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Synthesis and Chemistry of Binary Zerovalent Transition-Metal Phosphite Complexes

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Abstract: Reduction of molybdenum and tungsten chloride complexes with donor molecules followed by reaction with trimethyl phosphite yielded $Mo[P(OCH_3)_3]_6$ and $W[P(OCH_3)_3]_6$. Similar reductions of analogous rhenium halide complexes yielded a variety of products as a sensitive function of experimental conditions. Products included $Re_2[P(OCH_3)_3]_{10}$, $HRe[P(OCH_3)_3]_5$, $Re[P(OCH_3)_3]_5P(O)(OCH_3)_2$, $H_3Re[P(OCH_3)_3]_4$, and $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$. One common property of the binary phosphite complexes $Mo[P(OCH_3)_3]_6$, $W[P(OCH_3)_3]_6$, and $Re_2[P(OCH_3)_3]_{10}$ was the facile reaction with protic acids to give a series of cationic and hydridic products with yields dependent upon reaction conditions. Products included the following complexes: $\{HM[P(OCH_3)_3]_6^+\}$ (M = Mo, W), $\{M[P(OCH_3)_3]_5P(OCH_3)_2^+\}$ (M = Mo, W), $HM[P(OCH_3)_3]_4[O_2CCF_3]$ (M = Mo, W), $H_2Re[P(OCH_3)_3]_5^+$, and $H_2Re[P(OCH_3)_3]_3(O_2CCF_3)$. All were stereochemically nonrigid species with $\{M[P(OCH_3)_3]_5P(OCH_3)_2^+\}$ complexes showing intramolecular migration of OCH_3 groups. In $HM[P(OCH_3)_3]_4(O_2CCF_3)$, the character of the *permutational* mechanism for effective phosphite site exchange differs for molybdenum from that for the tungsten complex. All three binary metal phosphite complexes readily undergo substitution reactions through photodissociation of phosphite ligands; $W[P(OCH_3)_3]_6$ is especially photosensitive. Through photoactivation of the binary complexes in the presence of hydrogen, a series of hydrides was prepared: $H_2M[P(OCH_3)_3]_5$ and $H_4M[P(OCH_3)_3]_4$ (M = Mo and W), $HRe[P(OCH_3)_3]_5$, $H_3Re[P(OCH_3)_3]_4$, and $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$. Trimethyl phosphite thermally displaces hydrogen from the $H_4Mo[P(OCH_3)_3]_4$ complex to first form $H_2Mo[P(OCH_3)_3]_5$ and then $Mo[P(OCH_3)_3]_6$ whereas the tungsten analogue showed no evidence of phosphite displacement of hydrogen. Also described are the photoreactions of the binary phosphite complexes with CO, $(CN)_2$, and NO.

By formal analogy to transition-metal carbonyl chemistry, the area of binary zerovalent or low valent metal phosphite complexes should be quite large[1] and diverse. Development and elaboration of such chemistry has been a long-range goal for us. The status of the field concisely is as follows. Mononuclear nickel,[2] palladium,[3] and platinum[4] complexes typically of tetrahedral ML_4 form have been known for many years and are useful as reactants and as catalysts. In addition, several tris(triaryl phosphite) complexes of nickel[2b] have been isolated and characterized. Cobalt group complexes include $Co_2[P(OR)_3]_8$ (R = CH_3, C_2H_5, and *i*-C_3H_7),[5,6] $Rh_2[P(OCH_3)_3]_8$,[7] and an incompletely characterized iridium triphenyl phosphite complex.[8] Characterized zerovalent iron group complexes are $Fe[P(OR)_3]_5$ (R = CH_3, C_2H_5)[9-11] and $Ru[P(OCH_3)_3]_5$.[11] The only well-characterized manganese group complex is $Re_2[P(OCH_3)_3]_{10}$.[12,13] In group 6, $Mo[P(OCH_3)_3]_6$[14,15] and $W[P(OCH_3)_3]_6$[16] are fully characterized, and $Cr[P(OCH_3)_3]_6$ is described in a patent.[17]

We present here the full synthesis details for the binary phosphites of molybdenum, tungsten, and rhenium and also the reactions of these complexes with simple reagents like protic acids, hydrogen, carbon monoxide, and nitric oxide. One very distinctive[18] property of these more electropositive transition-metal complexes of phosphites is photoactivation whereby phosphite ligand dissociation ensues.

Experimental Section

Materials. Molybdenum pentachloride and tungsten hexachloride were purchased from Alfa Division of Ventron Corp. and were sublimed under a dynamic vacuum prior to use. Rhenium pentachloride (99.9% metals basis) was purchased from Alfa Division of Ventron Corp. and was used without further purification. Ammonium perrhenate was obtained from the Nuclear Chemistry Division of the Lawrence Livermore Laboratory and was used as received. Potassium metal was purchased either from J. T. Baker Chemical Co. or from Mallinckrodt Chemical Co. and was washed with hexane prior to use. Potassium iodide (analytical reagent grade), purchased from Mallinckrodt Chemical Co., was dried in an oven at 100 °C and was stored under an inert atmosphere. Mercury was either purchased from Quicksilver Products, Inc., and was used without further purification or was recycled by following procedures which are described by Shriver.[19] Trimethyl phosphite (97%, Aldrich Chemical Co.), pyridine (analytical reagent grade, Mallinckrodt Chemical Co.), tetrahydrofuran (analytical reagent grade, Mallinckrodt Chemical Co.), acetonitrile (99%, Aldrich Chemical Co.), and trifluoroacetic acid (99%, Aldrich Chemical Co.) were dried prior to use according to established procedures as described in General Procedures. Carbon monoxide (99.5% min), hydrogen (99.95%), deuterium (99.5%

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(1) One potential and significant constraint to the scope has a purely steric basis. The alkyl and aryl phosphite ligands are substantially larger than carbon monoxide. Hence the instability of binary polynuclear metal phosphite complexes may complicate their isolation and study. It is, however, encouraging that the binuclear cobalt and rhenium complexes, $Co_2[P(OR)_3]_8$ and $Re_2[P(OR)_3]_{10}$ possess relatively high thermal stabilities.

(2) (a) Leading references for NiL_4 complexes are as follows: Olechowski, J. R.; McAlister, G. G.; Clark, R. F. *Inorg. Chem.* **1965**, *4*. 246. Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956. Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *Ibid.* **1974**, *96*, 53 and references therein. (b) Three NiL_3 complexes have been characterized by Gosser and co-workers: Gosser, L. W.; Tolman, C. A. *Inorg. Chem.* **1970**, *9*, 2350. Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.

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(17) Ittel, S. D.; Tolman, C. A. U.S. Patent, 4 155 925, 1979.

(18) We have found most of the binary metal phosphite complexes to be susceptible to this type of photoactivation but the photosensitivities of the late transition-metal phosphite complexes are much lower than for those of the early transition metals. $W[P(OCH_3)_3]_6$ is affected by ordinary laboratory light.

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min), nitric oxide (99.0% min), and cyanogen (98.5% min) were purchased from Matheson Gas Products and were used without further purification. Nitrogen (99.996+%) and acetylene were purchased from Liquid Carbonics and were used without further purification. ^{13}CO (91.2% ^{13}C) was purchased from Bio-Rad Laboratories and was used without further purification.

Neutral aluminum oxide (Alumina Woelm N, activity grade I) for column chromatography was purchased from ICN Nutritional Biochemicals (Woelm Pharma) and was treated with trimethyl phosphite prior to use. The procedure which was followed is described in General Procedures.

General Procedures. All manipulations were carried out under an inert atmosphere of argon or nitrogen, except as noted. Trimethyl phosphite was refluxed over sodium and was distilled prior to use. Pyridine was treated with KOH, refluxed over BaO, and distilled prior to use. Acetonitrile was refluxed over CaH_2 and was distilled prior to use. Trifluoroacetic acid was stirred with activated Molecular Sieve 13X and was vacuum distilled prior to use. All other solvents were dried with sodium and benzophenone and were distilled prior to use.

Potassium metal was scraped clean and weighed immediately prior to charging a reaction vessel. Potassium iodide was ground by using a mortar and pestle and was added to the reaction mixture as a fine powder. Potassium–mercury amalgam was prepared by carefully stirring a mixture of potassium and mercury under an inert atmosphere. Extreme caution was exercised in mixing. The amalgamation process was very exothermic and sometimes violent.

Trimethyl phosphite deactivated alumina was prepared by slurrying Grade I neutral aluminum oxide in pure trimethyl phosphite. The excess trimethyl phosphite was removed under vacuum, and the alumina was dried under an argon purge until the chromatographic material regained its flowing consistency.

Photolysis reactions were accomplished by employing a Hanovia medium-pressure mercury lamp with a 450-W power supply. In the preparations which used a quartz reaction vessel, the light source was approximately 3 cm from the reaction solution. In all other preparations, the light was filtered through Pyrex glass, and the light source was approximately 5 cm from the reaction solution.

Analytical Procedures. Elemental analyses were performed at the University of California Berkeley Microanalytical Laboratory and at the Pascher Mikroanalytisches Laboratorium in Bonn, West Germany. Nuclear magnetic resonance data were obtained with the Varian EM 390 spectrometer for ^1H (90 MHz) and ^{19}F (84.7 MHz), a modified Bruker 42 kG multinuclear pulse-FT spectrometer equipped with Nicolet Technology Corp. hardware for ^1H (180 MHz) and ^{31}P (72.9 MHz), and a Cryomagnet Systems 59 kG multinuclear pulse-FT spectrometer equipped with Nicolet hardware for ^1H (250 MHz) and ^{13}C (63.1 MHz). ^1H NMR chemical shifts are reported with a negative sign for resonances which are observed at higher field than tetramethylsilane standard reference at δ 0. ^{31}P NMR chemical shifts are reported with a negative sign for resonances which are observed at lower field than the trimethyl phosphite standard reference at δ 0. ^{13}C NMR chemical shifts are reported with a positive sign for resonances which are observed at lower field than tetramethylsilane standard reference at δ 0. ^{19}F NMR chemical shifts are reported with a positive sign for resonances which are observed at higher field than $CFCl_3$ standard reference at δ 0.

Computer simulations of complex multiplet resonance patterns were obtained with the NTCSIM program in NTCFT-1180 (Nicolet Technology Corp.).

All infrared spectra were recorded with a Perkin-Elmer 283 infrared spectrophotometer. Mass spectrometric data were obtained with an AEI 12 mass spectrometer employing electron impact at 50 eV. Electronic spectra were recorded with a Varian Cary 118 ultraviolet–visible spectrophotometer.

Preparation of $MoCl_4(OC_4H_8)_2$.[20] Molybdenum pentachloride (16.0 g, 59 mmol) was added slowly as a solid to 200 mL of CH_3CN with stirring, and the reaction mixture was further stirred for 2 days. Red-purple $MoCl_4(NCCH_3)_2$ was isolated by filtration. The dark red-purple solids were then stirred in 100 mL of tetrahydrofuran for 2 h. The resultant orange mixture was filtered, and the solids were washed with tetrahydrofuran. $MoCl_4(OC_4H_8)_2$ (11.4 g, 30 mmol, 51% based on $MoCl_5$) was isolated as an orange powder and was used for the reduction reactions without further purification. Yields generally ranged from 50 to 60% based on molybdenum pentachloride.

Preparation of the Pyridine Adduct of Molybdenum Chloride. Molybdenum pentachloride (6.3 g, 23 mmol) was added as a solid to 50 mL of pyridine while being continuously stirred. A vigorous exothermic reaction ensued, and after 6 h of stirring, the reaction mixture was filtered and the olive green powder (10.5 g, 23 mmol, 99% yield based on molybdenum pentachloride) was isolated. The elemental analyses for different preparations were invariant and best fitted the following formulation: $MoOCl_3(NC_5H_5)_3$. Anal. Calcd for $C_{15}H_{15}Cl_3MoN_3O$: C, 39.5; H, 3.3; Cl, 23.3; N, 9.2. Found: C, 39.5; H, 3.3; Cl, 22.9; N, 9.3. The infrared spectrum (KBr) of this complex showed a strong absorption at 1060 cm^{-1} that could be ascribed to a multiply bonded Mo–O stretching frequency. The apparent presence of oxygen in the product was attributed to the difficulty in obtaining oxygen-free molybdenum pentachloride. The pyridine adduct of molybdenum chloride was used for the reduction reactions without further characterization.

Preparation of $Mo[P(OCH_3)_3]_6$. Three separate synthetic procedures produced similar or higher yields of hexakis(trimethyl phosphite)molybdenum than was previously reported.[14,15]

Procedure A. In a 250-mL three-neck round-bottom flask, $MoCl_4(OC_4H_8)_2$ (10 g, 26 mmol), K (4.5 g, 115 mmol), KI (4.5 g, 27 mmol), and 50 mL of benzene were stirred and heated to reflux (80 °C) for 2 h. The reaction mixture was then cooled, and the solvent was removed by evacuation. To the resultant pink residue was added $P(OCH_3)_3$ (50 mL, 53 g, 427 mmol), and the mixture was stirred and heated to reflux (112 °C) for 30 min. The reaction temperature was then reduced to ca. 70 °C, and that temperature was maintained for 20 h. The reaction mixture was then cooled, and the volatiles were removed under vacuum. The resultant brown residue was extracted with hexane, and the solution was filtered. The vacuum removal of hexane from the filtrate produced light-colored solids which were chromatographed on a $P(OCH_3)_3$ deactivated alumina column (20 cm × 5 cm diameter) employing hexane as the eluant. The first fraction contained $Mo[P(OCH_3)_3]_6$ (8.0 g, 9 mmol, 18% yield based on molybdenum pentachloride), which when recrystallized from hexane at −40 °C was obtained as colorless crystals: ^1H NMR (C_6D_6) δ 3.7 (m, J_{HP} = 9.6 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −32.1 (s with satellite sextet, J_{PMo} = 254 Hz (^{95}Mo, $I = {}^5/_2$, 15.7% natural abundance; ^{97}Mo, $I = {}^5/_2$, 9.5% natural abundance)). Anal. Calcd for $C_{18}H_{54}MoO_{18}P_6$: C, 25.7; H, 6.5; P, 22.1. Found: C, 25.8; H, 6.5; P, 22.6.

Procedure B. The pyridine adduct of molybdenum chloride (6.1 g, 13 mmol) was used in place of $MoCl_4(OC_4H_8)_2$ in a procedure which was similar to the one described in procedure A. The product was purified by column chromatography on trimethyl phosphite deactivated alumina and by recrystallizations from hexane. Isolated yield of colorless crystals of $Mo[P(OCH_3)_3]_6$ was 2.5 g (3.0 mmol, 23% yield based on molybdenum pentachloride). ^1H and ^{31}P NMR spectra were identical with those of the $Mo[P(OCH_3)_3]_6$ prepared by procedure A. Anal. Calcd for $C_{18}H_{54}MoO_{18}P_6$: C, 25.7; H, 6.5; Mo, 11.4; N, 0.0; P, 22.1. Found: C, 26.0; H, 6.6; Mo, 11.0; N, 0.0; P, 22.0.

Procedure C. In a 250-mL three-neck round-bottom flask, the pyridine adduct of molybdenum chloride (5.0 g, 11 mmol) and 50 mL of benzene were stirred. Freshly prepared potassium amalgam which contained 2.0 g (51 mmol) of K in 50 mL of mercury was added slowly, and the reaction mixture was stirred at ~20 °C for 12 h. The solvent and other volatiles were then removed by evacuation, and to the resultant purple-gray residue was added 25 mL (26 g, 210 mmol) of $P(OCH_3)_3$. After 24 h of stirring at ambient temperatures, the mercury was separated from the reaction mixture by employing a 250-mL separatory funnel. The solvent was then removed by vacuum from the reaction mixture by evacuation, and the resultant purple solids were extracted with hexane. The product was purified by column chromatography on trimethyl phosphite deactivated alumina and by recrystallization from hexane. Isolated yield of colorless crystals of $Mo[P(OCH_3)_3]_6$ was 2.1 g (2.5 mmol, 23% yield based on molybdenum pentachloride). ^1H and ^{31}P NMR spectra were identical with those of $Mo[P(OCH_3)_3]_6$ prepared by procedure A. Anal. Calcd for $C_{18}H_{54}MoO_{18}P_6$: C, 25.7; H, 6.5; Mo, 11.4; N, 0.0; P, 22.1; Cl, 0.0. Found: C, 25.8; H, 6.4; Mo. 11.1; N, 0.1; P, 21.9; Cl, 0.0.

Preparation of $H_2Mo[P(OCH_3)_3]_5$ and $H_4Mo[P(OCH_3)_3]_4$. A 100-mL Pyrex reaction vessel was charged with 100 mg (0.12 mmol) of $Mo[P(OCH_3)_3]_6$, 10 mL of tetrahydrofuran, and 1-atm total pressure of hydrogen at ~20 °C. The reaction mixture was exposed to a photon source for 30 min during which time the solution remained clear but gained a slight brown hue. The solvent and excess hydrogen were removed under vacuum, and the remaining off-white solids were characterized by ^1H NMR spectroscopy, by $^{31}P\{^1H\}$ NMR spectroscopy, and by $^{31}P\{^1H_{CH}\}$ NMR spectroscopy.

$H_2Mo[P(OCH_3)_3]_5$: ^1H NMR (C_7D_8) δ −5.8 (sextet, J_{HP} = 34 Hz); $^{31}P\{^1H\}$ NMR (C_7D_8) δ −46.6 (s); $^{31}P\{^1H_{CH}\}$ NMR (C_7D_8) δ −46.6 (t, J_{PH} = ca. 34 Hz). As expected J_{PH} was dependent on the decoupling power and the narrowness of the decoupling frequency band. J_{HMo} and J_{PMo} were not observed.

$H_4Mo[P(OCH_3)_3]_4$: ^1H NMR (C_7D_8) δ −4.6 (quintet, J_{HP} = 33 Hz); $^{31}P\{^1H\}$ NMR (C_7H_8) δ −55.0 (s); $^{31}P\{^1H_{CH}\}$ NMR (C_7H_8) δ −55.0 (quintet, J_{PH} = ca. 33 Hz; J_{HMo} and J_{PMo} were not observed).

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Thermal Decomposition of $H_4Mo[P(OCH_3)_3]_4$. A NMR tube containing 0.5 mL of C_7D_8 (toluene-d_8) and 50 mg (0.08 mmol) of $H_4Mo[P(OCH_3)_3]_4$ was monitored by ^1H and ^{31}P NMR spectroscopy over several days at ~20 °C for decomposition. Initially, the ^1H NMR spectrum showed only one hydride quintet resonance at δ −4.6. After 2 days at ~20 °C, another hydride (sextet) resonance at δ −5.8 was observed with a concomitant diminution of the intensity of the quintet resonance at δ −4.6. After 7 days, the original hydride quintet resonance was lost in the base line, and the only hydride resonance observed was the sextet resonance of $H_2Mo[P(OCH_3)_3]_5$ at δ −5.8. Consistently, the $^{31}P\{^1H\}$ NMR spectrum showed, after 7 days at ambient temperatures, a singlet resonance of the dihydride at δ −46.6 and a small singlet resonance of $Mo[P(OCH_3)_3]_6$ at δ −32.1.

Reaction of $H_4Mo[P(OCH_3)_3]_4$ with $P(OCH_3)_3$. Excess (0.1 mL, 0.9 mmol) $P(OCH_3)_3$ was added to a 5-mm NMR tube which contained 0.5 mL of C_7D_8 and 50 mg (0.08 mmol) of $H_4Mo[P(OCH_3)_3]_4$. The ^1H NMR spectrum showed that all traces of the $H_4Mo[P(OCH_3)_3]_4$ hydride quintet resonance had disappeared in 5 min, and the $^{31}P\{^1H\}$ NMR spectrum showed a singlet resonance for $Mo[P(OCH_3)_3]_6$ at δ −32.1 with the accompanying six satellite resonances, J_{PMo} = 254 Hz, and a singlet resonance of $P(OCH_3)_3$ at δ 0.

Reaction of $Mo[P(OCH_3)_3]_6$ and CO. A 100-mL reaction vessel was charged with 100 mg (0.12 mmol) of $Mo[P(OCH_3)_3]_6$, 10 mL of benzene, and 1-atm total pressure of carbon monoxide. The reaction mixture was exposed to a photon source for 30 min during which time the solution remained clear and colorless. The solvent and excess carbon monoxide were removed under vacuum, and the off-white residue was analyzed and characterized by NMR spectroscopy and by infrared spectroscopy.

$Mo[P(OCH_3)_3]_5(CO)$: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −35.1 (d of intensity 4), −24.5 (quintet of intensity 1, $J_{P_AP_B}$ = 48 Hz); IR (C_6H_6) ν_{CO} 1860 cm^{-1}.

trans-$Mo[P(OCH_3)_3]_4(CO)_2$: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −39.1 (s); IR (C_6H_6) ν_{CO} 1900 cm^{-1}. A small amount of *mer*-$Mo[P(OCH_3)_3]_3(CO)_3$ was also observed. *mer*-$Mo[P(OCH_3)_3]_3(CO)_3$: $^{31}P\{^1H\}$ NMR (C_7H_8) δ −34.8 (d of intensity 2), −28.4 (t of intensity 1, $J_{P_AP_B}$ = 47 Hz). ^{13}C-enriched CO (1-atm total pressure) was introduced into a 100-mL reaction vessel which contained 100 mg (0.12 mmol) of $Mo[P(OCH_3)_3]_6$ and 10 mL of tetrahydrofuran. The reaction mixture was exposed to a photon source for 30 min, during which time the solution remained clear and colorless. The solvent and excess carbon monoxide were removed under vacuum, and the off-white residue was analyzed and characterized by $^{31}P\{^1H\}$ NMR spectroscopy and by $^{13}C\{^1H\}$ NMR spectroscopy.

trans-$Mo[P(OCH_3)_3]_4(^{13}CO)_2$: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −39.1 (t, J_{PC} = 14 Hz); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 215 (quintet, J_{CP} = 14 Hz). *mer*-$Mo[P(OCH_3)_3]_3(^{13}CO)_3$: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −34.8 (m of intensity 2), −28.4 (m of intensity 1); $^{31}P\{^1H, {}^{31}P_{trans\text{-}PP}\}$ NMR (C_7D_8) δ −28.4 (approximate d, $J_{PC\text{-}trans}$ = ~25 Hz); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 220 (m, $J_{CP\text{-}trans}$ = ~25 Hz, $J_{CP\text{-}cis}$ = ~15 Hz) (coupling constants were estimated by computer spectral simulation). A small amount of $Mo[P(OCH_3)_3]_5(^{13}CO)$ was also observed. $Mo[P(OCH_3)_3]_5(^{13}CO)$: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −35.1 (obscured by the resonance of *mer*-$Mo[P(OCH_3)_3]_3(^{13}CO)_3$), −24.5 (quintet of doublets, $J_{P_AP_B}$ = 48 Hz, $J_{PC\text{-}trans}$ = 39 Hz); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 222 (d, quintet fine structure was not resolved, $J_{CP\text{-}trans}$ = 39 Hz).

Photochemical Reaction of $Mo[P(OCH_3)_3]_6$ under Nitrogen Purge. In a quartz reaction vessel, 100 mg (0.12 mmol) of $Mo[P(OCH_3)_3]_6$, which was dissolved in 100 mL of tetrahydrofuran, was exposed to a photon source for 30 min while continuously bubbling N_2 through the solution. During the course of the reaction, the colorless solution gained a light brown color. All volatiles were removed from the reaction solution under vacuum, and the off-white residue was analyzed by NMR spectroscopy: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −46.7 (m of intensity 1), −34.6 (m of intensity 1), −32.1 (s of intensity 1, with six satellite resonances, J_{PMo} = 254 Hz), −6.9 (m of intensity 1). Selective homonuclear ^{31}P decoupling determined that the multiplet resonance at δ −46.7 was coupled to the multiplet resonances at δ −34.6 and at δ −6.9 and that all other resonances were not coupled to any other ^{31}P resonance. The singlet resonance at δ −32.1 was assigned to recovered $Mo[P(OCH_3)_3]_6$, and the resonances at δ −46.7, −34.6, and −6.9 were tentatively assigned to $Mo[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$.

As a control, a 5-mm (diameter) NMR tube was charged with 50 mg (0.06 mmol) of $Mo[P(OCH_3)_3]_6$ and 0.5 mL of C_6D_6 (benzene-d_6). The $^{31}P\{^1H\}$ NMR spectrum which showed only one singlet resonance for $Mo[P(OCH_3)_3]_6$ was recorded, and then the solution was exposed to a photon source for 10 min, during which time the clear colorless solution changed to a clear dark brown solution. The appearance of uncoordinated $P(OCH_3)_3$ was observed in the $^{31}P\{^1H\}$ NMR spectrum, and this appearance was accompanied by the diminution of the resonance for $Mo[P(OCH_3)_3]_6$. Several other resonances were observed in the coordinated trimethyl phosphite region, but specific assignments were not attempted due to the complexity of the spectrum.

Reaction of $Mo[P(OCH_3)_3]_6$ with NO. A 100-mL reaction vessel was charged with 100 mg (0.12 mmol) of $Mo[P(OCH_3)_3]_6$, 10 mL of tetrahydrofuran, and 1-atm total pressure of nitric oxide. The reaction mixture became brown upon mixing, and after 1 h at ~20 °C, dark brown precipitates were evident. The solvent and excess nitric oxide were removed by vacuum, and the dark brown residue was partially characterized by NMR spectroscopy: $^{31}P\{^1H\}$ NMR (C_7D_8–CD_2Cl_2) δ −19.5 (d of intensity 4, $J_{P_AP_B}$ = 58 Hz), +12.7 (quintet of intensity 1, $J_{P_AP_B}$ = 58 Hz). These resonances were tentatively assigned to $Mo[P(OCH_3)_3]_5(NO)^+$. Also observed were singlet resonances corresponding to uncoordinated $P(OCH_3)_3$, three sets of multiplet resonances tentatively assigned to $Mo[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$, and a singlet resonance at δ −21.4 which was not assigned but could be due to $Mo[P(OCH_3)_3]_3(NO)_2$. The IR spectrum (dichloromethane) of the reaction product showed a very strong, broad absorption at 1655 cm^{-1} assignable to $\{Mo[P(OCH_3)_3]_5NO^+\}$, and a weaker, broad absorption at 1780 cm^{-1} that could have been due to the dinitrosyl derivative.

Preparation of the Pyridine Adduct of Tungsten Chloride. Tungsten hexachloride (12.0 g, 30 mmol) was added as a solid to 50 mL of pyridine with continuous agitation of the reaction mixture. A vigorous exothermic reaction ensued which resulted in the formation of orange-brown solids. After 1 day of stirring, the reaction mixture was filtered, and the light tan powder (14.3 g, 30 mmol, 99% yield based on tungsten hexachloride) was isolated. The elemental analyses of different samples consistently best fitted the following formulation: $WOCl_3(NC_5H_5)_3 \cdot {}^1/_3(NC_5H_5)$. Anal. Calcd for $C_{16.6}H_{16.6}Cl_3N_{3.3}OW$: C, 35.0; H, 2.9; Cl, 18.7; N, 8.1. Found: C, 35.0; H, 2.8; Cl, 18.7; N, 8.2. The apparent presence of oxygen in the product was attributed to the difficulty in obtaining oxygen-free tungsten hexachloride. The pyridine adduct of tungsten chloride was used for the reduction reactions without further characterization.

Preparation of $W[P(OCH_3)_3]_6$. In a 250-mL three-neck round-bottom flask, 14.7 g (26 mmol) of the pyridine adduct of tungsten chloride, 5.1 g (130 mmol) of K, 5.1 g (31 mmol) of KI, and 50 mL of benzene were stirred and heated to reflux (80 °C) for 2 h. The reaction mixture was then cooled, and the solvent was removed by evacuation. To the resultant residue was added 50 mL (427 mmol) of $P(OCH_3)_3$, and this slurry was stirred and heated to reflux (112 °C) for 30 min. The reaction temperature was then reduced to ca. 70 °C, and that temperature was maintained for 16 h. The volatiles were then removed from the reaction mixture under vacuum, and the resultant brown residue was extracted with hexane. The vacuum removal of hexane from the extract yielded solids which were recrystallized from hexane at −40 °C. The crude product was chromatographed on a trimethyl phosphite deactivated alumina column with hexane as the eluant. The first fraction contained $W[P(OCH_3)_3]_6$ (3.4 g, 4 mmol, 14% yield based on tungsten hexachloride), which after recrystallization from hexane, was obtained as colorless crystals. $W[P(OCH_3)_3]_6$ was sensitive to ordinary light both in the solid form and in solutions: ^1H NMR (C_6D_6) δ 3.7 (m, J_{HP} = 9.6 Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −3.3 (s with satellite d, J_{PW} = 449 Hz (^{183}W, $I = {}^1/_2$, 14.4% natural abundance)); mp 153 °C dec; electronic spectrum (C_5H_{12}), 228 nm (m, ϵ = ca. 1.5×10^4 L/(mol cm)); mass spectrum (EI, 50 eV) calcd for $W[P(OCH_3)_3]_6$, envelope of appropriate masses for the isotopes of tungsten (^{182}W, ^{183}W, ^{184}W, and ^{186}W) centered around *m/e* 928, found, envelope of appropriate masses centered around *m/e* 928 for $W[P(OCH_3)_3]_6$ and masses corresponding to successive losses of six $P(OCH_3)_3$ including masses at *m/e* 897 and 882 corresponding to $W[P(OCH_3)_3]_5[P(OCH_3)_2]$ and $W[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$, respectively. Anal. Calcd for $C_{18}H_{54}O_{18}P_6W$: C, 23.3; H, 5.9; O, 31.0; P, 20.0; W, 19.8. Found: C, 23.6; H, 5.7; O, 28.4; P, 19.7; W, 19.7. (Oyxgen analysis was obtained by Pascher through the combustion with indulines and the value may be low because of the interference by phosphorus and tungsten.)

Preparation of $\{W[P(OCH_3)_3]_5[P(OCH_3)_2]^+\}(CF_3COO^-) \cdot CF_3COOH$. In a 100-mL round-bottom flask, 1.7 g (1.8 mmol) of $W[P(OCH_3)_3]_6$ was stirred in 25 mL of diethyl ether. To the clear colorless solution was added 0.15 mL (1.9 mmol) of CF_3COOH, whereupon the reaction solution immediately gained a red hue and within 5 min, began to precipitate pale red-orange solids. The reaction mixture was filtered, and the pale red-orange $\{W[P(OCH_3)_3]_5[P(OCH_3)_2]^+\}(CF_3COO^-) \cdot CF_3COOH$ (0.9 g, 0.8 mmol, 44% yield based on tungsten, 84% based on trifluoroacetic acid) was isolated: ^1H NMR (CD_2Cl_2, 25 °C) δ 3.6 (s), 17.5 (br s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ −57.6 (d of quintets of intensity 1, $J_{PP\text{-}trans}$ = 252 Hz (d), $J_{PP\text{-}cis}$ = 46 Hz (quintet)), −5.0 (t with satellite d of t of intensity 4, $J_{PP\text{-}cis}$ = 49 Hz (av), J_{P_W} = 417 Hz), +7.7 (d of quintets of intensity 1, $J_{PP\text{-}trans}$ = 251 Hz (d), $J_{PP\text{-}cis}$ = 53 Hz (quintet)). Anal. Calcd for $C_{21}H_{52}F_6O_{21}P_6W$: C, 22.4; H, 4.7; P, 16.5. Found: C, 23.2; H, 4.8; P, 15.8.

Reaction of $W[P(OCH_3)_3]_6$ with Excess CF_3COOH. In a 100-mL round-bottom flask, 1.0 g (1.1 mmol) of $W[P(OCH_3)_3]_6$ was stirred in

20 mL of ethylene glycol dimethyl ether. To the clear, colorless solution was added 0.45 mL (5.7 mmol) of CF_3COOH, whereupon the solution immediately gained a burgundy-red hue. The reaction solution was heated to reflux (83 °C) for 10 min and then was stirred at ~20 °C for 18 h. The volatiles were then removed under vacuum, and the resultant red-brown oil was partially characterized by variable-temperature ^1H NMR spectroscopy: ^1H NMR (CD_2Cl_2, 25 °C) δ −5.9 (quintet with satellite d, $J_{HP} = 42$ Hz, $J_{HW} = 6$ Hz); ^1H NMR (CD_2Cl_2, −60 °C) δ −6.1 (t of t, $J_{HP} = 68$ Hz, $J_{HP'} = 14$ Hz); ^{19}F NMR (CD_2Cl_2, 25 °C) δ +73.5 (s) (^{19}F NMR chemical shift of CF_3COOH is δ +76.6). These resonances were assigned to $HW[P(OCH_3)_3]_4(O_2CCF_3)$. Also spectroscopically observed, but not isolated, in this reaction was the cationic seven-coordinate monohydride complex $HW[P(OCH_3)_3]_6^+$: ^1H NMR (CD_2Cl_2) δ −4.7 (septet, $J_{HP} = 22$ Hz).

Photochemical Activation of $W[P(OCH_3)_3]_6$. In a 5-mm (diameter) NMR tube was placed 50 mg (0.05 mmol) of $W[P(OCH_3)_3]_6$ and 0.5 mL of C_6D_6 (benzene-d_6). The $^{31}P\{^1H\}$ NMR spectrum which showed only one singlet (with the accompanying satellite doublet) resonance for $W[P(OCH_3)_3]_6$ was recorded, and then the solution was exposed to a photon source for 10 min, during which time the clear, colorless solution turned clear dark brown. The $^{31}P\{^1H\}$ resonance for uncoordinated $P(OCH_3)_3$ appeared (which was concomitant with a diminution of the resonance for $W[P(OCH_3)_3]_6$). Several other resonances were observed in the coordinated trimethyl phosphite region, but specific assignments were not attempted due to the complexity of the spectrum.

Preparation of $H_4W[P(OCH_3)_3]_4$. In a quartz reaction vessel, 2.0 g (2.2 mmol) of $W[P(OCH_3)_3]_6$ which was dissolved in 100 mL of hexane was exposed to a photon source for 45 min while hydrogen was continuously bubbled through the reaction solution. After the photolysis reaction, the volatiles were removed under vacuum, and the resultant off-white solids were chromatographed on a trimethyl phosphite deactivated alumina column with hexane as the eluant. Upon vacuum removal of the solvent from the first fraction, colorless crystals of $H_4W[P(OCH_3)_3]_4$ (1.2 g, 1.8 mmol, 80% based on tungsten) were isolated: mp 101 °C (reversible melting); ^1H NMR (C_7D_8) δ 3.6 (m, $J_{HP} = 10.5$ Hz), −4.8 (quintet with satellite d, $J_{HP} = 33$ Hz, $J_{HW} = 30$ Hz (^{183}W, $I = ^1/_2$, 14.4% natural abundance)); $^{31}P\{^1H\}$ NMR (C_7D_8) δ −26.1 (s with satellite d, $J_{PW} = 285$ Hz); $^{31}P\{^1H_{CH}\}$ NMR (C_7D_8) δ −26.1 (quintet with satellite d of quintets, J_{PH} = ca. 33 Hz (J_{PH} was dependent on the decoupling power and the narrowness of the decoupling frequency band)); mass spectrum (EI, 50 eV) calcd for $^{186}WH_4[P(OCH_3)_3]_4$, *m/e* 686, found, *m/e* 686 for $^{186}WH_4[P(OCH_3)_3]_4$, and masses corresponding to successive losses of four hydrogen atoms and four trimethyl phosphite molecules. Anal. Calcd for $C_{12}H_{40}O_{12}P_4W$: C, 21.1; H, 5.9; P, 18.1. Found: C, 21.4; H, 5.8; P, 18.0.

Preparation of $H_2W[P(OCH_3)_3]_5$ and $H_2W[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$. In a 100-mL Pyrex reaction vessel, 100 mg (0.11 mmol) of $W[P(OCH_3)_3]_6$, 10 mL of tetrahydrofuran, and hydrogen (1-atm total pressure at ambient temperature) were mixed, and the solution was exposed to a photon source for 2 h, after which time the clear, colorless solution gained an orange-brown hue. The solvent and excess hydrogen were removed under vacuum, and the residue was characterized by ^1H NMR spectroscopy, by $^{31}P\{^1H\}$ NMR spectroscopy, and by selective methoxy proton decoupled $^{31}P\{^1H_{CH}\}$ NMR spectroscopy. The major products were $H_4W[P(OCH_3)_3]_4$ and $H_2W[P(OCH_3)_3]_5$.

$H_2W[P(OCH_3)_3]_5$: ^1H NMR (C_7D_8) δ 3.6 (m, $J_{HP} = 10$ Hz), −6.3 (sextet with satellite d, $J_{HP} = 36$ Hz, $J_{HW} = 19$ Hz (^{183}W, $I = ^1/_2$, 14.4% natural abundance)); $^{31}P\{^1H\}$ NMR (C_7D_8) δ −18.3 (s with satellite d, $J_{PW} = 398$ Hz); $^{31}P\{^1H_{CH}\}$ NMR (C_7D_8) δ −18.3 (t, J_{PH} = ca. 36 Hz (the observed J_{PH} was dependent on the decoupling power and the narrowness of the decoupling frequency band)).

$H_2W[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$: ^1H NMR (C_7D_8) δ 3.6 (complex multiplet), −5.6 (t of quartets, $J_{HP} = 40$ Hz (quartet)), $J_{HP'} =$ 27 Hz (t)); $^{31}P\{^1H\}$ NMR (C_7D_8) δ −17.4 (t of intensity 3, $J_{PP'} = 30$ Hz), +14.6 (quartet of intensity 2, $J_{PP'} = 30$ Hz).

Reaction of $W[P(OCH_3)_3]_6$ with ^{13}CO. A 100-mL reaction vessel was charged with 100 mg (0.11 mmol) of $W[P(OCH_3)_3]_6$, 10 mL of tetrahydrofuran, and 1-atm total pressure at ~20 °C of ^{13}C enriched carbon monoxide. The reaction mixture was exposed to a photon source for 30 min, and then the solvent and other volatiles were removed by evacuation. The residue was partly characterized by $^{31}P\{^1H\}$ NMR spectroscopy and by $^{13}C\{^1H\}$ NMR spectroscopy: $^{31}P\{^1H\}$ NMR (C_7D_8) for *trans*-$W[P(OCH_3)_3]_4(^{13}CO)_2$, δ −11.5 (t, $J_{PC} = 10$ Hz), for $W[P(OCH_3)_3]_5(^{13}CO)$, δ −7.9 (d of d, $J_{PP} = 37$ Hz, $J_{PC} = 12$ Hz), −2.0 (d, quintet fine structure not resolved, $J_{PC} = 39$ Hz) (unassigned resonances were found at δ −9.2 (m) and 7.0 (m); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 210 (complex multiplet for *trans*-$W[P(OCH_3)_3]_4(^{13}CO)_2$), 213 (complex multiplet for $W[P(OCH_3)_3]_5(^{13}CO)$), 244 (complex multiplet which was not assigned).

Photochemical Reaction of $W[P(OCH_3)_3]_6$ under Nitrogen Purge. In a quartz reaction vessel, 1.0 g (1.1 mmol) of $W[P(OCH_3)_3]_6$, which was dissolved in 100 mL of tetrahydrofuran, was exposed to a photon source for 90 min while nitrogen was continuously bubbled through the reaction solution. The initially clear, colorless solution changed during the photolysis reaction to a clear dark brown. The solvent and other volatiles were removed under vacuum from the reaction solution, and the resultant residue was characterized by NMR spectroscopy: $^{31}P\{^1H\}$ NMR (C_7D_8) δ −21.5 (m of intensity 1), −6.6 (m of intensity 1), −3.3 (s with accompanying satellite d, $J_{PW} = 449$ Hz), +30.5 (m of intensity 1). Selective homonuclear ^{31}P decoupling established that the multiplet resonances at δ −21.5, −6.6, and +30.5 were all spin coupled to each other. These resonances were tentatively assigned to $W[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$. The singlet resonance at δ −3.3 was assigned to unreacted $W[P(OCH_3)_3]_6$.

Preparation of the Pyridine Adduct of Rhenium Chloride. Rhenium pentachloride (10.0 g, 27.5 mmol) was carefully added as a solid to 100 mL of freshly dried pyridine, whereupon a vigorous and exothermic reaction ensued. The mixture was stirred at ~20 °C for 2 days, after which the dark reaction mixture was filtered. The solids were washed with pyridine and tetrahydrofuran, and the green-black solids (4.4 g, 6.8 mmol, 25% yield based on rhenium pentachloride) were isolated. Anal. Calcd for $C_{20}H_{20}Cl_4N_4Re$: C, 37.3; H, 3.1; N, 8.7; Cl 22.0. Found: C, 40.3; H, 3.4; N, 8.7; Cl, 23.7. This solid which approximately analyzed for $ReCl_4(NC_5H_5)_4$ was used for the reduction reactions without further characterization.

Preparation of $ReOCl_3(NC_5H_5)_2$.[21] $ReOCl_3[P(C_6H_5)_3]_2$[22a] (5.9 g, 7.1 mmol) was added to 50 mL of pyridine, and the mixture was stirred at ~20 °C for 1 day. After filtration, lime-green solids (2.1 g, 4.5 mmol, 65% yield based on rhenium) were isolated. Anal. Calcd for $C_{10}H_{10}Cl_3N_2ORe$: C, 25.7; H, 2.2; N, 6.0; Cl, 22.8. Found: C, 27.4; H, 2.1; N, 6.1; Cl, 22.3. $ReOCl_3(NC_5H_5)_2$ was used for the reduction reactions without further characterization.

Preparation of $Re_2[P(OCH_3)_3]_{10}$ and $HRe[P(OCH_3)_3]_5$. Several procedures proved to be effective in the synthesis of decakis(trimethyl phosphite)dirhenium and hydridopentakis(trimethyl phosphite)rhenium. Four procedures are described.

Procedure A. In a 250-mL three-neck round-bottom flask, 2.3 g (3.5 mmol) of the pyridine adduct of rhenium chloride, 0.8 g (20.1 mmol) of K, 0.8 g (4.8 mmol) of KI, and 50 mL of benzene were stirred and heated to reflux (80 °C) for 1 h. The reaction mixture was then cooled, and the solvent was removed under vacuum. To the resultant residue was added 50 mL (427 mmol) of $P(OCH_3)_3$, and this slurry was stirred and heated to reflux (112 °C) for 30 min. The reaction temperature was then reduced to ca. 70 °C, and that temperature was maintained for 16 h. The solid, which remained after unreacted trimethyl phosphite and other volatiles were removed, was extracted with hexane, and then this extract was chromatographed on a trimethyl phosphite deactivated alumina column using hexane as the eluant. Hexane recrystallization of the first colorless and light yellow fractions yielded small amounts of $Re_2[P(OCH_3)_3]_{10}$ and $HRe[P(OCH_3)_3]_5$.

Procedure B. The general procedure as described in procedure A was followed using $ReOCl_3(NC_5H_5)_2$ in place of the pyridine adduct of rhenium chloride. Hexane recrystallization of the chromatographed products yielded small amounts $Re_2[P(OCH_3)_3]_{10}$ and $HRe[P(OCH_3)_3]_5$.

Procedure C. Rhenium pentachloride (10.0 g, 27.5 mmol) was added to 100 mL of pyridine, and the mixture was stirred at ~20 °C for 1 day. Unreacted pyridine was removed under vacuum, and to the resultant green-black slurry was added 5.4 g (138 mmol) of K, 4.6 g (27.7 mmol) of KI, and 100 mL of benzene. This reaction mixture was stirred and heated to reflux (80 °C) for 1.5 h, and then the solvent was removed under vacuum. Excess trimethyl phosphite (50 mL, 427 mmol) was added. The mixture was heated to 112 °C for 30 min, and then the reaction temperature was lowered to 70 °C. After 20 h, unreacted trimethyl phosphite and other volatiles were vacuum removed, and the remaining solid was extracted with hexane. The extract was chromatographed on a trimethyl phosphite deactivated alumina column using hexane as the eluant. The first fractions contained the desired products which were isolated after recrystallization from hexane at −40 °C (yield, ca. 10% based on rhenium). Anal. Calcd for $C_{15}H_{45}O_{15}P_5Re$: C, 22.3; H, 5.6; P, 19.2. Found: C, 23.5; H, 5.7; P, 18.9.

$Re_2[P(OCH_3)_3]_{10}$: ^1H NMR (C_7D_8) δ 3.7 (m); $^{31}P\{^1H\}$ NMR (C_7D_8) δ +15.8 (d of intensity 4, $J_{PP} = 28$ Hz), +19.5 (quintet of intensity 1, $J_{PP} = 28$ Hz); mass spectrum (EI, 50 eV) calcd for $^{187}Re_2[P(OCH_3)_3]_{10}$, *m/e* 1614, found, *m/e* 807 for $^{187}Re[P(OCH_3)_3]_5$ and *m/e* 805 for

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$^{185}Re[P(OCH_3)_3]_5$, *m/e* 776 for $^{187}Re[P(OCH_3)_3]_4[P(OCH_3)_2]$ and *m/e* 774 for $^{185}Re[P(OCH_3)_3]_4[P(OCH_3)_2]$.

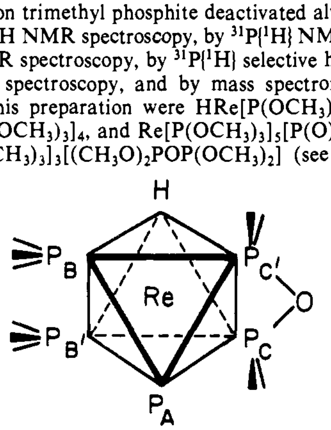
$HRe[P(OCH_3)_3]_5$: ^1H NMR (C_7D_8) δ 3.7 (m, J_{HP} = 10.2 Hz), −9.5 (quintet of d, $J_{HP\text{-trans}}$ = 12 Hz, $J_{HP\text{-cis}}$ = 24 Hz); $^{31}P\{^1H\}$ NMR (C_7D_8) δ +1.0 (d of intensity 4, J_{PP} = 28 Hz), +7.2 (quintet of intensity 1, J_{PP} = 28 Hz); $^{31}P\{^1H_{CH}\}$ NMR (C_7D_8) δ +1.0 (t, $J_{PP} + J_{PH}$ = ca. 52 Hz (the observed J_{PH} was dependent on the decoupling power and the narrowness of the decoupling frequency band)); mass spectrum (EI, 50 eV) calcd for $^{187}ReH[P(OCH_3)_3]_5$, *m/e* 808, found, *m/e* 808 for $^{187}ReH[P(OCH_3)_3]_5$ and *m/e* 806 for $^{185}ReH[P(OCH_3)_3]_5$, *m/e* 777 for $^{187}ReH[P(OCH_3)_3]_4[P(OCH_3)_2]$ and *m/e* 775 for $^{185}ReH[P(OCH_3)_3]_4[P(OCH_3)_2]$.

Procedure D. Decakis(trimethyl phosphite)dirhenium and hydridopentakis(trimethyl phosphite)rhenium were co-products in the potassium–mercury amalgam reduction procedures which were employed in the syntheses of $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$ and $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$ (vide infra).

Preparation of $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$. A 500-mL round-bottom flask was charged with 10.0 g (27.5 mmol) of rhenium pentachloride and 150 mL of tetrahydrofuran. To the dark solution was added 50 mL (427 mmol) of $P(OCH_3)_3$, and the mixture was stirred at ~20 °C for 1 day. The solvent and the unreacted trimethyl phosphite were removed under vacuum, and to the resultant red-brown residue was added another 50 mL (427 mmol) of $P(OCH_3)_3$. Freshly prepared potassium–mercury amalgam, which contained 5.6 g (143 mmol) of K in 50 mL of mercury, was slowly added to the phosphite slurry while agitation was continuously maintained. The reaction mixture was magnetically stirred at ambient temperatures for 1 day, and then the mercury was separated from the reaction mixture by employing a 250-mL separatory funnel. The solvent was then removed from the reaction mixture by evacuation, and the resultant gray solids were extracted with hexane. The product was purified by column chromatography on trimethyl phosphite deactivated alumina and by recrystallization from hexane at −40 °C. Isolated yield of colorless crystals of $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$ was 2.0 g (2.2 mmol, 8% yield based on rhenium pentachloride): mp 226–229 °C dec; ^1H NMR (C_7D_8) δ 3.7 (complex m); $^{31}P\{^1H\}$ NMR (C_7D_8) δ +20.0 (m, J_{PP} = ca. 40 Hz), +53.2 (approximately d of quintets, $J_{PP\text{-trans}}$ = ca. 250 Hz) (missing was another set of resonances for a unique phosphorus ligand; presumably this set was partially obscured by near overlap with the large triplet); mass spectrum (EI, 50 eV) calcd for $^{187}Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$ *m/e* 916, found, highest mass observed was *m/e* 870 (and *m/e* 868 with the appropriate rhenium isotope ratio). $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$ reacted with methyl iodide[22b] to form $\{Re[P(OCH_3)_3]_6^+\}I^-$. Anal. Calcd for $C_{17}H_{51}O_{18}P_6Re$: C, 22.3; H, 5.6; P, 20.3. Found: C, 22.4; H, 5.6; P, 19.9.

Preparation of $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$. Rhenium pentachloride (10.0 g, 27.5 mmol) was slowly added as a solid to 50 mL of pyridine with constant agitation. After 1 day of reaction at ~20 °C, the solvent and other volatiles were removed under vacuum, and to the resultant dark-green slurry was added 50 mL of benzene. Freshly prepared potassium–mercury amalgam, which contained 6.1 g (156 mmol) of K in 50 mL of mercury, was slowly added to the stirred benzene solution. After 3 h, when the reaction mixture changed from the initially dark green color to a blue-purple hue, the solvent was removed under vacuum, and 50 mL (427 mmol) of $P(OCH_3)_3$ was added to the reaction mixture. After 1 day of stirring at ~20 °C, the mercury was separated from the reaction mixture by employing a 250-mL separatory funnel. The solvent was then removed under vacuum, and the resultant purple solids were extracted with hexane. The products were purified by column chromatography on trimethyl phosphite deactivated alumina and were characterized by ^1H NMR spectroscopy, by $^{31}P\{^1H\}$ NMR spectroscopy, by $^{31}P\{^1H_{CH}\}$ NMR spectroscopy, by $^{31}P\{^1H\}$ selective homonuclear ^{31}P decoupled NMR spectroscopy, and by mass spectrometric analysis. Co-products in this preparation were $HRe[P(OCH_3)_3]_5$, $Re_2[P(OCH_3)_3]_{10}$, $H_3Re[P(OCH_3)_3]_4$, and $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$.

fac-$HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$ (see **1**): ^1H NMR



(C_7D_8) δ 3.7 (m), −8.8 (m); $^{31}P\{^1H\}$ NMR (C_7D_8) δ −8.2 (m of intensity 2, P_B and $P_{B'}$), −1.5 (m of intensity 1, P_A), +40.5 (m of intensity 2, P_C and $P_{C'}$, approximate coupling constants from computer simulation, $J_{P_BP_C} = J_{P_{B'}P_{C'}}$ = ~250 Hz, $J_{P_BP_{C'}} = J_{P_{B'}P_C} = J_{P_AP_C} = J_{P_AP_{C'}}$ = ~30 Hz, $J_{P_AP_B} = J_{P_AP_{B'}}$ = ~25 Hz); $^{31}P\{^1H_{CH}\}$ NMR (C_7D_8) multiplet resonances observed at δ −8.2 and at +40.5, which were each approximately a doublet of doublets in the $^{31}P\{^1H\}$ NMR spectrum. were approximately each a doublet of triplets; the multiplet resonance observed at δ −1.5 only broadened with selective decoupling (selective homonuclear ^{31}P decoupling established that the multiplet resonances at δ −8.2, −1.5, and +40.5 were all coupled to each other); mass spectrum (EI, 50 eV) calcd for $^{187}ReH[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$, *m/e* 762. Found, *m/e* 762 and 760 in appropriate ratio for the isotopes of rhenium.

Reaction of $Re_2[P(OCH_3)_3]_{10}$ and $HRe[P(OCH_3)]_5$ with CF_3COOH. To a 5-mm NMR tube, which contained 50 mg (0.06 mmol of rhenium) of a mixture of $Re_2[P(OCH_3)_3]_{10}$ and $HRe[P(OCH_3)_3]_5$ dissolved in 0.5 mL of CD_2Cl_2, was added 0.1 mL (1.3 mmol) of CF_3COOH. The pale yellow solution did not visibly change in color, but all traces of the dirhenium decakis(trimethyl phosphite) and of the hydridopentakis(trimethyl phosphite)rhenium vanished in 2 min, which was the time required to record the first NMR spectrum: ^1H NMR (CD_2Cl_2) δ 9.2 (br s), 4.0 (s), 3.6 (complex m), −7.2 (quartet. J_{HP} = 20 Hz), −7.5 (sextet, J_{HP} = 20 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ +15.8 (br s), +16.8 (s). At −60 °C, only one singlet was observed in the $^{31}P\{^1H\}$ NMR spectrum. The hydride sextet resonance at δ −7.5 and the ^{31}P singlet resonance at δ +16.8 were tentatively assigned to $\{H_2Re[P(OCH_3)_3]_5^+\}$. The hydride quartet resonance at δ −7.2 and the ^{31}P broad singlet resonance at δ +15.8 were tentatively assigned to $H_2Re[P(OCH_3)_3]_3(O_2CCF_3)$.

Reaction of $Re_2[P(OCH_3)_3]_{10}$ with H_2. A 100-mL Pyrex reaction vessel was charged with 100 mg (0.06 mmol) of $Re_2[P(OCH_3)_3]_{10}$, 10 mL of tetrahydrofuran, and hydrogen (1-atm total pressure at ~20 °C). The reaction solution was exposed to a photon source for 30 min. During the course of the reaction, the initially pale orange solution gained a dark purple hue. The solvent and excess hydrogen were removed under vacuum, and the dark residue was characterized by ^1H NMR spectroscopy, by $^{31}P\{^1H\}$ NMR spectroscopy, and by $^{31}P\{^1H_{CH}\}$ NMR spectroscopy. $H_3Re[P(OCH_3)_3]_4$: ^1H NMR (C_7D_8) δ 3.7 (m), −8.1 (quintet, J_{HP} = 18 Hz); $^{31}P\{^1H\}$ NMR (C_7D_8) δ −2.8 (s); $^{31}P\{^1H_{CH}\}$ NMR (C_7D_8) δ −2.8 (quartet, J_{PH} = ca. 18 Hz). Also present in the reaction mixture were $HRe[P(OCH_3)_3]_5$ and $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$.

Reaction of $Re_2[P(OCH_3)_3]_{10}$ with ^{13}CO. A 100-mL reaction vessel was charged with 100 mg (0.06 mmol) of $Re_2[P(OCH_3)_3]_{10}$, 10 mL of tetrahydrofuran, and ^{13}C-enriched carbon monoxide (1-atm total pressure at ~20 °C). The reaction solution was exposed to a photon source for 30 min, during which time the solution remained clear and pale orange. The solvent and other volatiles were removed under vacuum, and the residue was characterized by ^1H NMR, $^{31}P\{^1H\}$ NMR, and $^{13}C\{^1H\}$ NMR spectroscopy. *trans*-$HRe[P(OCH_3)_3]_4(^{13}CO)$: ^1H NMR (C_7D_8) δ 3.7 (complex multiplet), −7.4 (m, J_{HP} = ca. 25 Hz, J_{HC} = ca. 5 Hz); $^{31}P\{^1H\}$ NMR (C_7D_8) δ −2.8 (d, J_{PC} = 9 Hz); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 200 (quintet, J_{CP} = 9 Hz). Also present in the reaction mixture were $HRe[P(OCH_3)_3]_5$ and a small amount of $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$.

Results and Discussion

Synthesis. In developing the chemistry of zerovalent transition-metal phosphite chemistry, we have attempted to establish synthesis systematics and to gain some understanding of reaction mechanism in the reduction sequence. A reaction sequence for the nickel, cobalt, and iron group metal halides[23] is as shown in eq 1. For the equilibrium between the four- and five-coordinate phosphite complexes of the metal dihalides, the magnitude of K_{eq} is typically large for compact phosphites like trimethyl phosphite and small for bulky phosphites like triisopropyl phosphite.[5,6,10] In addition, autoionization of these covalent complexes will occur in some solvents to give $\{M[P(OR)_3]_x^{+,2+}\}(MCl_4^{2-})$ species. Information about the complexes present after the first one-electron reduction is limited to the cobalt system in which the $\{Co[P(OCH_3)_3]_5^+\}$ complex has been isolated as Cl^- and $\{Co[P(OCH_3)_3]_4^-\}$ salts.[6] Where the phosphite was bulky, as in the case of triisopropyl phosphite, the major cationic species was $\{Co[P(OR)_3]_4^+\}$.[6] The second one-electron reduction generates the

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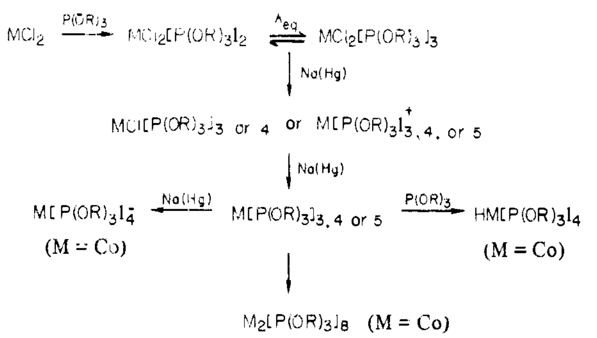
[23] Sodium amalgam with an ethereal solution of the trialkyl phosphite is the most general and convenient, high yield synthesis of iron and cobalt group complexes from the metal dihalide–phosphite complexes. Synthesis of nickel group complexes is very simple, and a wide range of simple reducing agents can be used; in fact, the reaction of nickel(II) chloride and excess trialkyl phosphite directly yields the NiL_4 complex.



(1)

zerovalent complexes ML_x, where x is 3, 4, or 5 depending on the metal and bulkiness of the phosphite ligand,[24] and the third one-electron reduction for cobalt gives $\{Co[P(OCH_3)_3]_4^-\}$.[6] Unknown is the mechanism of the dimer $Co_2[P(OR)_3]_8$ formation; it does not simply comprise dimerization of the $Co[P(OR)_3]_4$ radical.[6]

The synthesis of molybdenum, tungsten, and rhenium zerovalent or low valent phosphite complexes is formally analogous to that of iron, cobalt, and nickel group complexes discussed above although generally the temperatures required were explicably higher for the earlier and more electropositive transition metals. Parallels between the odd-electron cobalt and rhenium systems are really quite striking if the fine details of synthetic procedure and reaction temperatures are ignored. All the products isolated from the cobalt and from the rhenium reduction systems are fully analogous. In parallel to cobalt, the reduction scheme for rhenium is shown in Scheme I. The only rhenium species, noted in the scheme, that have not been characterized are the radical intermediates like $Re[P(OCH_3)_3]_5$ or $Re[P(OCH_3)_3]_4$ and the octahedral cation $\{Re[P(OCH_3)_3]_6^+\}$.[25,26] One rather interesting product is $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$.[27a] Formation of this very stable octahedral rhenium(I) complex from the putative 19-electron $Re[P(OCH_3)_3]_6$ intermediate by loss of a methyl radical is a plausible process.[27b] Furthermore, the generation of a methyl radical could account for the observed formation of tetramethyl diphosphite, as a ligand in the chelate complex $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$.[28]

$$CH_3\cdot + P(OCH_3)_3 \rightarrow C_2H_6 + \cdot OP(OCH_3)_2$$

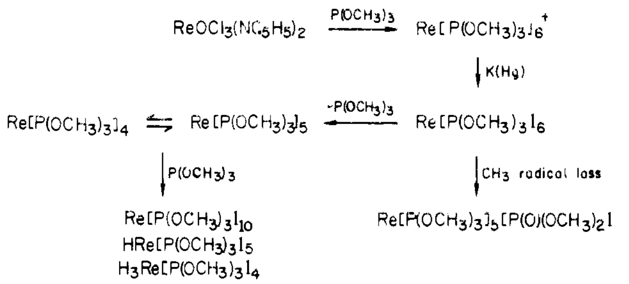
$$\cdot OP(OCH_3)_2 + P(OCH_3)_3 \rightarrow (CH_3O)_2P\text{–}O\text{–}P(OCH_3)_2 + CH_3O\cdot$$

$$CH_3O\cdot + P(OCH_3)_3 \rightarrow CH_3OCH_3 + \cdot OP(OCH_3)_2$$

Previously, the formation of the $OP(OCH_3)_2$ radical, as both a monodentate[29,30] and bidentate[31] ligand, has been observed in reactions of the phosphite with metal complexes under very mild reaction conditions.

The actual yields of the above cited rhenium(0) and rhenium(I) phosphite complexes is a sensitive function of reaction conditions which are described in the experimental section. At this point, the only variable that we can intelligently comment on is the relative yields of products from the one-electron reduction of $Re[P(OCH_3)_3]_6^+$. If the temperature of the reaction medium during this reduction step is high, then phosphite dissociation from the radical $Re[P(OCH_3)_3]_6$ should be relatively fast and the major products are $Re_2[P(OCH_3)_3]_{10}$ and $HRe[P(OCH_3)_3]_5$—if low, then the methyl radical loss may be dominant so as to form primarily $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$. Although $P(O)(OCH_3)_2$ analogue complexes should be preparable for molybdenum and tungsten, these are not direct products of the reductive syntheses ostensibly because none of the zerovalent intermediates or products is an odd electron species.

Scheme I



The procedural sequence in the reductive synthesis of transition-metal complexes is crucial for the molybdenum, tungsten, and rhenium systems and affects product distribution rather dramatically. Generally, we have found that for optimal yields of the zerovalent complexes of the more electropositive transition metals it is essential to reduce a metal halide–ether or –pyridine complex before introducing the phosphite. In fact, for the molybdenum and tungsten systems, no $M[P(OCH_3)_3]_6$ complex has been detected or isolated from reductions of the metal halide in the presence of trimethyl phosphite. For these metals and for rhenium, the best reductant[32] examined to date has been the Rieke[33] reagent which comprises a mixture of potassium iodide and potassium.

General Properties of the Zerovalent Metal Phosphite Complexes. Spectroscopic properties of the new zerovalent transition-metal phosphite complexes are fully consistent with octahedral form for $Mo[P(OCH_3)_3]_6$ and $W[P(OCH_3)_3]_6$ and with biocta-hedral (vertex shared) form for $Re_2[P(OCH_3)_3]_{10}$. Salient NMR parameters are presented in Table I. All three complexes have basically a hydrocarbon exterior and, accordingly, have high solubilities in hydrocarbon solvents.[34] All three were sufficiently volatile at 50–80 °C and 10^{-8} torr to yield significant ions in mass spectrometric experiments. The tungsten complex gave the parent ion as well as substantial yields of all the ions resulting from the successive loss of trimethyl phosphite ligands. This behavior of the ionized molecule paralleled the relatively high thermal stability of these molecules. In contrast, $Re_2[P(OCH_3)_3]_{10}$ did not yield detectable quantities of the parent ion. The highest mass ion corresponded to $Re[P(OCH_3)_3]_5$ and other significant mass ions corresponded to those resulting from consecutive loss of trimethyl phosphite. Evidence for *thermal* generation of $Re[P(OCH_3)_3]_5$ fragments from the parent dimer is lacking, but this aspect of the rhenium dimer chemistry has not been extensively explored.

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(24) For nickel and cobalt, x will be 4 unless the phosphite is a very bulky ligand, whereas x will be 5 for iron with tri-*n*-alkyl phosphite ligands.

(25) We are confident that this octahedral species is present; our isolation attempts continue.

(26) This cation has been prepared, isolated, and characterized as I^- and PF_6^- salts by reaction of $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$ and CH_3I; Muetterties, E. L.; Yang, Z.-Y., to be submitted for publication.

(27) (a) The cobalt analogue $Co[P(OCH_3)_3]_4[P(O)(OCH_3)_2]$ also has been isolated from a sodium amalgam reduction reaction and has been fully characterized.[6] (b) Alternatively, $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$ may be generated in the reaction of the 17-electron $Re[P(OCH_3)_3]_5$ complex with trimethyl phosphite. A precedent for this reaction is[30]

$$\{C_5H_5Cr(CO)_2P(OCH_3)_3\}_2 \rightarrow C_5H_5Cr(CO)_2P(OCH_3)_3 \xrightarrow{P(OCH_3)_3} C_5H_5Cr[P(O)(OCH_3)_2](CO)_2P(OCH_3)_3 + C_5H_5CrCH_3(CO)_2P(OCH_3)_3$$

(28) The radical reaction sequence is described for free phosphite but some of this radical chemistry must involve coordinated phosphite.

(29) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970**, *24*, 725.

(30) Goh, L.-Y.; D'Aniello, M. J., Jr.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192.

(31) Burch, R. R., Muetterties, E. L., unpublished observations on rhodium(I) cluster chemistry.

(32) The oxidation state of the transition metal after the reduction step is not known. Colors of the residue from the reduction step range from white with a pinkish or violet tinge for molybdenum and tungsten to dark brown or purple for rhenium.

(33) Rieke, R. D.; Öfele, K.; Fischer, E. O. *J. Organomet. Chem.* **1974**, *76*, C19.

(34) Generally, all the phosphite complexes and the various neutral derivatives of them were very soluble in most organic solvents. These solubility properties led to substantial difficulties in separations from reactions that produced several products. In many cases, column chromatography did not provide quantitative separations. For example, separation of $Re_2[P(OCH_3)_3]_{10}$ from $HRe[P(OCH_3)_3]_5$ was never quantitative although highly enriched samples of either complex were obtained by using a phosphite-deactivated alumina column.

Table I. Nuclear Magnetic Resonance Data for the Hydride Complexes of Molybdenum and Tungsten Phosphites and Related Complexes[a]

	^{1}H NMR			^{31}P{^{1}H} NMR	
	δ_{MH}	J_{HP}, Hz	J_{HM}, Hz	δ_P	J_{PM}, Hz
$Mo[P(OCH_3)_3]_6$[15]	...	...		−32.1 (s)	254 ($I = {}^5/_2$)[b]
$H_2Mo[P(OCH_3)_3]_5$	−5.8 (sx)	34		−46.6 (s)	
$H_4Mo[P(OCH_3)_3]_4$	−4.6 (p)	33		−55.0 (s)	
$HMo[P(OCH_3)_3]_4(O_2CCF_3)$[15]	−9.8 (tt)	16 62		−23.4 (t) −55.9 (t)	62 ($J_{P_AP_B}$)
$W[P(OCH_3)_3]_6$	...	...		−3.3 (s)	449 ($I = {}^1/_2$)
$H_2W[P(OCH_3)_3]_5$	−6.3 (sx)	36	19	−18.3 (s)	398
$H_4W[P(OCH_3)_3]_4$	−4.8 (p)	33	30	−26.1 (s)	285
$H_2W[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$	−5.6 (tq)	40 (q) 27 (t)		−17.4 (t) +14.6 (q)	30 ($J_{P_AP_B}$, av)
$HW[P(OCH_3)_3]_4(O_2CCF_3)$	−6.1 (tt)	14 68			

[a] Abbreviations: s, singlet; t, triplet; q, quartet; p, quintet; sx, sextet; tq, triplet of quartets, and tt, triplet of triplets. [b] Averaged value for ^{95}Mo-P and ^{97}Mo-P.

The chemistry of these zerovalent metal complexes is dominated by three general characteristics: (i) protonation to give a series of products, (ii) relative resistance to thermal dissociation of a phosphite ligand, and (iii) facile photoactivation of phosphite ligand dissociation in $Mo[P(OCH_3)_3]_6$ and $W[P(OCH_3)_3]_6$ and of metal–metal bond scission in $Re_2[P(OCH_3)_3]_{10}$. These distinctive features are discussed summarily in following sections and the dynamic stereochemistry of the derivative complexes is presented in the last section.

Protonation Reactions. Electrophilic attack of $Mo[P(OCH_3)_3]_6$[15] and $W[P(OCH_3)_3]_6$ is a distinguishing reaction—in fact, it is a ubiquitous reaction of all zerovalent metal phosphite complexes and understandably so in light of the strong donor properties of the phosphite ligand. However, in the case of the molybdenum and tungsten complexes, the unique feature of electrophilic attack or specifically the protonation reaction was the dominant process whereby methanol was eliminated to form the octahedral and diamagnetic d^4 {$M[P(OCH_3)_3]_5[P(OCH_3)_2]^+$} complexes.[35] These same complexes were formed in the alkylation (CH_3^+) of the $M[P(OCH_3)_3]_6$ complexes. Also formed in low yields from the protonation reactions[15] were the seven-coordinate hydrides {$HM[P(OCH_3)_3]_6^+$} which were the expected products based on simple extrapolation from the later transition-metal zerovalent complexes where the corresponding hydrides were formed in near quantitative yields, e.g., {$HFe[P(OCH_3)_3]_5^+$} from $Fe[P(OCH_3)_3]_5$[9,10] and {$HNi[P(OR)_3]_x^+$} from $Ni[P(OR)_3]_x$.[36] These two types of products in the protonation reaction appear to be kinetically controlled products; facile interconversion of {$M[P(OCH_3)_3]_5[P(OCH_3)_2]^+$} and {$HM[P(OCH_3)_3]_6^+$} was not observed.[15] Reaction course with excess acid, specifically trifluoroacetic acid, was different with the *hexakis* phosphite complexes—the major product was $HM[P(OCH_3)_3]_4[O_2CCF_3]$ for both the molybdenum and tungsten systems.[15]

Protonation of $Re_2[P(OCH_3)_3]_{10}$ with trifluoroacetic acid gave primarily {$H_2Re[P(OCH_3)_3]_5^+$} and $H_2Re[P(OCH_3)_3]_3(O_2CCF_3)$ which are formal analogues of the protonation products, respectively, {$HM[P(OCH_3)_3]_6^+$} and $HM[P(OCH_3)_3]_4[O_2CCF_3]$ in the molybdenum and tungsten systems. NMR parameters of the hydride complexes are presented in Table I.

Photochemistry. By formal analogy to transition-metal carbonyl chemistry, an extensive photochemistry might be anticipated for the zerovalent metal phosphite complexes. This photochemistry would be of the form

$$M[P(OCH_3)_3]_6 \xrightarrow{h\nu} M[P(OCH_3)_3]_5 + P(OCH_3)_3$$

$$Re_2[P(OCH_3)_3]_{10} \xrightarrow{h\nu} 2Re[P(OCH_3)_3]_5$$

$$Re[P(OCH_3)_3]_5 \rightleftharpoons Re[P(OCH_3)_3]_4 + P(OCH_3)_3$$

This chemistry was realized but unanticipated was the extreme photosensitivity of $W[P(OCH_3)_3]_6$. The tungsten complex is colorless; the electronic spectrum consists of a set of absorptions that are centered around 228 nm and tail into the edge of the visible spectrum. Crystals and solutions of $W[P(OCH_3)_3]_6$ quickly discolored on exposure to laboratory light—coloration was initially purple and dark brown after long exposure. On exposure to ultraviolet light, solutions turned dark brown. ^{31}P NMR studies of photolyzed solutions of $W[P(OCH_3)_3]_6$ showed the presence of free trimethyl phosphite, which increased in concentration with time of exposure as the signal for $W[P(OCH_3)_3]_6$ decreased, and also the presence of the chelate complex $W[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$. The majority of the species generated in the photolysis were unidentified. All were highly colored, extremely soluble in hydrocarbon solvents and not readily separable by chromatographic techniques.

In contrast, the molybdenum complex was far less photosensitive. No coloration or decomposition of $Mo[P(OCH_3)_3]_6$ as a solid or in solution was observed with long exposures to laboratory light. Nevertheless, irradiation of solutions with a Hanovia medium-pressure mercury lamp did lead to photolytic dissociation of trimethyl phosphite and a set of products analogous to those described above for the tungsten complex.

The facile photodissociation of phosphite ligand for the *hexakis* phosphite complexes was utilized in the synthesis of a series of hydrides by photolysis of the complexes in the presence of hydrogen. For molybdenum, broad-band irradiation with a Pyrex filter led to the formation of $H_2Mo[P(OCH_3)_3]_5$ and $H_4Mo[P(OCH_3)_3]_4$. A similar chemistry was observed for the tungsten complex. Irradiation through quartz gave a relatively selective synthesis of $H_4W[P(OCH_3)_3]_4$ and, through Pyrex, a mixture of $H_2W[P(OCH_3)_3]_5$, $H_4W[P(OCH_3)_3]_4$, and $H_2W[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$ with the first complex the major product. There was no evidence that these *hexakis* phosphite complexes thermally react with hydrogen: $Mo[P(OCH_3)_3]_6$ did not react detectably with H_2 up to 100 °C above which temperature thermal decomposition of the complex prevailed. Similarly, the tungsten complex, in the absence of light, was unreactive toward hydrogen.

A distinguishing feature in this hydride chemistry between the molybdenum and the tungsten systems was the displacement of hydrogen from the hydride complexes by free trimethyl phosphite. Reaction of $H_4Mo[P(OCH_3)_3]_4$ with excess phosphite quantitatively yielded $Mo[P(OCH_3)_3]_6$ within 5 min. In sharp contrast, neither $H_4W[P(OCH_3)_3]_4$ nor $H_2W[P(OCH_3)_3]_5$ reacted with trimethyl phosphite. Thermal reactivity of $H_4Mo[P(OCH_3)_3]_4$ was correspondingly high. A solution of the complex in toluene (sealed tube) was monitored by NMR spectroscopy at ~25 °C. After 2 days at 25 °C, the presence of $H_2Mo[P(OCH_3)_3]_5$ was discernible, and after 7 days, all of the tetrahydride complex had disappeared—the major solution species at that point was the dihydride complex with small amounts of $Mo[P(OCH_3)_3]_6$.[37]

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[35] In these d^4 complexes, the diamagnetic behavior can be ascribed to the noninnocent $P(OCH_3)_2$ ligand which is formally a three-electron donor, a postulate supported by crystallographic data for the molybdenum complex.

[36] Drinkard, W. C.; Eaton, D. R.; Jesson, J. P.; Lindsey, R. V., Jr. *Inorg. Chem.* **1970**, *9*, 392.

[37] Stoichiometric considerations require another molybdenum species, "deficient" in phosphite, to be present, but none was spectroscopically detected.

Clearly, hydrogen dissociation (reductive elimination) from the molybdenum hydride complexes is far more facile than with the analogous tungsten hydrides.

Although $Re_2[P(OCH_3)_3]_{10}$ does not react thermally with hydrogen,[38] it does with photoactivation. Photolysis (Pyrex filter) of $Re_2[P(OCH_3)_3]_{10}$ and hydrogen mixtures produced $H_3Re[P(OCH_3)_3]_4$ and $HRe[P(OCH_3)_3]_5$ as well as a small amount of $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$. Hence, fragmentation of the dimer is a facile photochemical process as is phosphite dissociation in $HRe[P(OCH_3)_3]_5$.

Important NMR parameters of the hydrides obtained in the photolysis are presented in Table I.

Photolysis of the zerovalent molybdenum and tungsten phosphite complexes in the presence of carbon monoxide (^{12}C and ^{13}C labeled) yielded mixtures of $M[P(OCH_3)_3]_5CO$, *trans*-$M[P(OCH_3)_3]_4(CO)_2$, and *mer*-$M[P(OCH_3)_3]_3(CO)_3$.[39] The trisubstituted derivative was observed only in the molybdenum case. These results establish the selective trans activation of the phosphite dissociation by the carbon monoxide in the photolysis reaction of $M[P(OCH_3)_3]_5CO$; the cis isomer of the dicarbonyl product was not detected by NMR spectroscopy. Another product in the tungsten reaction system may be a dinuclear complex because there was a very low field ^{13}C NMR carbonyl resonance (δ 244), a region characteristic of bridged metal carbonyl ligands. Analogous photolysis of $Re_2[P(OCH_3)_3]_{10}$ and CO gave as the major product $HRe[P(OCH_3)_3]_5$ and *trans*-$HRe[P(OCH_3)_3]_4CO$ (no cis isomer); the hydride ligand was generated by the common process of hydrogen atom abstraction from the solvent by ReL_5 or ReL_4 "radical" complexes. Presumably the reaction sequence was

$$Re_2[P(OCH_3)_3]_{10} \xrightarrow{h\nu} 2Re[P(OCH_3)_3]_5 \rightleftharpoons 2Re[P(OCH_3)_3]_4 + P(OCH_3)_3$$

$$Re[P(OCH_3)_3]_4 \xrightarrow{\text{solvent}} HRe[P(OCH_3)_3]_4 \xrightarrow{P(OCH_3)_3} HRe[P(OCH_3)_3]_5$$

$$HRe[P(OCH_3)_3]_4 + CO \rightarrow \textit{trans}\text{-}HRe[P(OCH_3)_3]_4CO$$

with selective trans activation by the hydride ligand in the phosphite photodissociation step.

In reactions with other small molecules like NO, CH_3NC, $(CN)_2$, and PF_3, $W[P(OCH_3)_3]_6$ was unreactive in the absence of light whereas $Mo[P(OCH_3)_3]_6$ was reactive. Most notably, NO reacted instantaneously with $Mo[P(OCH_3)_3]_6$ to yield largely $Mo[P(OCH_3)_3]_5NO^+$. As a general characterization of this chemistry, we can describe the tungsten complex as relatively nonreactive thermally but very reactive photochemically while the molybdenum complex has moderate reactivity in both a thermal and a photochemical context.

Dynamic Stereochemistry. The octahedral zerovalent or low valent molybdenum, tungsten, and rhenium phosphite complexes[40] were stereochemically rigid molecules within the context of DNMR spectroscopic studies with the exception of the cationic d^4 $\{M[P(OCH_3)_3]_5[P(OCH_3)_2]^+\}$ complexes. As discussed in detail in an earlier article[15] for the $\{Mo[P(OCH_3)_3]_5[P(OCH_3)_2]^+\}$ complex, the DNMR ^1H, ^{31}P, and ^{13}C data indicate that there is a rapid (10^2 s^{-1}) site exchange of methoxy groups about all *six* phosphorus ligands at temperatures above ~−50 °C; a similar NMR behavior has been noted here for the tungsten analogue.

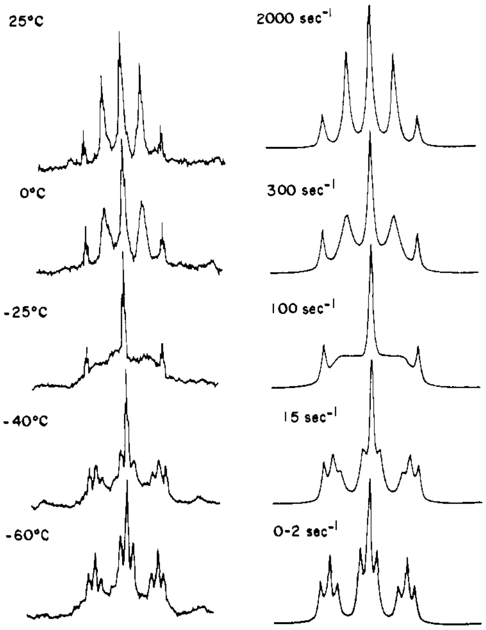
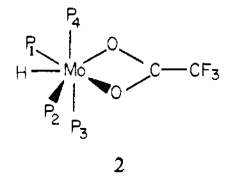


Figure 1. On the left are the observed ^1H DNMR spectra for $HW[P(OCH_3)_3]_4(O_2CCF_3)$ in the metal hydride region (δ −6.1) and on the right are the theoretical spectra[42] based on a pairwise permutational mechanism. The fine structure in the experimental spectra are presumed to arise from $^{183}W-^1H$ spin coupling. For the permutational analysis of this hydride under C_{2v} symmetry constraint, see **2** for the labeled structure; the permutations for identity and inverse are (12)(34) and (12)(34), for pairwise exchange are (13)(24), (1324), (1423), and (14)(23), and for nonpairwise exchange are (23), (234), (132), (1342), (123), (13), (1234), (134), (243), (24), (1432), (142), (1243), (143), (124), and (14).

Interestingly, the formally related d^6 rhenium complex $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$ showed no evidence of any dynamic process (the AB_4C ^{31}P spectrum was invariant from low temperatures to +50 °C). A crystallographic study of $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$ will be made for a detailed structural comparison with $Mo[P(OCH_3)_3]_5[P(OCH_3)_2]^+$.[15]

Expectedly, all the seven- and eight-coordinate hydridometal phosphite complexes were stereochemically nonrigid. ^1H and ^{31}P NMR spectra for $H_2M[P(OCH_3)_3]_5$ (M = Mo, W, and Re^+) and for $H_4M[P(OCH_3)_3]_4$ (M = Mo, W) showed spectroscopic equivalence of H and P ligand atoms down to −90 °C, the temperature limits of our spectrometer systems (−60 °C for the rhenium complexes). In addition, the molybdenum and tungsten $HM[P(OCH_3)_3]_4(O_2CCF_3)$ complexes were stereochemically nonrigid, but limiting spectra for both were observed below 0 °C. An earlier crystallographic study[41] of the molybdenum complex established that the complex approximated pentagonal-bipyramidal form, **2**. Permutationally, there are only two exchange mechanisms: pairwise exchange of phosphorus atoms, e.g., (13)(24) and nonpairwise exchange, e.g., (23). The earlier DNMR studies of the molybdenum complexes established nonpairwise exchange to be the dominant process.[41] We show in Figure 1 that pairwise exchange is the dominant process for the tungsten complex. We can present no reasonable explanation for these differences in the



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[38] The precise dimensions and details of thermal reactivity of this dimer with respect to metal–metal and metal–phosphorus bond scission has not been fully defined and is under investigation.

[39] The thermal reactions of CO with the zerovalent metal phosphite complexes have not been explored. Generally, the thermal dissociation of phosphite is a relatively slow process; ligand exchange between $Mo[P(OCH_3)_3]_6$ and $P(OC_2H_5)_3$ to give $Mo[P(OCH_3)_3]_5P(OC_2H_5)_3$ was only 10% complete within 24 h at 20 °C.

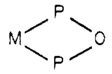
[40] These included $Mo[P(OCH_3)_3]_5CO$, $Mo[P(OCH_3)_3]_4(CO)_2$, $Mo[P(OCH_3)_3]_3(CO)_3$, $Mo[P(OCH_3)_3]_5NO^+$, $Mo[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$, $W[P(OCH_3)_3]_5CO$, $W[P(OCH_3)_3]_4(CO)_2$, $W[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$, $HRe[P(OCH_3)_3]_5$, $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$, and $HRe[P(OCH_3)_3]_4CO$. The $M[P(OCH_3)_3]_6$ are also presumed to be relatively stereochemically rigid, but there was no NMR probe for intramolecular ligand exchange in these presumed octahedral species.

[41] Wreford, S. S.; Kouba, J. K.; Kirner, J. F.; Muetterties, E. L.; Tavanaiepour, I.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1558.

[42] Program 65, Quantum Chemistry Program Exchange, Indiana University; cf. Bushweller, C. H.; Bhat, G.; Letendre, L. J.; Brunelle, J. A. Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65.

dominant exchange mechanism between the molybdenum and tungsten complexes. Pairwise exchange as observed for the tungsten complex is consistent with previously proposed idealized pathways based on the interconversion of pentagonal-bipyramidal, capped octahedral, and capped trigonal prismatic geometries.[43,44]

The Chelate $(CH_3O)_2POP(OCH_3)_2$ Ligand. To our knowledge, tetramethyl diphosphite has never been described in the literature either as the free molecule or as a ligand in a transition-metal complex although the closely related diphosphite $(C_2H_5O)_2POP(OC_2H_5)_2$ has been prepared and utilized to prepare transition-metal complexes in which the diphosphite serves as a bridging ligand between two metal atoms.[45-47] All the $(CH_3O)_2POP(OCH_3)_2$ derivatives of molybdenum, tungsten, and rhenium described in this article have been colored—brown for the first two metals and purple for $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$—whereas the strict "per" trimethyl phosphite analogues were colorless. Apparently, the presence of the four-membered cycle introduces electronic or steric features whereby electronically excited states are readily accessible by thermal activation.[48]



We presently seek a direct synthesis of the diphosphite to enable a more detailed study of the chelate chemistry.

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Registry No. $Mo[P(OCH_3)_3]_6$, 37478-27-6; $W[P(OCH_3)_3]_6$, 73411-63-9; $H_2Mo[P(OCH_3)_3]_5$, 79815-40-0; $H_4Mo[P(OCH_3)_3]_4$, 79803-06-8; $H_2W[P(OCH_3)_3]_5$, 73411-64-0; $H_4W[P(OCH_3)_3]_4$, 73460-89-6; $Mo[P(OCH_3)_3]_5(CO)$, 37478-26-5; $W[P(OCH_3)_3]_5(CO)$, 37478-28-7; *trans*-$Mo[P(OCH_3)_3]_4(CO)_2$, 79854-39-0; *trans*-$W[P(OCH_3)_3]_4(CO)_2$, 79854-40-3; *mer*-$Mo[P(OCH_3)_3]_3(CO)_3$, 15631-23-9; $Mo[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$, 79803-07-9; $W[P(OCH_3)_3]_4[(CH_3O)_2POP(OCH_3)_2]$, 79803-08-0; $Mo[P(OCH_3)_3]_5(NO)^+$, 79803-09-1; $Mo[P(OCH_3)_3]_3(NO)_2$, 79803-10-4; $\{W[P(OCH_3)_3]_5[P(OCH_3)_2]^+\}(CF_3COO^-)$, 79803-12-6; $HW[P(OCH_3)_3]_4(O_2CCF_3)$, 79815-39-7; $HW[P(OCH_3)_3]_6^+$, 79803-13-7; $H_2W[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$, 79803-14-8; $Re_2[(P(OCH_3)_3]_{10}$, 76281-32-8; $HRe[P(OCH_3)_3]_5$, 76428-28-9; $Re[P(OCH_3)_3]_5[P(O)(OCH_3)_2]$, 79815-41-1; $HRe[P(OCH_3)_3]_3[(CH_3O)_2POP(OCH_3)_2]$, 79803-15-9; $H_3Re[P(OCH_3)_3]_4$, 79803-16-0; $H_2Re[P(OCH_3)_3]_5^+$, 79803-17-1; $H_2Re[P(OCH_3)_3]_3(O_2CCF_3)$, 79803-18-2; *trans*-$HRe[P(OCH_3)_3]_4(CO)$, 79803-19-3; $MoCl_5$, 10241-05-1; WCl_6, 13283-01-7; $ReCl_5$, 13596-35-5; $MoOCl_3(NC_5H_5)_3$, 79803-20-6; $MoCl_4(OC_4H_8)_2$, 16998-75-7; $WOCl_3(NC_5H_5)_3$, 79803-21-7; $ReCl_4(NC_5H_5)_4$, 79803-22-8; $ReOCl_3(NC_5H_5)_2$, 18195-83-0; CF_3COOH, 76-05-1.

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(44) As discussed in ref 41, the geometry of the molybdenum complex can be considered as a hydride (equatorial) edge capped trigonal bipyramid if the trifluoroacetic ligand is treated as a unidentate ligand. In this structural approximation of a trigonal-bipyramidal pseudo-five-coordinate species with axial and equatorial sets of phosphorus ligands, the expected polytopal rearrangement involving a square-pyramidal intermediate or transition state would also be a pairwise exchange process.

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Reaction of Bicyclo[3.2.1]octa-2,6-diene with 1,2,4-Triazoline-3,5-diones: Competitive Dipolar and Homocycloaddition

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Contribution from the Institute of Organic Chemistry, University of Würzburg, D-8700 Würzburg, Am Hubland, West Germany, the Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931, and the Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, West Germany. *Received February 2, 1981. Revised Manuscript Received July 13, 1981*

Abstract: The nonconjugated bicyclo[3.2.1]octa-2,6-diene (**1**) affords with 1,2,4-triazolin-3,5-diones the homocycloadducts **6**. An X-ray structure determination confirms cyclopropane formation as the preferred mode of homoreactivity. Dipolar cycloaddition takes place both at the C_2–C_3 and the C_6–C_7 sites, leading to the rearranged urazoles **7** and **8** (major product), respectively. As expected, attack at the more strained double bond (C_6–C_7 attack) predominates. Ene reactions and [2 + 2] cycloadditions are not observed. The urazoles **6–8** have been converted to their respective azoalkanes **10–12** via oxidative hydrolysis.

Bicyclo[3.2.1]octa-2,6-diene (**1**) should be an interesting and useful substrate for exploring competitive cycloaddition behavior in view of its great diversity in possible reaction modes with dienophiles. Although [2 + 4] cycloaddition is not possible since **1** is a nonconjugated diene, it could undergo [2 + 2], ene, homo, and dipolar reactions with suitable dienophiles (Figure 1). When triazolinediones (TAD) are used as dienophiles, these various cycloaddition modes would afford a maximum of nine products, i.e., urazoles **2–9**. For example, [2 + 2] cycloadditions[1] at the

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