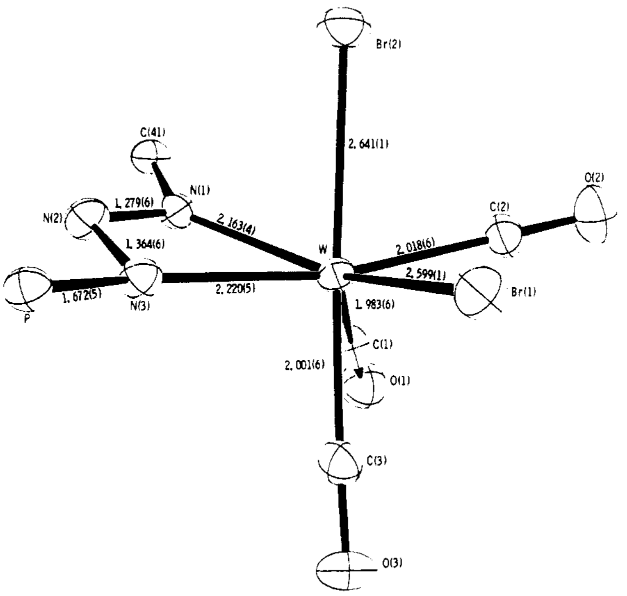

Figure 2. Coordination sphere of $WBr_2(CO)_3(p\text{-}CH_3C_6H_4N_3PPh_3)$. The three phenyl groups and all tolyl atoms but C(41) have been omitted. Vibrational ellipsoids are drawn at the 50% probability level.

The Phosphazide Ligand. The tetraarylphosphazide ligand is attached to the metal in a chelating fashion through N(1) and N(3), forming a four-membered metallacycle (Figure 2). The tungsten–nitrogen bond lengths of 2.163 (4) (W–N(1)) and 2.220 (5) Å (W–N(3)) are indicative of normal metal–nitrogen single-bond lengths. We expect an unencumbered W–N(sp^2) single bond to be about 2.15 Å. The W–N(1) distance is close to this value, and the W–N(3) distance is lengthened somewhat by the carbonyl (C(2)–O(2)) in the trans position. The phosphazide complex is slightly congested at the metal as a result of the high coordination number, but this is not a serious problem. The bulky PPh_3 group is far enough from the metal and other ligands so that it does not wield much steric influence. The planar tolyl group is twisted about the N(1)–C(41) bond out of the N_3 plane by 11°. The carbon atom C(41) lies in the N_3 plane while the W and P atoms are only 0.2 Å out of the N_3 plane.

The N(1)–N(2) and N(2)–N(3) bond lengths of 1.279 (6) and 1.364 (6) Å both imply bond orders greater than unity. With it known that N—N single bonds are about 1.45 Å (hydrazines)[20] and N═N double bonds are about 1.23 Å (diazenes)[21] in length, the two respective N—N bond lengths correspond to approximate bond orders of 1.7 and 1.3. The P—N(3) distance of 1.672 (5) Å is intermediate between the values expected for single and double bonds. Although there are less structural data on P—N bond lengths, we estimate that P—N single bonds should be about 1.77 Å[22] and P═N double bonds should be about 1.56 Å (phosphoranimines)[23] in length. On this basis, the P—N(3) distance corresponds to a bond order of 1.4. The metrical parameters of the coordinated phosphazide do not correspond to any of the valence bond structures (E–G) of the molecule, but rather to an equal mixture of all three forms. The presence of the tungsten atom or any Lewis acid, for that matter, probably stabilizes F and G at the expense of E. Furthermore, the W(II) seems to

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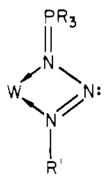
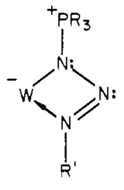
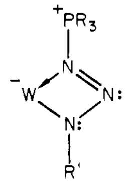


E

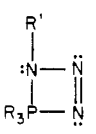


F

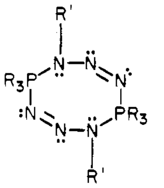


G

promote the delocalized bonding found in stable triazenido (RN$_3$R$^-$) complexes. The much greater stability of the coordinated phosphazide relative to the free molecule is certainly related to the inability of the rigidly bound chelate to form the proper intermediates such as I or possibly H, which allow N$_2$ extrusion and phosphoranimine formation. The N–W–N (57°), W–N–N (97°, 102°), and N–N–N (104°) angles in the phosphazide chelate are normal for four-membered metallacycles, and the metrical parameters for the PPh$_3$ portion of the phosphazide ligand are typical.



H



I

A comparison of the infrared spectra (Nujol mulls) of WBr$_2$(CO)$_3$(tol^{14}N^{14}N^{15}NPPh$_3$) and its unlabeled analogue showed that three bands shifted to lower energy upon ^{15}N labeling. No shifts in bands above 1200 cm^{-1} were observed, but bands at 1130 (vs), 1032 (s), and 864 (m) cm^{-1} in the unlabeled complex were found at 1117 (vs), 1009 (s), and 859 (m) cm^{-1} in the labeled compound. The magnitudes of the isotopic shifts and the position of the absorption bands suggest that the band at 1130 cm^{-1} corresponds to ν_s(N$_3$), that the one at 1032 cm^{-1} corresponds to ν(PN), and that the 864-cm^{-1} band corresponds to δ(N$_3$). We had expected to observe both ν_{as}(N$_3$) (or ν(N(1)–N(2)), formalism F) and ν_s(N$_3$) (or ν(N(2)–N(3)), formalism F), but apparently only the lower energy band is observed to shift. In chelating triazenido ligands, only one band associated with ν(N$_3$) is observed in some complexes.[24] The low value of ν(PN) at 1032 cm^{-1} corresponds to the longer P–N distance of 1.67 Å (1.56 Å in tetraarylphosphoranimines). The respective values of ν(P=N) for Ph$_3$P=NPh,[24] Ph$_3$P=NC(O)Ph,[24] and (C$_6$H$_{11}$)$_3$P=NN=N-C(O)C$_4$H$_3$O[4] are found at 1344, 1332, and 1240 cm^{-1}. It should be noted that ν_s(N$_3$), ν_{as}(N$_3$), and ν(PN) are probably vibrationally coupled to an appreciable extent in phosphazides and that the observed bands do not correspond to pure vibrational modes.

The ^{31}P{^{1}H} NMR spectrum of WBr$_2$(CO)$_3$(tolN$_3$PPh$_3$) at ambient temperature exhibits a broad (14 Hz, fwhm) singlet at δ 42.0, which sharpens at −80 °C (1 Hz, fwhm). The spectrum of the labeled complex WBr$_2$(CO)$_3$(tol^{14}N^{14}N^{15}NPPh$_3$) showed a single resonance (doublet) in the same location with nearly the same peak widths at the different temperatures. The coupling to the ^{15}N is clearly evident with $^1J_{PN}$ = 24 Hz. The one-bond coupling constant can be compared to $^1J_{PN}$ in Ph^{15}N=PPh$_3$ (32 Hz)[24] and p-Me$_2$NC$_6$H$_4$^{14}N^{15}NP(p-C$_6$H$_4$OMe)$_3$$^+$ (57 Hz).[24] In the low-temperature spectra of the phosphazide complexes, tungsten satellites ($^2J_{WP}$ = 17 Hz) were observed, thus giving spectroscopic confirmation that the phosphorus atom was *not* directly bound to tungsten. These observations suggest that the broadening of the spectra at ambient temperatures is caused by some type of dynamic process, but the exact nature of this process cannot be determined with ^{1}H or ^{31}P spectroscopy for the compounds we have prepared.

We have shown that tetraarylphosphazides ((tetraarylphosphoranylidene)triazenes) can be stabilized by coordination to W(II) and Mo(II) and that one stable bonding mode is that of a three-membered chelate attached at the α- and γ-nitrogen atoms. The geometry of the coordinated phosphazide indicates that it acts as a four-electron σ-donor chelate and that its ground electronic state cannot be adequately described by a single valence-bond form. The similarities in the coordination geometries[25] of ArN$_3$Ar$^-$ and ArN$_3$PAr$_3$ ligands suggest that the four-membered (MN$_3$) metallacycles of this sort are stable even with respect to N$_2$ loss. However, the bonding modes of aroylphosphazide (ArC(O)N$_3$PAr$_3$) ligands, as found in cobalt complexes,[4] could involve the oxygen atom of the organic carbonyl.

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Registry No. WBr$_2$(CO)$_3$(tolN$_3$PPh$_3$), 80594-73-6; WBr$_2$(CO)$_3$(PhN$_3$PPh$_3$), 80594-68-9; MoBr$_2$(CO)$_3$(tolN$_3$PPh$_3$), 80594-69-0; WBr$_2$(CO)$_3$(tolNN^{15}NPPh$_3$), 80594-74-7; WBr$_2$(CO)$_2$(tolN=PPh$_3$)$_2$, 80594-70-3; [WBr(CO)$_2$(diphos)$_2$][Br], 80010-26-0; W(CO)$_2$(PPh$_3$)(S$_2$CN(CH$_2$)$_4$)$_2$, 80594-71-4; ReCl$_4$(PPh$_2$Me)$_2$, 36151-19-6; ReCl$_4$(PPh$_3$)$_2$, 34248-10-7; WBr$_2$(CO)$_3$(PPh$_3$)$_2$, 18130-07-9; MoBr$_2$(CO)$_3$(PPh$_3$)$_2$, 17250-41-8; tolN$_3$, 2101-86-2; PhN$_3$, 622-37-7; [MoBr$_2$(CO)$_4$]$_2$, 80594-72-5; tolNN^{15}N, 2101-86-2; ReCl$_3$(PPh$_2$Me)$_3$, 80656-01-5; ReCl$_3$(CH$_3$CN)(PPh$_3$)$_2$, 60899-23-2; PPh$_3$, 603-35-0; W(CO)$_6$, 14040-11-0.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes and Tables III and V giving root-mean-square amplitudes of vibration and structural parameters for H atoms (21 pages). Ordering information is given on any current masthead page.

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