Redox Chemistry of Hexakis(phenyl isocyanide) Complexes of Molybdenum and Tungsten: The Synthesis of the Seven-Coordinate Cations $[M(CNPh)_7]^{2+}$ and Their Electrochemistry and Substitution Reactions

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The reactions of the quadruply bonded tungsten complexes $W_2(mhp)_4$ and $W_2(dmhp)_4$ (mhp and dmhp are the anions of 2-hydroxy-6-methylpyridine and 2,4-dimethyl-6-hydroxypyrimidine, respectively) with excess phenyl isocyanide lead to reductive cleavage of the metal–metal bond and the formation of $W(CNPh)_6$. Oxidation of $M(CNPh)_6$ (M = Mo or W) with Ag^+ in the presence of free phenyl isocyanide yields the first examples of seven-coordinate, homoleptic aryl isocyanide complexes of molybdenum(II) and tungsen(II), $[M(CNPh)_7](PF_6)_2$. Oxidation of $M(CNPh)_6$ is also observed with I_2 and $NOPF_6$, reactions which yield $[M(CNPh)_6I]^+$ and $[M(NO)(CNPh)_5]PF_6$, respectively. The reactions of $[M(CNPh)_7]^{2+}$ (M = Mo or W) with a variety of mono- or bidentate phosphines generate seven-coordinate mixed-ligand cations of the types $[M(CNPh)_6(PR_3)]^{2+}$, $[M(CNPh)_5(PR_3)_2]^{2+}$, $[M(CNPh)_5(dppm)]^{2+}$, and $[M(CNPh)_5(dppe)]^{2+}$, where dppm = bis(diphenylphosphino)methane and dppe = 1,2-bis(diphenylphosphino)ethane. The cyclic voltammograms of these seven coordinate complexes are characterized by a single one-electron oxidation between +0.9 and +1.5 V and an irreversible two-electron reduction close to −1.0 V. Reduction of $[M(CNPh)_7]^{2+}$ with magnesium regenerates the six-coordinate homoleptic complexes $M(CNPh)_6$. Spectroscopic characterization of these complexes have included measurement of their ^1H NMR, IR, and electronic absorption spectra.

Introduction

The fission of metal–metal multiple bonds by π-acceptor ligands such as CO and NO and alkyl and aryl isocyanides is well documented.[1–10] One of the interesting features within this class of ligand induced cleavage reactions is the difference which exists between alkyl and aryl isocyanides in their reactions toward quadruply bonded dinuclear complexes such as $Cr_2(O_2CCH_3)_4$,[5] $Mo_2(O_2CCH_3)_4$,[6] and $W_2(mhp)_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine).[7] In the case of alkyl isocyanides, nonreductive cleavage yields the seven-coordinate cations $[M(CNR)_7]^{2+}$ (where M = Mo or W; R = CH_3, CMe_3, or C_6H_{11}), whereas for aryl isocyanide, reductive cleavage has been found to produce the six-coordinate complexes $M(CNAr)_6$ (where M = Cr or Mo). The formation of $Cr(CNPh)_6$ and $Mo(CNPh)_6$ by this latter procedure constitutes the most convenient synthetic route to these complexes.

In spite of the strong tendency for reductive cleavage to occur in the presence of ArNC ligands, it seemed to us that this should not preclude the formation of salts containing the seven-coordinate phenyl isocyanide cations $[M(CNPh)_7]^{2+}$. Following our discovery of a convenient preparation of $W(CNPh)_6$ we have now devised routes to $[Mo(CNPh)_7](PF_6)_2$ and $[W(CNPh)_7](PF_6)_2$ through the oxidation of $M(CNPh)_6$ in the presence of excess phenyl isocyanide. In the present report we describe these results along with details of the spectroscopic and electrochemical properties of these new compounds and their substitution chemistry. Preliminary details of certain of these results have been reported previously.[8]

Experimental Section

Starting Materials. The following compounds were prepared by standard literature procedures: $Mo(CNPh)_6$,[6] $W_2(mhp)_4$,[11] $W_2(dmhp)_4$,[12] and PhNC.[13] All monodentate and bidentate phosphines, 2-hydroxy-6-methylpyridine (Hmhp), 2,4-dimethyl-6-hydroxypyrimidine (Hdmhp), and other reagents and solvents were obtained from commercial sources. Solvents were of the highest purity commercially available and were used without further purification with the exception of acetone, which was dried over $CaSO_4$, and tetrahydrofuran, which was distilled from sodium benzophenone. Potassium hexafluorophosphate was recrystallized from aqueous solution. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was obtained by reacting tetra-*n*-butylammonium iodide with KPF_6 in hot water. The product was recrystallized from aqueous ethanol and dried in vacuo.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere, and all solvents were deoxygenated prior to use by purging with N_2 gas.

A. Preparation of $W(CNPh)_6$ from Quadruply Bonded Tungsten(II) Complexes. (i) $W_2(dmhp)_4$ (dmhp Is the Anion of 2,4-Dimethyl-6-hydroxypyrimidine). A quantity of $W_2(dmhp)_4$ (0.60 g, 0.70 mmol) was added with stirring to 25 mL of methanol which was cooled to −20 °C in a dry ice bath. To this was added an excess (10:1) of phenyl isocyanide. The resulting reaction mixture was stirred for 1 h and filtered and the resulting red solid washed sparingly with ethanol. The product was then dissolved in benzene and the solution passed through an alumina

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column using benzene as the eluant. This procedure was carried out in the dark to avoid photodecomposition. The solvent was removed under a stream of N_2, and red crystals of the complex were isolated; yield 0.30 g (27%). Anal. Calcd for $C_{42}H_{30}N_6W$: C, 62.85; H, 3.76. Found: C, 63.09; H, 3.80.

(ii) $W_2(mhp)_4$ (mhp Is the Anion of 2-Hydroxy-6-methylpyridine). A quantity of $W_2(mhp)_4$ (0.421 g, 0.52 mmol) was reacted by using a procedure analogous to that described in A(i); yield 0.24 g (29%). The resulting red crystals had the same spectroscopic properties as those of the sample of $W(CNPh)_6$ prepared in A(i).

B. Oxidation Reactions of $Mo(CNPh)_6$. (i) $[Mo(NO)(CNPh)_5]PF_6$. A quantity of $Mo(CNPh)_6$ (0.2 g, 0.28 mmol) was dissolved in 30 mL of freshly distilled tetrahydrofuran. Slightly more than a stoichiometric amount of $NOPF_6$ (0.06 g, 0.34 mmol) was added to the stirred solution via a side arm addition tube. The color of the solution changed immediately from bright red to dark purple. A small volume (10 mL) of deoxygenated hexane was then added to the reaction vessel. The dark purple solid which formed was collected, washed well with diethyl ether, and dried in vacuo; yield 0.20 g(90%). Anal. Calcd for $C_{35}H_{25}F_6MoN_6OP$: C, 53.44; H, 3.21; N, 10.69. Found: C, 53.11; H, 3.45; N, 10.78.

After removal of the dark purple product by filtration, the filtrate was taken to dryness. Recrystallization of the residue from acetone–diethyl ether yielded a small quantity of $[Mo(CNPh)_7](PF_6)_2$ as fine yellow needles; yield 0.029 g (9%). Anal. Calcd for $C_{49}H_{35}F_{12}MoN_7P_2$: C, 53.12; H, 3.19; N, 8.85. Found: C, 53.32; H, 3.41; N, 8.59. A higher yield synthesis of this complex is described in B(iv).

(ii) $[Mo(CNPh)_6I]PF_6$. A dichloromethane solution of iodine (0.180 g, 0.71 mmol) was added dropwise to a stirred dichloromethane solution of $Mo(CNPh)_6$ (0.5 g, 0.70 mmol). The color of the solution changed gradually from bright red to orange during this addition. Potassium hexafluorophosphate (0.25 g, 1.36 mmol) dissolved in acetone was then added to the reaction vessel. The solvent was removed under a stream of N_2, and the resulting solid residue was dissolved in benzene. Upon the addition of petroleum ether bright orange crystals separated. The product was washed well with water, 2-propanol, and diethyl ether and dried in vacuo; yield 52%. Anal. Calcd for $C_{42}H_{30}F_6IMoN_6P$: C, 51.13; H, 3.07; N, 8.52. Found: C, 50.89; H, 3.31; N, 8.34.

(iii) $[Mo(CNPh)_6I]BPh_4$. This complex was prepared in a manner similar to that of its analogous PF_6^- salt, except that an acetone solution of $NaBPh_4$ (0.4 g, 1.17 mmol) was added following the iodine oxidation. The addition of an excess of diethyl ether induced precipitation of the desired product. The orange solid was recrystallized from acetone–diethyl ether, washed well with ethanol and diethyl ether, and dried in vacuo; yield 79%. Anal. Calcd for $C_{66}H_{50}BIMoN_6$: C, 68.28; H, 4.35; N, 7.24. Found: C, 68.38; H, 4.35; N, 7.26.

(iv) $[Mo(CNPh)_7](PF_6)_2$. A mixture of $Mo(CNPh)_6$ (0.30 g, 0.42 mmol), $AgNO_3$ (0.17 g, 1.0 mmol), and KPF_6 (0.17 g, 0.92 mmol) was added to a 100-mL round-bottom flask followed by 25 mL of acetone and immediately thereafter 0.5 mL of phenyl isocyanide. The contents of the reaction flask were stirred at room temperature for 3 h in the dark. The reaction mixture was then filtered and diethyl ether added to the filtrate until precipitation of a yellow crystalline solid occurred. This was filtered off and washed successively with water, 2-propanol, and diethyl ether. Recrystallization was carried out by dissolving the product in acetone followed by the careful addition of diethyl ether; yield 0.33 g (71%). Anal. Calcd for $C_{49}H_{35}F_{12}MoN_7P_2$: C, 53.12; H, 3.19; N, 8.85. Found: C, 53.32; H, 3.32; N, 8.78.

Workup of the reaction filtrate afforded a small quantity of the nitrosyl derivative $[Mo(NO)(CNPh)_5]PF_6$ (yield less than 10%). Proof of its identity as the same complex as that prepared in B(i) was established by its spectroscopic and electrochemical properties.

C. Oxidation Reactions of $W(CNPh)_6$. (i) $[W(NO)(CNPh)_5]PF_6$. A quantity of $W(CNPh)_6$ (0.2 g, 0.249 mmol) was dissolved in 30 mL of acetone and a solution of $NOPF_6$ (0.044 g, 0.25 mmol) in acetone or dichloromethane (15 mL) added dropwise. This mixture was stirred for 45 min and diethyl ether than added to precipitate the purple product; yield 0.161 g (74%). Anal. Calcd for $C_{35}H_{25}F_6N_6OPW$: C, 48.07; H, 2.88; N, 9.61. Found: C, 47.92; H, 2.87; N, 9.50.

(ii) $[W(CNPh)_6I]BPh_4$. A quantity of $W(CNPh)_6$ (0.20 g, 0.249 mmol) was dissolved in dichloromethane (30 mL). To this stirred solution was added dropwise a dichloromethane solution containing iodine (0.063 g, 0.248 mmol). A similar procedure was followed to that described in B(iii); yield 0.217 g (70%). Anal. Calcd for $C_{66}H_{50}BIN_6W$: C, 63.47; H, 4.04. Found: C, 63.67; H, 4.21.

(iii) $[W(CNPh)_7](PF_6)_2$. A mixture of $W(CNPh)_6$ (0.700 g, 0.87 mmol), powdered $AgNO_3$ (0.30 g, 1.77 mmol), KPF_6 (0.33 g, 1.79 mmol), and phenyl isocyanide (~0.3 mL) was reacted in 30 mL of acetone in an analogous procedure to that described in B(iv); yield 0.72 g (69%). Anal. Calcd for $C_{49}H_{35}F_{12}N_7P_2W$: C, 49.24; H, 2.92; N, 8.20. Found: C, 49.06; H, 3.04; N, 7.95.

Workup of the reaction filtrate in a manner similar to B(iv) afforded a small crop of purple $[W(NO)(CNPh)_6]PF_6$ (yield <10%). Its identity as the same complex as that prepared in C(i) was established by its spectroscopic and electrochemical properties.

D. Interconversions between $[Mo(CNPh)_6X]PF_6$ (X = Halide) and $[Mo(CNPh)_7](PF_6)_2$. (i) The Preparation of $[Mo(CNPh)_6Cl]PF_6$. A mixture of $[Mo(CNPh)_6I]PF_6$ (0.28 g, 0.28 mmol) and LiCl (0.20 g, 4.7 mmol) was stirred and heated in ethanol for 20 min. The contents of the reaction flask were then cooled and filtered, and an orange solid was collected. This was washed several times with diethyl ether; yield 0.10 g (40%). The product was identified by its spectroscopic and electrochemical properties.

With an analogous procedure, the chloro derivative $[Mo(CNPh)_6Cl]PF_6$ was also prepared by the reaction of $[Mo(CNPh)_7](PF_6)_2$ with LiCl; yield 72%.

(ii) The Conversion of $[Mo(CNPh)_6Cl]PF_6$ to $[Mo(CNPh)_7](PF_6)_2$. A mixture of $[Mo(CNPh)_6Cl]PF_6$ (0.1 g, 0.11 mmol), KPF_6 (0.40 g, 2.2 mmol), and phenyl isocyanide (0.3 mL, 3.2 mmol) was stirred in ethanol at room temperature for 6 h. During this period the solution color changed from a yellow-orange to green. A yellow solid (0.10 g) was isolated upon filtering the reaction mixture and was washed successively with water, 2-propanol, and diethyl ether and dried in vacuo; yield 81%. Its identity as a pure sample of $[Mo(CNPh)_7](PF_6)_2$ was confirmed by using infrared spectroscopy and cyclic voltammetry.

E. Reactions of $[Mo(CNPh)_7](PF_6)_2$ with Phosphines and Phosphites. (i) $[Mo(CNPh)_5(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$. To a stirred slurry of $[Mo(CNPh)_7](PF_6)_2$ (0.18 g, 0.16 mmol) in ethanol was added tri-*n*-propylphosphine (0.6 mL, 3.0 mmol) under a nitrogen atmosphere. The solution was stirred at room temperature for 96 h, and the canary yellow solid was collected by filtration. The solid was washed well with diethyl ether and dried in vacuo. Recrystallization was accomplished by using an acetone–diethyl ether mixture; yield 0.058 g (30%). Anal. Calcd for $C_{53}H_{67}F_{12}MoN_5P_4$: C, 52.09; H, 5.53; N, 5.73. Found: C, 51.55; H, 4.94; N, 5.73.

(ii) $[Mo(CNPh)_5(PEt_3)_2](PF_6)_2$. Ethanol (30 mL) was added to $[Mo(CNPh)_7](PF_6)_2$ (0.30 g, 0.27 mmol), and the resulting solution was stirred and treated with an excess of triethylphosphine (0.50 mL, 3.4 mmol). When the solution was heated to just below boiling its color changed from yellow to dark brown. After 20 min the reaction mixture was cooled to room temperature and filtered. A canary yellow solid was collected, washed well with diethyl ether, and dried in vacuo. The product was recrystallized from an acetone–diethyl ether mixture; yield 0.20 g (65%). Anal. Calcd for $C_{47}H_{55}F_{12}MoN_5P_4$: C, 49.61; H, 4.88; N, 6.16. Found: C, 49.44; H, 4.78; N, 5.84.

(iii) $[Mo(CNPh)_5(PEt_2Ph)_2](PF_6)_2$. This complex was prepared in a manner similar to E(i); yield 83%. Anal. Calcd for $C_{55}H_{55}F_{12}MoN_5P_4$: C, 53.53; H, 4.50; N, 5.68. Found: C, 52.88; H, 4.70; N, 5.52.

(iv) $[Mo(CNPh)_5(PEtPh_2)_2](PF_6)_2$. This complex was prepared by using a procedure analogous to that used in E(ii). The yellow complex was recrystallized from an acetone–diethyl ether mixture; yield 60%. Anal. Calcd for $C_{63}H_{55}F_{12}MoN_5P_4$: C, 56.89; H, 4.18; N, 5.27. Found: C, 56.83; H, 4.04; N, 5.40.

(v) $[Mo(CNPh)_6(PPh_3)](PF_6)_2$. This monodentate phosphine derivative was prepared by reacting $[Mo(CNPh)_7](PF_6)_2$ (0.32 g, 0.29 mmol) with triphenylphosphine (0.40 g, 1.52 mmol). The reactants were dissolved in tetrahydrofuran and refluxed with stirring for 6 h. The color of the solution changed quickly from orange to a brilliant red and then more slowly to an orange-brown.

After the mixture was cooled to room temperature, the product was precipitated from solution as orange crystals by the addition of diethyl ether; yield 71%. Anal. Calcd for $C_{60}H_{45}F_{12}MoN_6P_3$: C, 56.88; H, 3.59; N, 6.63. Found: C, 56.61; H, 3.73; N, 6.35.

(vi) $[Mo(CNPh)_5(P(OEt)_3)_2](PF_6)_2$. This yellow complex was obtained by a procedure analogous to that used in E(v); yield 60%. ^1H NMR spectroscopy confirmed the stoichiometry of the complex.

(vii) $[Mo(CNPh)_5(dppe)](PF_6)_2$. $[Mo(CNPh)_7](PF_6)_2$ (0.19 g, 0.17 mmol) was reacted with 1,2-bis(diphenylphosphino)ethane (0.25 g, 0.63 mmol) in 25 mL of absolute ethanol under reflux conditions. The solution color changed from yellow to orange as the reaction progressed. After a 30-min reflux period the heat was removed and the reaction vessel allowed to cool to room temperature. Filtration yielded an orange solid which was washed well with diethyl ether and dried in vacuo; yield 55%. Anal. Calcd for $C_{61}H_{49}F_{12}MoN_5P_4$: C, 56.36; H, 3.81; N, 5.39. Found: C, 55.93; H, 4.42; N, 5.54.

(viii) $[Mo(CNPh)_5(dppm)](PF_6)_2$. This complex was prepared by combining $[Mo(CNPh)_7](PF_6)_2$ and bis(diphenylphosphino)methane in 30 mL of absolute ethanol. The solution was refluxed and stirred for 1 h. During this time the solution color changed from yellow to orange to a dark orange-brown. The reaction mixture was cooled to room temperature and filtered to yield an orange solid. The product was washed well with diethyl ether and dried in vacuo; yield 0.32 g (59%). Anal. Calcd for $C_{60}H_{47}F_{12}MoN_5P_4$: C, 56.04; H, 3.69; N, 5.45. Found: C, 55.84; H, 3.60; N, 5.48.

F. Reactions of $[W(CNPh)_7](PF_6)_2$ with Phosphines. (i) $[W(CNPh)_5(PEt_3)_2](PF_6)_2$. A quantity of $[W(CNPh)_7](PF_6)_2$ (0.19 g, 0.16 mmol) was reacted with triethylphosphine (0.6 mL, 4.06 mmol) by using a procedure analogous to that described in E(ii); yield 0.15 g (77%). The purity and stoichiometry of the compound were confirmed by using cyclic voltammetry and ^1H NMR spectroscopy.

(ii) $[W(CNPh)_5(PEtPh_2)_2](PF_6)_2$. A procedure analogous to that used in E(iv) was employed; yield 75%. The purity and stoichiometry of the compound were confirmed using cyclic voltammetry and ^1H NMR spectroscopy.

(iii) $[W(CNPh)_6(PPh_3)](PF_6)_2$. The reaction between $[W(CNPh)_7](PF_6)_2$ (0.2 g, 0.17 mmol) and triphenylphosphine (0.2 g, 0.76 mmol) was performed in a manner analogous to that described in E(v), except the reaction was carried out for 7 days; yield 0.163 g (72%). This complex can be recrystallized from acetone–diethyl ether mixtures. Anal. Calcd for $C_{60}H_{45}F_{12}N_6P_3W$: C, 53.19; H, 3.34. Found: C, 51.99; H, 3.30.

(iv) $[W(CNPh)_5(dppe)](PF_6)_2$. Using a procedure analogous to that used in the preparation of E(vii) yielded this complex as bright orange needles; yield 58%. Anal. Calcd for $C_{61}H_{49}F_{12}N_5P_4W$: C, 52.78; H, 3.56. Found: C, 52.24; H, 3.45.

G. Reduction of the Seven-Coordinate Molybdenum(II) and Tungsten(II) Species $[M(CNPh)_7](PF_6)_2$ to $M(CNPh)_6$. (i) $Mo(CNPh)_6$. The reduction of $[Mo(CNPh)_7](PF_6)_2$ to $Mo(CNPh)_6$ was accomplished by stirring a mixture of the starting material (1.0 mmol) with magnesium metal (2.0 mmol) (activated with 1,2-dibromoethane) in tetrahydrofuran. As the reaction progressed, the solution changed color from yellow to a dark brown. After the contents of the reaction vessel had been stirred for several hours, they were filtered and absolute ethanol was added to the filtrate. This precipitated the complex $Mo(CNPh)_6$; yield 80%. The identity of this complex was confirmed by a comparison of its spectroscopic and electrochemical properties with those of an authentic sample.

(ii) $W(CNPh)_6$. A procedure analogous to that in G(i) was used although it was essential that only a stoichiometric amount of the magnesium reducing agent was used. After complete reduction of the $[W(CNPh)_7](PF_6)_2$, the reaction mixture was added to an alumina column and eluted with deoxygenated benzene. Exposure to light was minimized during the entire process. The solvent was slowly removed from the orange eluate under a stream of N_2. The red crystalline solid was collected, washed with ethanol, and dried in vacuo; yield 0.3 g (70%). Its identity was confirmed by its spectroscopic and electrochemical properties.

H. Reduction Reactions of $[Mo(CNPh)_5(dppe)](PF_6)_2$ and $[Mo(CNPh)_5(PEtPh_2)_2](PF_6)_2$. The procedures used for reducing these two complexes were essentially the same so details are reported only for the dppe derivative. Magnesium metal (0.09 g, 3.7 mmol) (40 mesh) was added to a three-neck round bottom flask under a nitrogen atmosphere. Freshly distilled tetrahydrofuran (30 mL) was added via a cannula followed by 1,2-dibromoethane (0.15 mL, 1.7 mmol). After this mixture was stirred for 15 min, a second aliquot of 1,2-dibromoethane was added producing an immediate effervescence, thereby signaling the activation of the magnesium surface. The complex $[Mo(CNPh)_5dppe](PF_6)_2$ (0.225 g, 0.196 mmol) was added via a side arm addition tube and the resulting mixture stirred at room temperature in the dark for 4 h. The reaction mixture was then chromatographed on alumina and the orange band eluted by using benzene. The chromatography was conducted under oxygen-free conditions with minimal exposure to direct light. The orange eluate was collected from the column and the solvent removed under a stream of N_2. The resulting oil was treated with ethanol to help separate the red crystalline solid which was collected on a sintered frit and dried in vacuo; yield 0.089 g (50%). The product, which was very air sensitive, was formulated as $Mo(CNPh)_4(dppe)$ by using IR and ^1H NMR spectroscopy and cyclic voltammetry. A similar procedure when used to reduce $[Mo(CNPh)_5(PEtPh_2)_2](PF_6)_2$ afforded a red oil which we were unable to crystallize. This was characterized by using IR and ^1H NMR spectroscopy but the presence of contaminants precluded a definitive structural assignment.

Physical Measurements. Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded on dichloromethane solutions using a Varian series 634 spectrophotometer. Nuclear magnetic resonance spectra were recorded in acetone-d_6 with tetramethylsilane (Me_4Si) as an internal reference using a Perkin-Elmer R-32 90 MHz NMR spectrometer.

Electrochemical measurements were made on dichloromethane and acetonitrile solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) are referenced to the saturated potassium chloride calomel electrode (SCE) at 22 ± 2 °C and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed by using a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems Inc. Values of n, where n is the total number of equivalents of electrons transferred in exhaustive electrolysis at constant potentials, were calculated after measuring the total area under current vs. time curves for the complete reaction. The reactions were judged to be complete when the current had fallen below 1% of the initial value. Alternatively, values of n could be estimated by comparing the peak currents with the ferrocene–ferricinium couple with those arising from an equimolar solution of the complex of interest. All voltammetric measurements were made at a platinum bead electrode in solutions deaerated into a stream of dry nitrogen.

Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

As a consequence of our studies on the cleavage reactions of dinuclear complexes containing metal–metal multiple bonds, we have been able to develop a new synthetic route to $W(CNPh)_6$. The reductive cleavage of $W_2(dmhp)_4$ (dmhp is the anion of 2,4-dimethyl-6-hydroxypyrimidine) and $W_2(mhp)_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine) by phenyl isocyanide proceeds in a yield of ca. 30% which, while rather low, is still superior to that reported in existing procedures.[6,14] Furthermore, our method is convenient and quick and would seem, at least for the time being, to offer the easiest route to $W(CNPh)_6$. Thus, it is clear that like chromium and molybdenum

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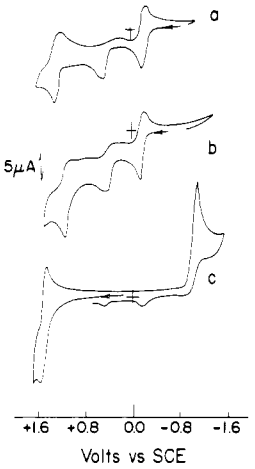

Figure 1. Cyclic voltammograms in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane of (a) Mo(CNPh)$_6$, (b) W(CNPh)$_6$, and (c) [Mo(CNPh)$_7$](PF$_6$)$_2$. Sweep rates for a and b are 200 mV/s and for c 300 mV/s, respectively.

quadruply bonded species, tungsten complexes containing the W_2^{4+} core are no exception to the general rule that alkyl and aryl isocyanides bring about facile cleavage of the metal–metal bond.[15]

Electrochemical and Chemical Oxidations of M(CNPh)$_6$ (M = Mo or W). With a ready source of W(CNPh)$_6$ and the availability of Mo(CNPh)$_6$ through the related reductive cleavage of $Mo_2(O_2CCH_3)_4$, we have carried out a study of the redox chemistry of these two homoleptic zerovalent metal complexes. Surprisingly, the electrochemical properties of these two complexes have not previously been reported, although photoredox reactions have been shown to occur when chloroform solutions of M(CNPh)$_6$ (M = Cr, Mo or W) are irradiated at 436 nm.[16,17] The resulting photo-oxidation products are the seven-coordinate cations [M(CNPh)$_6$Cl]$^+$. With the more sterically hindered M(CNIph)$_6$ derivatives (Iph = 2,6-diisopropylphenyl) photooxidation terminates at the [M(CNIph)$_6$]$^+$ stage.[16,17]

In contrast to the well-defined electrochemical processes which characterize the cyclic voltammograms for the chromium(0) aryl isocyanide derivatives Cr(CNAr)$_6$ (corresponding to the redox sequence [Cr]$^{3+}$ ← [Cr]$^{2+}$ ← [Cr]$^+$ ← [Cr]^0),[18] the CV's of Mo(CNPh)$_6$ and W(CNPh)$_6$ are significantly more complex (Figure 1). With 0.2 M Bu_4NPF_6 as supporting electrolyte, dichloromethane solutions of Mo(CNPh)$_6$ exhibit a reversible one-electron oxidation (n = 1.0 ± 0.1 by coulometry) at $E_{1/2}$ = −0.19 V vs. SCE. With switching potentials of +0.3 and −0.8 V, this couple is characterized by $i_{p,c}/i_{p,a}$ = 1 and $E_{p,a} - E_{p,c}$ ≃ 60 mV and the $i_p/v^{1/2}$ ratio was found to be constant for sweep rates (v) between 50 and 400 mV/s, in accord with diffusion control. A second oxidation at $E_{p,a}$ = +0.48 V vs. SCE (v = 200 mV/s) is irreversible and is followed by a chemical step in which an unidentified product ($E_{1/2}$ = +1.28 V vs. SCE) is formed (i.e., by an EEC mechanism). In the case of W(CNPh)$_6$ the corresponding oxidations are at $E_{1/2}$ = −0.18 V and $E_{p,a}$ = +0.44 V. However, the chemical product which is formed following the oxidation to [W(CNPh)$_6$]$^{2+}$ is characterized by a less reversible couple ($E_{p,a}$ = +1.16 V, $i_{p,c}/i_{p,a} \ll 1$) than is the case with the analogous molybdenum system (Figure 1).[19]

Bulk electrolysis of the Mo(CNPh)$_6$ solution at +0.6 V (i.e., positive of the irreversible oxidation) produced a lemon yellow solution whose CV displayed an oxidation wave at $E_{1/2}$ = +1.41 V and an irreversible reduction at $E_{p,c}$ = −1.12 V. In addition, another couple at $E_{1/2}$ ≃ 1.0 V showed that a second product was present which, on the basis of peak currents, was obviously a minor component of the system. From these results it was apparent that the chemical product ($E_{1/2}$ ≃ +1.2 V) which forms following the electrochemical oxidation of M(CNPh)$_6$ to [M(CNPh)$_6$]$^{2+}$ (Figure 1a) is itself sufficiently unstable that it cannot be obtained by bulk electrolysis. From a consideration of the known electrochemical properties of the seven-coordinate homoleptic alkyl isocyanide complexes [Mo(CNR)$_7$](PF$_6$)$_2$,[7] we felt that the species responsible for the electrochemical processes at $E_{1/2}$ = +1.41 V and $E_{p,c}$ = −1.12 V could be the seven-coordinate phenyl isocyanide cation [Mo(CNPh)$_7$]$^{2+}$.[20] Accordingly, we carried out a series of reactions aimed at the chemical oxidation of M(CNPh)$_6$ (M = Mo or W) to [M(CNPh)$_7$]$^{2+}$.

When $NOPF_6$ is added to a stirred solution of Mo(CNPh)$_6$ in tetrahydrofuran, there is an immediate color change from bright red to dark purple. Addition of hexane to the solution precipitates dark purple [Mo(NO)(CNPh)$_5$]PF$_6$ in very high yield. A comparable oxidation of W(CNPh)$_6$ produced the analogous [W(NO)(CNPh)$_5$]PF$_6$. By a careful workup of the filtrate from the reaction between Mo(CNPh)$_6$ and $NOPF_6$, we isolated a small crop of yellow needles which analyzed as the desired seven-coordinate complex [Mo(CNPh)$_7$](PF$_6$)$_2$. To optimize the yield of the latter complex, the presence of a mild oxidant, an excess of phenyl isocyanide, and an excess of hexafluorophosphate anion were judged to be necessary. Upon treating an acetone solution of Mo(CNPh)$_6$ with $AgNO_3$, KPF_6, and PhNC, we obtained [Mo(CNPh)$_7$](PF$_6$)$_2$ in 71% yield.[21] A comparable procedure was found to convert W(CNPh)$_6$ to [W(CNPh)$_7$](PF$_6$)$_2$ in yields close to 70%.

Undoubtedly, there are a variety of other oxidation procedures which will give similar results. However, the only other method we investigated involved the iodine oxidation of dichloromethane solutions of M(CNPh)$_6$. This afforded the orange cations [M(CNPh)$_6$I]$^+$ which could be crystallized as their PF_6^- or BPh_4^- salts. These new species are members of the class of molecules of the type [M(CNR)$_6$X]Y (X = halide, $SnCl_3^-$, or CN^-; Y = halide, PF_6^-, BPh_4^-, etc.) which was first prepared by Lippard and coworkers[22-24] and whose chemistry has been subsequently

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(19) The chemical product which is formed on the time scale of the cyclic voltammetry experiment and which is characterized by $E_{1/2}$ = +1.28 V in the case of Mo(CNPh)$_6$ and $E_{p,a}$ = +1.16 V for W(CNPh)$_6$ is not the mixed chloride–isocyanide species [M(CNPh)$_6$Cl]$^+$. Although this latter ion could conceivably be formed through reaction of [M(CNPh)$_6$]$^{2+}$ with the CH_2Cl_2 solvent, separate studies on the CV of authentic [Mo(CNPh)$_6$Cl]$^+$ have shown that the [Mo(CNPh)$_6$Cl]$^{+,2+}$ couple has an $E_{1/2}$ value of +0.99 V vs. SCE (see Table I).
(20) Our reasoning ran as follows. Since the $E_{1/2}$ value for the [Mo(CNR)$_7$]$^{2+,3+}$ couple (R = CH_3, CMe_3, or C_6H_{11}) is ≃+1.1 V vs. SCE, we would expect an $E_{1/2}$ value for [Mo(CNPh)$_7$]$^{2+,3+}$ which is appreciably greater than +1.1 V since PhNC is a better π acceptor than RNC and thus less able to stabilize the 3+ state. Paralleling this trend we would also anticipate that reduction of [Mo(CNPh)$_7$]$^{2+}$ would occur more readily than [Mo(CNR)$_7$]$^{2+}$. This expectation is realized by the appearance of a reduction wave at E_p = −1.1 V in the CV of the product which emanates from the irreversible electrochemical oxidation of Mo(CNPh)$_6$.
(21) Workup of the filtrate yielded a small crop of [Mo(NO)(CNPh)$_5$]PF$_6$ which is presumably formed through a secondary reaction involving reduction of the excess nitrate ion which is present.
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investigated quite extensively.[23-26] Accordingly, we have not carried out a detailed study of these cations other than noting the following two relevant points. First, reaction of $[Mo(CNPh)_6I]PF_6$ with the chloride ion results in halide exchange and the formation of $[Mo(CNPh)_6Cl]PF_6$. Second, reaction of the chloride complex with excess phenyl isocyanide produces $[Mo(CNPh)_7]^{2+}$, behavior which resembles that noted by Lippard[22,23,25] for the analogous alkyl isocyanide species (eq 1). Accordingly, we see here a close correspondence between the reaction chemistry of the analogous alkyl and aryl isocyanide derivatives.

$$[Mo(CNR)_6X]^+ + RNC \rightleftharpoons [Mo(CNR)_7]^{2+} + X^- \quad (1)$$

The identity of $[Mo(CNPh)_7](PF_6)_2$ as a genuine example of seven-coordinate molybdenum(II) has been established by a crystal structure determination, details of which will be reported elsewhere.[27]

A comparison of the CV of a dichloromethane solution of an authentic sample of $[Mo(CNPh)_7](PF_6)_2$ (Figure 1c) with the CV's of the solutions which are formed following the exhaustive electrolysis (at +0.6 V) of $Mo(CNPh)_6$ confirmed that this seven-coordinate cation is indeed present as a major product following the electrochemical oxidation of $Mo(CNPh)_6$. In addition to the one-electron oxidation $[Mo(CNPh)_7]^{2+} \rightarrow [Mo(CNPh)_7]^{3+} + e^-$ ($E_{1/2}$ = 1.41 V), there is an irreversible two-electron reduction at $E_{p,c}$ = −1.12 V in the CV of $[Mo(CNPh)_7](PF_6)_2$. The waves at $E_{p,a}$ = −0.18 V and $E_{p,a}$ = +0.44 V (Figure 1c) are due to the formation of $Mo(CNPh)_6$ following this reduction. This particular aspect of the redox chemistry of $[Mo(CNPh)_7](PF_6)_2$ and related species will be dealt with more fully later in the discussion. One final point of interest concerning a comparison between the CV's of $[Mo(CNPh)_7](PF_6)_2$ and the electrolyzed $Mo(CNPh)_6$ solutions is the presence of the additional couple at $E_{1/2} \simeq$ +1.0 V in the latter. We have ascertained that this is due to the formation of small amounts of $[Mo(CNPh)_6Cl]^+$ ($E_{1/2}$ = +0.99 V vs. SCE) through reaction of $[Mo(CNPh)_7]^{2+}$ with chloride ion which is generated at the auxiliary electrode and diffuses to the working electrode compartment.[28]

Acetonitrile solutions of $[Mo(CNPh)_7](PF_6)_2$ (0.2 M in Bu_4NPF_6) display similar electrochemical processes to those in dichloromethane (Table I), except that the oxidation at +1.4 V is now irreversible, no doubt due to reaction of $[Mo(CNPh)_7]^{3+}$ with the acetonitrile solvent. A dichloromethane solution of $[W(CNPh)_7](PF_6)_2$ displays very similar electrochemical behavior to that of its molybdenum analogue, with the reversible one-electron oxidation at $E_{1/2}$ = +1.32 V and the irreversible two-electron reduction at $E_{p,c}$ = −1.02 V vs. SCE (Table I).

The important features in the IR, ^1H NMR, and electronic absorption spectra of the complexes $[M(CNPh)_7](PF_6)_2$ (M = Mo or W), $[Mo(CNPh)_6X]PF_6$ (X = Cl or I), $[W(CNPh)_6I]BPh_4$, and $[M(NO)(CNPh)_5]PF_6$ (M = Mo or W) are presented by Table II and in all cases clearly serve to confirm the identity of these diamagnetic complexes through the similarity of their spectral properties to those of their alkyl isocyanide analogues $[M(CNR)_7]^{2+}$,[3,22,24] $[M(CNR)_6X]^+$,[22,24] (M = Mo or W; X = Cl or I), and $[Mo(NO)(CNR)_5]^+$.[29] The most noteworthy difference is the higher ν(NO) and lower ν(CN) frequencies in the IR spectra of $[M(NO)(CNPh)_5]^+$ (Table II) compared to those of the alkyl isocyanide derivatives $[Mo(NO)(CNR)_5]^+$.[29] This may be a further reflection of the better π-acceptor capabilities of PhNC relative to RNC.

Table I. Voltammetric Half-Wave Potentials for Phenyl Isocyanide Complexes of Molybdenum(II) and Tungsten(II)[a]

complex	$E_{1/2}$(ox)[b]	$E_{p,c}$(red)[b,c]
$[Mo(CNPh)_7](PF_6)_2$	+1.41	−1.12
	+1.40[d]	−1.06[d]
$[W(CNPh)_7](PF_6)_2$	+1.32	−1.02
$[Mo(NO)(CNPh)_5]PF_6$	+0.86	−1.72
	+1.02[d]	−1.43[d]
$[W(NO)(CNPh)_5]PF_6$	+0.85	−1.67
$[Mo(CNPh)_6Cl]PF_6$	+0.99	−1.44
$[Mo(CNPh)_6I]PF_6$	+1.06	−1.38
$[Mo(CNPh)_5(PEt_3)_2](PF_6)_2$	+1.27	−1.19
$[Mo(CNPh)_5(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$	+1.28	−1.22
$[Mo(CNPh)_5(PEt_2Ph)_2](PF_6)_2$	+1.29	−1.08
$[Mo(CNPh)_5(PEtPh_2)_2](PF_6)_2$	+1.30	−1.03
$[Mo(CNPh)_6(PPh_3)](PF_6)_2$	+1.43	−1.05
$[Mo(CNPh)_5(dppm)](PF_6)_2$	+1.31	−0.90
$[Mo(CNPh)_5(dppe)](PF_6)_2$	+1.34	−1.04
$[Mo(CNPh)_5(P(OEt)_3)_2](PF_6)_2$	+1.43	−1.18
$[W(CNPh)_5(PEt_3)_2](PF_6)_2$	+1.22	−1.14
$[W(CNPh)_5(PEtPh_2)_2](PF_6)_2$	+1.26	−1.04
$[W(CNPh)_5(dppe)](PF_6)_2$	+1.27	−1.12

[a] Measurements in CH_2Cl_2 with 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte unless stated otherwise. [b] Volts vs. SCE with a Pt-bead working electrode. [c] Values taken at a scan rate of 200 mV/s. [d] Measurements in CH_3CN.

The electrochemical properties of $[M(CNPh)_6X]^+$ (M = Mo or W) are similar to those of $[M(CNPh)_7]^{2+}$ in that the former complexes possess a reversible one-electron oxidation (n = 0.99 by coulometry for $[Mo(CNPh)_6I]PF_6$). However, the relevant $E_{1/2}$ values which characterize their CV's (Table I) are ~0.4 V less than those for the related oxidations of the homoleptic species, a trend which parallels that which has been found for the analogous pairs of alkyl isocyanide complexes $[M(CNR)_7]^{2+}$ vs. $[M(CNR)_6X]^{2+}$; the latter have $E_{1/2}$ values of $\simeq$ 1.1 and $\simeq$ 0.6 V, respectively.[7,28,30] The much lower electrode potentials of the halo derivatives (Table I) reflect the ability of halide ligands to better stabilize the higher oxidation states of molybdenum and tungsten in comparison to the phenyl isocyanide ligand.

The seven-coordinate aryl isocyanide complexes $[Mo(CNPh)_7](PF_6)_2$ and $[Mo(CNPh)_6X]PF_6$ (X = Cl or I) display three absorption bands in their electronic absorption spectra between 275 and 450 nm. These spectral features are reminiscent of those present in the related spectra of their alkyl isocyanide analogues[22,24] except that the absorptions for the alkyl isocyanide complexes occur at higher energies.

The 18-electron nitrosyl complexes $[M(NO)(CNPh)_5]PF_6$ exhibit electrochemical behavior which resembles qualitatively that of $[M(CNPh)_7]^{2+}$, namely, a one-electron oxidation (n = 0.92 by coulometry for M = Mo) and an irreversible reduction (Table I). The oxidation is much more accessible ($E_{1/2} \simeq$ +0.85 V vs. SCE) than that for either $[M(CNPh)_7]^{2+}$ or $[M(CNPh)_6X]^+$ but is strongly solvent dependent since an acetonitrile solution of [Mo-

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(30) Detailed studies have been undertaken of the dependence of the $E_{1/2}$ values for the $[M(CNR)_6X]^{+,2+}$ couple upon the nature of R and X (private communication from Professor S. J. Lippard). These results and their significance will be discussed in detail in due course.

Table II. Selected Spectroscopic Properties of Phenyl Isocyanide Complexes of Molybdenum(II) and Tungsten(II)

complex	^{1}H chem shifts in δ [a]			IR absorptns ν(C≡N),[b] cm^{-1}	electronic absorptn spectra,[c] nm
	alkyl	P(CH$_2$)$_n$P	phenyl		
[Mo(CNPh)$_7$](PF$_6$)$_2$			7.75 br, 7.60 m	2180 sh, 2170 sh, 2140 s 2140 s[f]	425 (4.5), 310 (61.1), 290 sh
[W(CNPh)$_7$](PF$_6$)$_2$			~7.70 br	2210 vw, 2170 sh, 2120 vs 2130 vs[f]	420 (7.7), 320 (65.0), 295 sh
[Mo(NO)(CNPh)$_5$]PF$_6$				2192 w, 2108 s, 1678 m[g] 2190 vw,[f] 2170 vw,[f] 2110 s,[f] 1680 m, br[f,g]	520 (1.4), 368 sh, 352 (41.0)
[W(NO)(CNPh)$_5$]PF$_6$				2195 w, 2160 w, 2090 vs, 1660 m[g]	528 (1.8), 375 sh, 360 (42.2)
[Mo(CNPh)$_6$Cl]PF$_6$				2130 s, 2100 s	440 sh, 320
[Mo(CNPh)$_6$I]PF$_6$				2195 w, 2110 s	438 sh, ~315 br
[W(CNPh)$_6$I]BPh$_4$				2190 w, ~2100 vs, br	450 sh, 335 sh, 310
[Mo(CNPh)$_5$(PEt$_3$)$_2$](PF$_6$)$_2$	2.48 m, 1.40 p		7.68 m	2130 sh, 2105 sh, 2075 s 2160 w,[f] 2090 s[f]	
[Mo(CNPh)$_5$(P-*n*-Pr$_3$)$_2$](PF$_6$)$_2$	2.33 m, 1.81 br, 1.00 t		7.68 m	2164 w, 2082 s	436 sh, 350 sh ?, 328 sh, 309
[Mo(CNPh)$_5$(PEt$_2$Ph)$_2$](PF$_6$)$_2$	2.80 m, 1.30 p		7.86 br, 7.52 m	2160 w, 2125 sh, 2092 s 2168 w,[f] 2098 s[f]	440–430 sh, 390 sh, 352 sh, 328 sh, 310
[Mo(CNPh)$_5$(PEtPh$_2$)$_2$](PF$_6$)$_2$	3.16 m, 1.31 p		7.78 br, 7.52 m, 7.24 m	2170 w, 2100 s	~430 sh, 353 sh, 325 (39.9)
[Mo(CNPh)$_6$(PPh$_3$)](PF$_6$)$_2$			7.80 br, 7.58 m	2195 w, 2170 sh, 2115 s 2190 w,[f] 2124 s, br[f]	438 sh, 376 sh, 326 sh
[Mo(CNPh)$_5$(dppm)](PF$_6$)$_2$		5.39 t[d]	7.95 br, 7.54 m, 7.33 m	2178 m, 2140 m-s, 2095 s	462, 386 sh, 342, 300
[Mo(CNPh)$_5$(dppe)](PF$_6$)$_2$		3.49 d[e]	7.93 br, 7.57 m, 7.29 m	2178 m-w, ~2140 sh, 2100 s 2170 m-w,[f] 2108 s[f]	425 sh, 344 sh, 307
[Mo(CNPh)$_5$(P(OEt)$_3$)$_2$](PF$_6$)$_2$				2188 m-w, 2165 m, 2095 s	
[W(CNPh)$_5$(PEt$_3$)$_2$](PF$_6$)$_2$	2.52 m, 1.37 p		7.67 m	2170 w, 2085 s	
[W(CNPh)$_5$(PEtPh$_2$)$_2$](PF$_6$)$_2$	3.25 m, 1.31 m		7.79 br, 7.53 m, 7.22 br	2168 w, 2120 sh, 2090 s	432 sh, 337 sh, 312 (49.2)
[W(CNPh)$_5$(dppe)](PF$_6$)$_2$		3.56 d[e]	7.90 br, 7.52 m, 7.21 m	2175 w, 2080 s, br 2175 w,[f] 2100 s,[f]	425 sh, 350 sh, 312 (53.7)
[W(CNPh)$_6$(PPh$_3$)](PF$_6$)$_2$				2200 w, 2110 s	450 sh, 318 sh, 302

[a] All ^{1}H NMR spectra were recorded in acetone-d_6. Abbreviations are as follows: br = broad, d = doublet, m = multiplet, p = pentet, q = quartet, t = triplet. [b] IR spectra recorded as Nujol mulls unless stated otherwise (see footnote *f*). [c] Electronic absorption spectra recorded on dichloromethane solutions. ϵ_{max} values (M^{-1} cm^{-1} × 10^{-3}) when recorded are given in parentheses. [d] J_{CH_2-P} = 11 Hz. [e] J_{CH_2-P} = 22 Hz. [f] Data recorded in dichloromethane. [g] ν(NO).

$(NO)(CNPh)_5]PF_6$ (with 0.2 M Bu_4NPF_6 as supporting electrolyte) has a CV with $E_{1/2}(ox) = +1.02$ V and $E_{p,c}(red) = -1.43$ V vs. SCE. This solvent effect is under further study at this time.

Substitution Chemistry: Reactions with Tertiary Phosphines and Phosphites. The close resemblance between the substitution chemistry of $[M(CNR)_7]^{2+}$ and $[M(CNPh)_7]^{2+}$ is seen not only in the existence of equilibria of the type shown in eq 1 (vide supra), involving replacement of one RNC or PhNC ligand by halide, but also in the ready formation of mixed phosphine–isocyanide complexes through substitution of up to two isocyanide ligands (eq 2 and 3). These products are isoelectronic with their

$$[M(CNPh)_7]^{2+} + xPR_3 \rightarrow [M(CNPh)_{7-x}(PR_3)_x]^{2+} + xPhNC \quad (2)$$

M = Mo or W; PR_3 = PEt_3, $P(OEt)_3$, P-*n*-Pr_3, PEt_2Ph, $PEtPh_2$ or PPh_3; x = 1 or 2

$$[M(CNPh)_7]^{2+} + Ph_2P(CH_2)_nPPh_2 \rightarrow [M(CNPh)_5(Ph_2P(CH_2)_nPPh_2)]^{2+} + 2PhNC \quad (3)$$

M = Mo or W; n = 1 or 2

precursor complexes $[M(CNPh)_7]^{2+}$, as well as with their alkyl isocyanide congeners.[4,7] Only the reactions of triphenylphosphine with $[M(CNPh)_7]^{2+}$ produced monosubstituted products, i.e., $[M(CNPh)_6(PPh_3)]^{2+}$. Steric crowding rather than electronic factors may be responsible for these reactions terminating at the monosubstitution stage, since the reaction of $[Mo(CNPh)_7]^{2+}$ with triethyl phosphite $P(OEt)_3$, a weaker Lewis base than PPh_3, readily yields a disubstituted product.

In all instances the spectroscopic properties of the mixed phosphine–phenyl isocyanide complexes (Table II) bear the same close relationship to $[Mo(CNPh)_7]^{2+}$ as do those of the mixed phosphine–alkyl isocyanide derivatives to $[M(CNR)_7]^{2+}$. One notable feature is a shift in the most intense ν(C≡N) mode to lower energy upon substituting phosphine for PhNC (Table II), a trend which reflects the transfer of electron density into the π^* orbitals of PhNC upon coordination of the better σ-donor phosphine ligands. Integration of the phenyl and alkyl resonances in the ^1H NMR spectra gave values in accord with the proposed stoichiometries of the complexes.

The electrochemical properties of the mixed-ligand complexes were studied by using the cyclic voltammetry technique. All complexes exhibited an accessible oxidation. The appropriate voltammetric half-wave potentials for all of the seven-coordinate complexes of the types $[M(CNPh)_5(PR_3)_2](PF_6)_2$, where M = Mo or W and PR_3 = PEt_3, P-*n*-Pr_3, PEt_2Ph, or $PEtPh_2$, $[M(CNPh)_5(dppm)](PF_6)_2$, and $[M(CNPh)_5(dppe)](PF_6)_2$ were substantially lower than the corresponding half-wave potentials for the homoleptic complexes $[M(CNPh)_7](PF_6)_2$. This reflects the greater ability of these phosphine ligands to stabilize the molybdenum(III) and tungsten(III) states in these complexes compared to the π-acceptor PhNC ligand. Note that with complexes containing the weaker bases PPh_3 and $P(OEt)_3$ the $E_{1/2}$ values (Table I) are comparable to those of $[M(CNPh)_7](PF_6)_2$.

For all the molybdenum(II) and tungsten(II) complexes, the current ratio $i_{p,c}/i_{p,a}$ for the one-electron couple was equal to unity (or very close to it) for sweep rates (v) between 50 and 400 mV/s, and plots of i_p vs. $v^{1/2}$ gave straight lines for sweep rates between 100 and 400 mV/s. The potential separation between the anodic and cathodic peaks ($\Delta E_p = E_{p,a} - E_{p,c}$) varied in the range from 67 to 112 mV for scan rates from 50 to 400 mV/s. From measurements on known reversible couples (e.g., ferrocene/ferricinium) using our experimental setup,[31] we believe that these electrochemical properties are best considered in a qualitative sense as being in accord with reversible electron transfer.

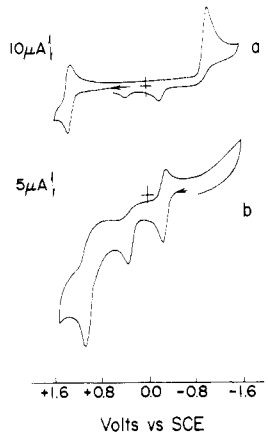

Figure 2. Cyclic voltammograms in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane of $[Mo(CNPh)_5(PEt_2Ph)_2](PF_6)_2$ (a) before and (b) after reduction at −1.2 V. Sweep rates for a and b are 200 mV/s.

Like $[M(CNPh)_7]^{2+}$, each of the mixed phosphine–isocyanide complexes also exhibit an electrochemically irreversible reduction close to −1.0 V, the CV's showing that this reduction is followed by the formation of zerovalent mixed ligand complexes as evidenced by the appearance of characteristic waves ($E_{p,a} \simeq +0.4$ and −0.2 V) at the end of the first scan. This is shown in Figure 2a in the CV of $[Mo(CNPh)_5(PEt_2Ph)_2](PF_6)_2$, where the oxidations at $E_{p,a}$ = +0.36 and −0.24 V demonstrate that a molybdenum(0) species (vide infra) is formed following the two-electron reduction of the seven-coordinate molybdenum(II) complex. A similar phenomenon is seen in the CV of $[Mo(CNPh)_7](PF_6)_2$ (Figure 1c) where reduction leads to the formation of $Mo(CNPh)_6$. The chemical and electrochemical reductions of these mixed-ligand complexes and their homoleptic parents are dealt with further in the following section.

Reduction of Seven-Coordinate M(II) to Six-Coordinate M(0). As discussed in previous sections, all the seven-coordinate (phenyl isocyanide)molybdenum(II) and -tungsten(II) complexes, whether homoleptic, mixed halide–phenyl isocyanide, or mixed phosphine–phenyl isocyanide have cyclic voltammograms which display a two-electron reduction wave at ca. −1.0 V vs. SCE. Furthermore, these CV's display, on the return scan, product waves at ca. +0.4 and −0.2 V vs. SCE (see Figures 1c and 2a). Electrochemical reduction of $[M(CNPh)_7](PF_6)_2$ in dichloromethane yields solutions whose cyclic voltammograms are characteristic of $M(CNPh)_6$. The chemical reduction of $[M(CNPh)_7](PF_6)_2$ to $M(CNPh)_6$ in high yield was accomplished by using activated magnesium as the reducing agent (see Experimental Section).

Similar results were obtained upon carrying out the electrolytic reduction of $[Mo(CNPh)_5(PEt_2Ph)_2](PF_6)_2$ at a potential of −1.2 V. As shown in Figure 2b, the resultant orange solution has a CV which is characteristic of a phenyl isocyanide complex of molybdenum(0). The oxidations at $E_{p,a}$ = +0.36 V and $E_{1/2}$ = −0.28 V vs. SCE are clearly different from those of $Mo(CNPh)_6$ itself ($E_{1/2}$ = +0.48 V and $E_{p,a}$ = −0.19 V), thereby signifying that phosphine ligands must be present in the product. Upon carrying out

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the chemical reduction of $[Mo(CNPh)_5(PEtPh_2)_2](PF_6)_2$ using magnesium metal (alternatively, sodium can be used), we produced a red oil which proved difficult to characterize. However, the corresponding magnesium reduction of $[Mo(CNPh)_5(dppe)](PF_6)_2$ produced an air-sensitive red solid whose CV displayed oxidations at $E_{p,a}$ = +0.42 V and $E_{1/2}$ = −0.27 V vs. SCE as well as a couple at $E_{1/2}$ = +1.16 V which heralded the formation of a chemical product following the irreversible oxidation at +0.42 V. The IR spectrum of this complex (CH_2Cl_2 solution) had ν(C≡N) modes at 1955 (vs) and 1810 (sh) cm^{-1}, and its ^1H NMR spectrum (in CD_2Cl_2) displayed phenyl resonances at δ ~8.4 (br) and ~7.78 (m) and $-C_2H_4-$ resonances at δ 3.13 (d, J_{CH_2-P} = 20 Hz), the latter feature implying the presence of bidentate dppe. The most likely formulation for this unstable molecule is $Mo(CNPh)_4$(dppe), based upon an integration of the above signals in the ^1H NMR spectrum.

These reduction reactions are of interest from two points of view. First, they provide an alternative strategy to that already available[32] for the synthesis of mixed phosphine–isocyanide complexes of molybdenum(0).[33] Second, the metal-based reductions of $[M(CNR)_7]^{2+}$ and $[M(CNR)_{7-x}(PR_3)_x]^{2+}$ proceed by a different mechanism from that which occurs in the zinc reduction of $[Mo(CNCMe_3)_6I]^+$.[26,34] The latter reduction leads to the reductive coupling of two adjacent isocyanide ligands to afford the $[Mo(CNCMe_3)_4(Me_3CNHCCNHCMe_3)]^+$ cation.[26,34] The factors which govern the latter reaction course are currently under further study.[35]

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Registry No. $Mo(CNPh)_6$, 14154-60-0; $W(CNPh)_6$, 14128-11-1; $[Mo(NO)(CNPh)_5]PF_6$, 78653-92-6; $[Mo(CNPh)_7](PF_6)_2$, 78653-88-0; $[Mo(CNPh)_6I]PF_6$, 79721-63-4; $[Mo(CNPh)_6I]BPh_4$, 79721-64-5; $[W(NO)(CNPh)_5]PF_6$, 78653-94-8; $[W(CNPh)_6I]BPh_4$, 79721-66-7; $[W(CNPh)_7](PF_6)_2$, 78653-90-4; $[Mo(CNPh)_6Cl]PF_6$, 79721-70-3; $[Mo(CNPh)_5(P\text{-}n\text{-}Pr_3)_2](PF_6)_2$, 79734-82-0; $[Mo(CNPh)_5(PEt_3)_2](PF_6)_2$, 79734-84-2; $[Mo(CNPh)_5(PEt_2Ph)_2](PF_6)_2$, 79721-72-5; $[Mo(CNPh)_5(PEtPh_2)_2](PF_6)_2$, 79721-74-7; $[Mo(CNPh)_6(PPh_3)](PF_6)_2$, 79721-76-9; $[Mo(CNPh)_5(P(OEt)_3)_2](PF_6)_2$, 79721-78-1; $[Mo(CNPh)_5(dppe)](PF_6)_2$, 79721-80-5; $[Mo(CNPh)_5(dppm)](PF_6)_2$, 79734-86-4; $[W(CNPh)_5(PEt_3)_2](PF_6)_2$, 79721-82-7; $[W(CNPh)_5(PEtPh_2)_2](PF_6)_2$, 79721-84-9; $[W(CNPh)_6(PPh_3)](PF_6)_2$, 79721-86-1; $[W(CNPh)_5(dppe)](PF_6)_2$, 79721-88-3; $W_2(dmhp)_4$, 69351-88-8; $W_2(mhp)_4$, 67634-84-8.

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Synthesis of Cyclic Aminooxo- and Dioxocarbenes from Carbonyl Ligands in Complexes of Iron and Manganese

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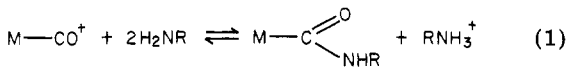
Electrophilic CO ligands in metal carbonyl complexes are converted to cyclic aminooxo- or dioxocarbene ligands by the following reactions: $M{-}C{\equiv}O^+ + H_3NCH_2CH_2Br^+ + 2B \rightarrow M{-}\overline{COCH_2CH_2NH}^+ + 2BH^+ + Br^-$; $M{-}C{\equiv}O^+ + HOCH_2CH_2Br + B \rightarrow M{-}\overline{COCH_2CH_2O}^+ + BH^+ + Br^-$. The base B used in these reactions is frequently NaH, but Et_3N and K_2CO_3 can also be successfully applied in certain cases. It is suggested that the reactions proceed by nucleophilic attack of the amine or alkoxide on a CO carbon atom to give a carbamoyl or alkoxycarbonyl intermediate, which cyclizes intramolecularly to yield the carbene products. One CO group in each of the following complexes has been observed to undergo one or both of these reactions: $FeCp(CO)_3^+$, $MnCp(NO)(CO)_2^+$, $MnCp(NO)(P(OPh)_3)(CO)^+$, $MnCp(NO)(CNC_6H_{11})(CO)^+$, and $Fe(CO)_5$. The reaction of $MnCp(NO)(CO)_2^+$ with $HOCH_2CH_2Br$ is the only one which leads to a dicarbene complex, $MnCp(NO)(\overline{COCH_2CH_2O})_2^+$. On the basis of studies of these and other metal carbonyl complexes, it appears that only CO groups that are sufficiently electropositive and have ν(CO) force constants equal to or greater than 17.0 mdyn/Å participate in these reactions. The amino group in $FeCp(CO)_2(\overline{COCH_2CH_2NH})^+$ is deprotonated by NaH or K_2CO_3 to give the imine complex $FeCp(CO)_2(\overline{COCH_2CH_2N})$ which reacts with $PdCl_2(NCMe)_2$ to yield the di-chloro-bridged dimer *sym,-trans*-$[FeCp(CO)_2(\overline{COCH_2CH_2N})Pd(\mu\text{-}Cl)Cl]_2$ in which the imine complexes are coordinated to the Pd(II) via their N atoms. Trends in the infrared and ^1H and ^{13}C NMR spectra of the complexes are discussed.

Introduction

Aliphatic amines react with electrophilic carbonyl ligands to give carbamoyl complexes (eq 1).[2,3] The reactivity



(1)

of a given CO ligand depends upon its electron density, which is reflected in its C–O stretching force constant.[4] Those CO ligands with force constants greater than approximately 17.2 mdyn/Å readily form carbamoyl com-

(1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.
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