NMR analysis showed to be 90% **4**, 5% **3**, and 5% **6**. To determine the stability of **3** under solvolysis conditions, we heated **3** (0.028 g, 0.10 mmol), 3,5-dinitrobenzoic acid (0.022 g, 0.10 mmol), 1.0 mL of water, and 4.0 mL of acetone at 45–50 °C. Comparison of a sample with drawn after 72 h with one withdrawn prior to heating by TLC (silica gel/benzene) showed that no change had occurred.

Reaction of 3 with H_2SO_4 and HBr. Alcohol **3** dissolved in cold 98% H_2SO_4 with some gas evolution to give a brown solution. This solution was poured immediately into an ice-water mixture and the mixture extracted with ether. Washing, drying ($MgSO_4$), and evaporation of the ether layer left a yellow oil whose IR and NMR spectra were identical with those of **6**. Treatment of **3** in SO_2 at −78 °C with excess HBr gave a black solution from which no organic products could be isolated.

(2,3,4-Trimethylpentadienyl)tricarbonyliron Fluoroborate (10). Alcohol **5** (500 mg) was added to a solution of trifluoroacetic anhydride (14 g) and 48% fluoroboric acid (2.5 g), and the mixture was stirred at room temperature under an atmosphere of carbon monoxide for 3 h. This mixture was poured into cold ether to precipitate the product as a pale yellow solid: 190 mg (25%); mp 260 °C; IR (CH_3NO_2) 3675, 2125, 2080, 1060 cm^{-1}; NMR (acetone-d_6) δ 3.85 (d, 2, $J_{syn,anti}$ = 3 Hz, $H_{1\text{-}syn}$), 2.80 (s, 3, 3-CH_3), 2.60 (s, 6, 2-CH_3), 1.4 (br, 2, $H_{1\text{-}anti}$); NMR (SO_2 at −20 °C) δ 3.58 (br, 2, $H_{1\text{-}syn}$), 2.68 (br s, 3, 3-CH_3), 2.53 (br s, 6, 2-CH_3), 8.37 (br, 2, $H_{1\text{-}anti}$). Further purification of this material was not possible, and hydrolysis and methanolysis gave no identifiable products. Lower reaction temperatures gave the same product in lower yield. A perchlorate salt, IR [(CH_3NO_2) 3675, 2125, 2075, 2050, and 1050 cm^{-1}] and NMR spectra identical with those of **10**, was prepared in 56% yield by dropwise addition of 60% $HClO_4$ in acetic anhydride to a stirred solution of **3** in acetic anhydride at 0 °C.

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Registry No. 3, 52472-512; **3-ODNB**, 78782-43-1; **4**, 52472-54-5; **5**, 52472-53-4; **6**, 52472-52-3; **7**, 78782-44-2; **8**, 78791-21-6; **10**, 78791-23-8; **11**, 78791-24-9; diiron enneocarbonyl, 15321-51-4; 3-methyl-2-(1-methylethenyl)-2-buten-1-ol, 52385-60-1; (2,3,4-trimethylpentadienyl)tricarbonyliron perchlorate, 78791-25-0.

Improved Synthesis of Seven-Coordinate Molybdenum(II) and Tungsten(II) Isocyanide Complexes. Dealkylation of Coordinated *tert*-Butyl Isocyanide[1,2]

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A general, high-yield synthesis of seven-coordinate cations $[M(CNR)_6X]^+$, $[Mo(CNR')_6I]^+$, and $[M(CNR)_7]^{2+}$, where M = Mo, W; R = alkyl; R′ = aryl; X = Cl, I, CN, has been developed. The synthetic procedure includes the oxidation of the appropriate $M(CNR)_3(CO)_3$ species with a mild reagent, followed by displacement of carbon monoxide with isocyanide. The oxidant $PhICl_2$ was found to be especially convenient in this procedure. This method can be used to prepare 1–20 g of crystalline products in good yields. Mixed halo–carbonyl–isocyanide products $(CO)_yX_z{}^{(2-z)+}$, $x + y + z = 7$, may also be obtained by this synthetic route. A novel dealkylation reaction of a coordinated *t*-BuNC ligand occurs when heptakis(*tert*-butyl isocyanide)molybdenum(II) or -tungsten(II) is refluxed in ethanol. The products are the cyanohexakis(*tert*-butyl isocyanide)metal(II) cations.

During studies of the reductive coupling[2,3] of alkyl isocyanide ligands in seven-coordinate molybdenum(II) and tungsten(II) complexes, we found it desirable to develop improved syntheses of compounds having the general formulas $[M(CNR)_6X]^+$[4,5] and $[M(CNR)_7]^{2+}$[5–9] (M = Mo, W; R = alkyl, aryl; X = halide) which have been known for a number of years. These compounds have been prepared by a variety of methods, including reductive alkylation[4,5] of molybdenum(IV) cyanide complexes, chemical oxidation[5,10] of metal(0) carbonyl or isocyanide complexes followed by displacement of the carbonyl ligands by isocyanide, and photochemical[11] oxidation of metal(0) isocyanide complexes in $CHCl_3$. Recently reported syntheses[7–9] of $[M(CNR)_7]^{2+}$ and $M(CNR)_5X_2$ (X = $CF_3CO_2^-$, Cl^-) involve cleavage of the quadruply bonded $Mo_2{}^{4+}$ core by alkyl isocyanide.

This paper describes high-yield preparations of the desired compounds through oxidation of $M(CNR)_x(CO)_{6-x}$ ($1 \le x \le 3$; R = alkyl, aryl; M = Mo, W) with mild oxidants such as $PhICl_2$ and I_2 followed by displacement of the carbon monoxide ligand with isocyanide. Conditions have been developed so that either the $[M(CNR)_6X]^+$ or the $[M(CNR)_7]^{2+}$ complexes may be prepared. These reactions require inexpensive starting materials, can be conducted on a large (1–20 g) scale, and produce good to excellent quantities of isolated crystalline product. The procedure

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(1) Part 14 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 13, see ref 2.

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also allows the synthesis of mixed halo–carbonyl–isocyanide complexes such as $Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2$, the W(II) analogue of which has been previously reported.[10] The unique ligand in the $[M(CNR)_6X]^+$ cations (X = $SnCl_3^-$, halide) can be displaced,[5b,12] and this reaction has been employed here to prepare the $[M(CNR)_6(CN)]^+$ (from X = halide) and $[Mo(CNR)_7]^{2+}$ (from X = $SnCl_3^-$) complexes. X-ray crystallographic studies of these complexes have been described elsewhere.[12,13] Finally, a novel dealkylation reaction of the coordinated *tert*-butyl isocyanide ligand to form coordinated cyanide has been observed in the complex $[M(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$ (M = Mo, W). This generally unrecognized reaction may be relatively common among cationic isocyanide complexes when the alkyl group can form a stable carbonium ion as is the case when R is *tert*-butyl or benzyl.

Experimental Section

General Procedures. All reactions were carried out with the highest purity reagents commercially available. Molybdenum hexacarbonyl was obtained from Climax Molybdenum or Pressure Chemical Co., and tungsten hexacarbonyl was obtained from Pressure Chemical Co. Isocyanides were prepared by standard procedures[14] from the appropriate amine or *N*-alkylformamide. Iodobenzene dichloride was prepared by the method of Lucas and Kennedy.[15] $M(CNR)_3(CO)_3$ compounds were synthesized by literature procedures.[16] Microchemical analyses were performed by Galbraith Laboratories, Knoxville, TN. Nuclear magnetic resonance spectra were taken on a Bruker WP-80 or a Perkin-Elmer R32 spectrometer. A Perkin-Elmer 621 or a Jasco infrared spectrometer was used to record infrared spectra. Electronic spectra were recorded on a Cary 118C spectrophotometer. All chromatographic separations were carried out by using "flash" chromatography as described by Still, Kahn, and Mitra.[17]

Mixed Halo–Carbonyl–Isocyanide Complexes. $Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2$. A solution of 1.26 g (5.0 mmol) of I_2 in 25 mL of benzene was added dropwise to 2.14 g (5.0 mmol) of $Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_3$ dissolved in 50 mL of benzene. If, toward the end of the addition, the solution began to darken rapidly with each drop of I_2, the addition was discontinued. The benzene was removed under reduced pressure to yield a brown powder. Dark brown crystals were obtained by vapor diffusion of *n*-pentane into 15 mL of a benzene solution of the compound under an inert atmosphere. Over a period of 2 days, 2.22 g (68% yield) of $Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2$ was deposited. IR ($CHCl_3$) 2985 (m), 2210 (m), 2173 (sh), 2155 (s), 1995 (s), 1935 (s), 1375 (m), 1235 (w), 1205 (m), 572 (w), 530 (w) cm^{-1}. Anal. Calcd for $C_{17}H_{27}N_3O_2MoI_2$: C, 31.17; H, 4.15; N, 6.41; Mo, 14.64; I, 38.74. Found: C, 30.78; H, 4.22; N, 6.29; Mo, 14.27; I, 37.83.

$[W(CN\text{-}t\text{-}C_4H_9)_4(CO)I_2]\cdot CHCl_3$. A solution of 2.0 g (7.9 mmol) of iodine in 50 mL of methanol was added dropwise over a 5-min period to a solution of 4.17 g (8.1 mmol) of $W(CN\text{-}t\text{-}C_4H_9)_3(CO)_3$ and 2.1 g (25 mmol) of *tert*-butyl isocyanide dissolved in 500 mL of methanol. The reaction was allowed to stir at room temperature for 30 min. The solvent was removed under reduced pressure, leaving 6.4 g of solid. Unoxidized starting material (1.4 g), $[W(CN\text{-}t\text{-}C_4H_9)_6I]I$, and $[W(CN\text{-}t\text{-}C_4H_9)_7]I_2$ were isolated as solids by vapor diffusion of ether into a methanol solution of the residue. The filtrates were combined and the solvents removed under reduced pressure. The resultant solid was divided into batches, and X-ray quality crystals were eventually obtained by vapor diffusion of pentane into a $CHCl_3$ solution. The formulation of the product was confirmed by X-ray crystallography.[18] IR (KBr pellet) 2155 (s, br), 1905 (s) cm^{-1}. Anal. Calcd for $WC_{21}H_{36}I_2N_4O\cdot CHCl_3$: C, 28.80; H, 4.06; N, 6.11; W, 20.04; I, 27.66. Found: C, 29.01; H, 4.29; N, 6.36; W, 20.19; I, 29.38.

$[M(CNR)_6X]^+$ Complexes. $[Mo(CNCH_3)_6I]BF_4$. A solution of 1.55 g (6.1 mmol) of I_2 dissolved in 10 mL of toluene was added dropwise with stirring to 1.86 g (6.1 mmol) of $Mo(CNCH_3)_3(CO)_3$ dissolved in 400 mL of toluene. After 5 min, 0.755 g (18.4 mmol) of methyl isocyanide was added to the solution. After 24 h of stirring, the solvent was removed under reduced pressure. The solid residue was dissolved in 250 mL of methanol and purged with N_2 for 30 min. The purging was continued for an additional hour while the solution was photolyzed with a Pyrex-jacketed 450-Watt medium-pressure Hanovia lamp. The methanol solution was concentrated to about 30 mL, and 1.3 g of $NaBF_4$ was added. Bright orange crystals precipitated in a few minutes. Further concentration and chilling to −20 °C produced more crystals (total yield 1.45 g, 40%). The $[Mo(CNCH_3)_6I]BF_4$ compound was recrystallized from hot absolute ethanol: mp 171–175 °C dec; IR (KBr pellet) 2923 (w), 2155 (s), 1451 (w), 1405 (m), 1050 (s), 690 (w), 499 (w), 483 (w), cm^{-1}. Anal. Calcd for $C_{12}H_{18}N_6MoIBF_4$: C, 25.92; H, 3.26; N, 15.12; Mo, 17.26; I, 22.83. Found: C, 26.02; H, 3.42; N, 14.98; Mo, 17.00; I, 22.63.

$[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$. A mixture of 5.25 g (19.9 mmol) of $Mo(CO)_6$ and 11.7 g (141 mmol) of *tert*-butyl isocyanide was heated to reflux in an oil bath with stirring under nitrogen. Sublimation of $Mo(CO)_6$ was minimized by adjusting the level of the oil bath to be below the liquid level in the flask and by heating the reaction slowly (~45 min) from room to reflux temperature. Gas evolution occurred as the solution heated up and the $Mo(CO)_6$ dissolved. The oil bath temperature was maintained at about 120 °C for an additional hour after all the $Mo(CO)_6$ had dissolved, and then it was allowed to cool. To the cool solution was added 200 mL of nitrogen-purged methanol. A solution of 5.05 g (19.9 mmol) of I_2 dissolved in 75 mL of methanol was added with stirring over 10-min. The iodine color dissipated almost immediately with concomitant gas evolution. This solution was heated to reflux for 8 h. The solvent was removed under reduced pressure and replaced with 250 mL of absolute ethanol. The bright orange[19] solution was purged with nitrogen for 30 min and then photolyzed with a Pyrex-jacketed 450-Watt medium-pressure Hanovia mercury lamp for 1 h.[20] The solvent was removed to yield 12.5 g of $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$ (74%) which was recrystallized by vapor diffusion of Et_2O into an ethanol solution of the complex. If NMR spectroscopy showed the conversion to pure $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$ to be incomplete, the photolysis step was repeated. No more than three repetitions of the photolysis was ever required to achieve complete conversion to $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$; mp 183–188 °C dec. The product was identified by its NMR, optical, and IR spectra.[5b] IR (KBr pellet) 2973 (m), 2924 (w), 2175 (w), 2114 (s), 2040 (sh), 1450 (w), 1367 (m), 1232 (m), 1190 (m), 520 (m) cm^{-1}.

$[Mo(CN\text{-}c\text{-}C_6H_{11})_6I]I$. A mixture of 2.6 g (9.9 mmol) of $Mo(CO)_6$ and 8.6 g (79.0 mmol) of cyclohexyl isocyanide ($CN\text{-}c\text{-}C_6H_{11}$) under nitrogen was heated in an oil bath at 120 °C with stirring for 6 h. After the solution had cooled, the mixture was diluted with 200 mL of methanol. A solution of 2.5 g (9.9 mmol) of I_2 dissolved in 50 mL of methanol was added to the solution. Gas evolution was observed and the solution was allowed to stir at room temperature for 24 h. The resulting solution was filtered and the solvent removed under reduced pressure leaving a brown oil. The brown oil was chromatographed on a 6 cm × 50 cm silica gel column eluted with 3% $EtOH/CHCl_3$. The unoxidized pale yellow mixed isocyanide–carbonyl molybdenum(0) species were eluted first and discarded. An orange band containing a mixture of $[Mo(CN\text{-}c\text{-}C_6H_{11})_6I]I$ and $[Mo(CN\text{-}c\text{-}C_6H_{11})_7]I_2$ was collected,

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[19] If the solution was brown at this point it was "flash" chromatographed[17] on silica gel to remove the impurities. Approximately 3% $EtOH/CHCl_3$ is a suitable elution solvent.

[20] The conversion of $[ML_7](I)_2$ to $[ML_6I]I$ does not require light, but it is vastly accelerated by it.

the solvent was removed under reduced pressure, and the residue was dried under vacuum overnight. The resulting oil was redissolved in isoamyl alcohol, purged with nitrogen for 30 min, and photolyzed by a Pyrex-jacketed 450-Watt medium-pressure Hanovia lamp for 1.5 h. The solvent was removed under reduced pressure. If TLC of the product showed a spot corresponding to [Mo(CN-c-C_6H_{11})$_7$]I_2, the photolysis was repeated. Orange platelike crystals (2.18 g, 22% yield) were obtained by vapor diffusion of petroleum ether into the [Mo(CN-c-C_6H_{11})$_6$I]I product dissolved in acetone: mp 167–168.5 °C; IR (KBr pellet) 2932 (m), 2856 (m), 2185 (sh), 2130 (s), 1450 (m), 1362 (m), 1351 (m), 1320 (m), 1270 (w), 1238 (w), 1145 (w), 1122 (w), 1035 (w), 1015 (w), 990 (w), 960 (w), 695 (w), 645 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.54 (m), 1.82 (m), 4.15 (m). Anal. Calcd for $C_{42}H_{66}N_6MoI_2$: C, 50.21; H, 6.62; N, 8.36; I, 25.26. Found: C, 49.96; H, 6.74; N, 8.27; I, 25.65.

[W(CN-*t*-C_4H_9)$_6$I]I. A solution of 0.234 g (0.92 mmol) of iodine dissolved in 10 mL of methanol was added dropwise with stirring to a solution containing 0.484 g (0.94 mmol) of W(CN-*t*-C_4H_9)$_3$(CO)$_3$ dissolved in 25 mL of methanol. After the addition was complete, 0.26 g (3.1 mmol) of *tert*-butyl isocyanide was added, and the reaction was refluxed for 12 h. The methanol and any free isocyanide was removed under reduced pressure. The resultant solid was photochemically[19,20] converted to [W(CN-*t*-C_4H_9)$_6$I]I and purified as described in the synthesis of [Mo(CN-*t*-C_4H_9)$_6$I]I above. A total of 0.64 g of [W(CN-*t*-C_4H_9)$_6$I]I (74% yield) was collected (mp 179–180 °C dec) and identified by its NMR and IR spectroscopic properties.[5b] IR (KBr pellet) 2925 (w), 2875 (m), 2110 (s), 1370 (w), 1190 (m), 1155 (w) cm^{-1}.

[Mo(CN-*t*-C_4H_9)$_6$Cl]Cl. The starting material, Mo(CN-*t*-C_4H_9)$_3$(CO)$_3$, was prepared in situ by using 18.7 g (71 mmol) of Mo(CO)$_6$ and 35.4 g (426 mmol) of *tert*-butyl isocyanide as described above in the procedure for [Mo(CN-*t*-C_4H_9)$_6$I]I. The product of the reaction was dissolved in 750 mL of toluene that was purged with nitrogen for 30 min. While the solution was being vigorously stirred, 19.4 g (71 mmol) of $PhICl_2$ was added in four batches. Vigorous gas evolution occurred. The reaction was allowed to stir at room temperature under nitrogen for 48 h during which time yellow [Mo(CN-*t*-C_4H_9)$_6$Cl]Cl precipitated. The precipitate was filtered, washed with toluene, and dried under vacuum overnight to obtain 35 g of [Mo(CN-*t*-C_4H_9)$_6$Cl]Cl (74% yield). The product was identified by its NMR spectrum.[5b] IR (KBr pellet) 2999 (w), 2149 (s), 2130 (sh), 1390 (w), 1255 (w), 1218 (w), 550 (w) cm^{-1}.

[Mo(CNC_6H_4-*p*-Cl)$_6$I]I. A solution containing 0.96 g (3.8 mmol) of I_2 in 20 mL of benzene was added dropwise to a stirred solution of 10 mL of benzene containing 2.19 g (3.7 mmol) of Mo(CNC_6H_4-*p*-Cl)$_3$(CO)$_3$. After the gas evolution had subsided, 3.1 g (22.5 mmol) of *p*-chlorophenyl isocyanide was added. After about 1 h a precipitate had formed. The solution was stirred at room temperature for approximately 12 h, and then the orange brown precipitate was collected. This material (presumably the triiodide salt) was "flash" chromatographed[17] on a 5 cm × 10 cm silica gel column eluted with $CHCl_3$. A purple I_2 band and an orange-brown band were followed by a large deep orange band which, upon removal of the solvent, was found to be [Mo(CNC_6H_4-*p*-Cl)$_6$I]I (2.68 g, 62% yield, based on molybdenum). The product was recrystallized from methylene chloride/*n*-pentane. Anal. Calcd for $C_{42}H_{24}N_6Cl_6MoI_2$: C, 42.93; H, 2.06; N, 7.15; Mo, 8.16; Cl, 18.10; I, 21.60. Found: C, 42.67; H, 2.22; N, 7.01; Mo, 8.38; Cl, 17.90; I, 21.30.

[Mo(CNC_6H_4-*p*-Cl)$_6$I](PF_6). To a solution containing 1.0 g (0.9 mmol) of [Mo(CNC_6H_4-*p*-Cl)$_6$I]I in 900 mL of methanol was added 2 g (12 mmol) of NH_4PF_6. A bright yellow precipitate formed immediately which was allowed to stand 45 min before collecting and drying under vacuum to yield 0.8 g (75%) of [Mo(CNC_6H_4-*p*-Cl)$_6$I](PF_6): mp 188–193 °C dec; IR (KBr pellet) 2115 (s), 1485 (m), 1090 (m), 1010 (m), 840 (m) cm^{-1}.

[Mo(CNC_6H_4-*p*-CH_3)$_6$I](PF_6). A solution containing 0.476 g (1.9 mmol) of iodine in 15 mL of toluene was added dropwise to 0.996 g (1.9 mmol) of Mo(CNC_6H_4-*p*-CH_3)$_3$(CO)$_3$ dissolved in 20 mL of toluene. After the gas evolution had subsided, 0.76 g (6.5 mmol) of *p*-tolyl isocyanide was added, and the reaction was stirred at room temperature for 48 h. The solvent was removed under vacuum and the resultant red-orange oil dissolved in 150 mL of 95% ethanol and layered over 60 mL of a 50% ethanol/water solution containing 1 g of $NaPF_6$. Over the course of several hours 1.63 g (80% yield) of [Mo(CNC_6H_4-*p*-CH_3)$_6$I](PF_6) plates formed and was collected: mp 98–106 °C dec; IR (KBr pellet) 2925 (m), 2130 (s), 1503 (m), 840 (m) cm^{-1}. Anal. Calcd for $C_{48}H_{42}N_6MoIPF_6$: C, 53.84; H, 3.95; N, 7.85; Mo, 8.96; I, 11.85. Found: C, 52.75; H, 3.97; N, 7.65; Mo, 8.75; I, 11.92.

[Mo(CN-*t*-C_4H_9)$_6$(CN)](PF_6). Method A. A 0.21-g (43 mmol) portion of NaCN was added to 150 mL of methanol containing 2.15 g (2.5 mmol) of [Mo(CN-*t*-C_4H_9)$_6$I]I. The reaction mixture was stirred at room temperature for 8 h during which time the color changed from orange to yellow. This solution was added to 150 mL of CH_2Cl_2 and washed four times with a saturated NaCl solution. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure, leaving 1.37 g (2.1 mmol, 84% yield) of a yellow powder. This product was converted to the PF_6^- salt by passing a 1:1 H_2O/methanol solution of [Mo(CN-*t*-C_4H_9)$_6$(CN)]Cl through 35 mL of Dowex 2-X8 20–50 mesh anion exchanger converted to the PF_6^- form by standard procedures. X-ray quality crystals were formed in the dark by vapor diffusion of Et_2O into methanol containing [Mo(CN-*t*-C_4H_9)$_6$(CN)](PF_6): mp 167–176 °C dec; IR (KBr pellet) 2927 (m), 2935 (m), 2114 (s), 2045 (sh), 1462 (m), 1402 (w), 1369 (m), 1237 (m), 1190 (s), 1041 (w), 925 (w), 873 (sh), 833 (sh), 558 (s), 527 (s) cm^{-1}. Anal. Calcd for $C_{31}H_{54}N_7MoPF_6$: C, 48.63; H, 7.11; N, 12.80; Mo, 12.53; P, 4.05. Found: C, 48.59; H, 7.29; N, 13.04; Mo, 11.21; P, 3.90. The formula has also been confirmed in an X-ray crystal structure determination.[13]

Method B. A suspension of 0.2 g (0.2 mmol) of [Mo(CN-*t*-C_4H_9)$_7$](PF_6)$_2$ was placed in 50 mL of absolute ethanol and refluxed for 3 days. After the heat was removed, 0.1 g of $NaPF_6$ (0.6 mmol) was added. A yellow precipitate (0.025 g) formed which was collected and identified as starting material by its ^1H NMR and electronic spectra. The ethanol was removed under reduced pressure and the residue chromatographed on silica gel by eluting with 3% ethanol/chloroform. A yellow band (33 mg) with ^1H NMR, IR, and UV spectra identical with those of [Mo(CN-*t*-C_4H_9)$_6$(CN)](PF_6) (0.044 mmol, 22% yield) prepared by method A was collected.

[W(CN-*t*-C_4H_9)$_6$(CN)](H_2PO_4). A suspension of 0.5 g (0.47 mmol) of [W(CN-*t*-C_4H_9)$_7$](PF_6)$_2$ in 25 mL of ethanol with 0.2 mL of pyridine was heated to reflux under nitrogen for 3 days. The solution was filtered and the solvent removed under reduced pressure. The yellow-brown product was dissolved in 15 mL of ethanol and crystallized by vapor diffusion of Et_2O into this solution. Yellow crystals (135 mg, 35% yield) of [W(CN-*t*-C_4H_9)$_6$(CN)]H_2PO_4 were collected and identified by analytical and spectroscopic (especially the P–O stretch at 1055 cm^{-1}; the $H_2PO_4^-$ anion presumably arose through hydrolysis of PF_6^-) data: IR (KBr pellet) 2988 (m), 2945 (m), 2101 (s), 2045 (sh), 1460 (m), 1398 (m), 1370 (m), 1232 (m), 1190 (s), 1055 (s), 840 (m), 520 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (s). Anal. Calcd for $C_{31}H_{56}N_7WPO_4$: C, 46.22; H, 7.01; N, 12.17; W, 22.82. Found: C, 46.25; H, 7.02; N, 11.48; W, 20.92.

Attempted Synthesis of [Mo(CN-*t*-C_4H_9)$_6$Cl]Cl. Method A by Oxidation of Mo(CO)$_6$ with $PhICl_2$ followed by Addition of CNR. To a stirred, nitrogen-purged solution of 0.8 g (3 mmol) of Mo(CO)$_6$ in 20 mL of toluene was added 0.83 g (3 mmol) of $PhICl_2$. Once gas evolution had subsided, 1.2 g (14 mmol) of *tert*-butyl isocyanide was added. Gas evolution occurred and a gummy, water-soluble precipitate formed. This solution was filtered and an additional 0.78 g (9 mmol) of *tert*-butyl isocyanide was added to the solution. After 3 days at room temperature, 44 mg of [Mo(CN-*t*-C_4H_9)$_6$Cl]Cl (2% yield) formed and was collected by filtration and identified by its ^1H NMR spectrum (δ 1.55 in $CDCl_3$).[5b]

Method B by Oxidation of Mo(CO)$_6$ with $PhICl_2$ in the Presence of CNR. When the oxidation above was carried out in the presence of CN-*t*-C_4H_9, a gummy, water-soluble precipitate was the only observed product.

Method C by Addition of Mo(CO)$_6$ to a Solution Containing $PhICl_2$ and CNR. When the $PhICl_2$ was added to a toluene solution of *tert*-butyl isocyanide and followed by addition of Mo(CO)$_6$, no immediate reaction occurred. After 10 min the solution turned blue. [Mo(CN-*t*-C_4H_9)$_6$Cl]Cl was not isolated from this solution even after several days of standing. The blue products have not yet been characterized.

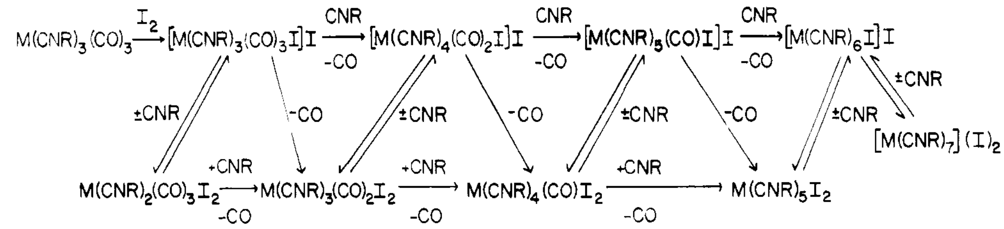

Figure 1. Possible scheme depicting the synthesis and interconversion reactions of seven-coordinate molybdenum(II) and tungsten(II) halo–carbonyl–isocyanide complexes.

[MoL$_7$]$^{2+}$ Complexes. [Mo(CN-c-C$_6$H$_{11}$)$_7$](PF$_6$)$_2$. Mo(CN-c-C$_6$H$_{11}$)$_3$(CO)$_3$ was prepared from 1.0 g (3.8 mmol) of Mo(CO)$_6$ and 4.4 g (40 mmol) of cyclohexyl isocyanide in a manner identical with that for Mo(CN-*t*-C$_4$H$_9$)$_3$(CO)$_3$ described in the [Mo(CN-*t*-C$_4$H$_9$)$_6$I]I synthesis. The product was dissolved in 125 mL of methanol, and 1.0 g (3.6 mmol) of PhICl$_2$ was added with concomitant gas evolution. The reaction was allowed to stand at room temperature for 24 h before 2.5 g (14.9 mmol) of NaPF$_6$ was added to the solution. The solution was cooled to 0 °C for 4 days. Yellow plates of [Mo(CN-c-C$_6$H$_{11}$)$_7$](PF$_6$)$_2$ were collected by filtration (3.24 g, 2.8 mmol, 74% yield): mp 137–138.5 °C; IR (KBr pellet) 2935 (s), 2862 (m), 2143 (s), 1455 (m), 1369 (m), 1353 (m), 1321 (m), 1155 (w), 1125 (w), 1020 (w), 930 (w), 897 (m), 835 (s), 648 (w) cm^{-1}. Anal. Calcd for C$_{49}$H$_{77}$N$_7$MoP$_2$F$_{12}$: C, 51.17; H, 6.75; N, 8.53; P, 5.39. Found: C, 51.07; H, 6.78; N, 8.45; P, 5.55.

[Mo(CN-*t*-C$_4$H$_9$)$_7$](PF$_6$)$_2$. This compound[5b] was prepared in 80% yield in a manner analogous to that described above for [Mo(CN-c-C$_6$H$_{11}$)$_7$](PF$_6$)$_2$; mp 190–200 °C dec.

[W(CN-*t*-C$_4$H$_9$)$_7$](PF$_6$)$_2$. In this case the W(CO)$_6$ and *tert*-butyl isocyanide must be heated for 96 h to produce the W(CN-*t*-C$_4$H$_9$)$_3$(CO)$_3$. The procedure was the same as that described for [Mo(CN-c-C$_6$H$_{11}$)$_7$](PF$_6$)$_2$ in every other respect, and [W-(CN-*t*-C$_4$H$_9$)$_7$](PF$_6$)$_2$[5b] was produced in 60% yield; mp 190–195 °C dec.

[Mo(CN-*t*-C$_4$H$_9$)$_7$](BPh$_4$)$_2$. To a stirred suspension of 0.10 g (0.1 mmol) of [Mo(SnCl$_3$)(CN-*t*-C$_4$H$_9$)$_6$](PF$_6$) in 15 mL of methanol was added 0.3 g (3.6 mmol) of *tert*-butyl isocyanide. The solution turned bright yellow over a 4-h period. Upon addition of 0.25 g (0.7 mmol) of Na(BPh$_4$), 0.137 g (0.1 mmol, 100% yield) of [Mo(CN-*t*-C$_4$H$_9$)$_7$](BPh$_4$)$_2$ precipitated from solution: ^{1}H NMR (acetone-*d*$_6$) 6.8 (m), 7.4 (m), 1.64 (s) (ratio of aromatic to aliphatic protons 40:62; theoretical, 40:63); IR (KBr pellet) 3152 (m), 2980 (m), 2925 (w), 2135 (s), 1580 (w), 1475 (w), 1455 (w), 1425 (w), 1370 (m), 1230 (w), 1185 (m), 1030 (w), 840 (w), 740 (m), 730 (m), 700 (m) 530 (m) cm^{-1}.

Oxidation of *tert*-Butyl Isocyanide with PhICl$_2$. A 12.5-g (45 mmol) portion of iodobenzene dichloride was added with stirring to a solution of 3.9 g (47 mmol) of *tert*-butyl isocyanide in 40 mL of CH$_2$Cl$_2$. An exothermic reaction occurred, the iodobenzene dichloride dissolved, and the solution turned brown. At the end of the reaction (5–10 min after the addition of the iodobenzene dichloride) the solution abruptly turned clear amber. The solution was distilled under nitrogen. After the CH$_2$Cl$_2$ was removed, a fraction boiling at 108 °C was collected (4.9 g) which contained *tert*-butyl isocyanide dichloride (δ 1.6 (s)) and *tert*-butyl isocyanate (δ 1.4 (s)) as a 1:9 mixture as determined from proton NMR spectral integration. The infrared spectrum showed a band at 2260 cm^{-1} attributed to *tert*-butyl isocyanate (a hydrolysis product of *tert*-butyl isocyanide dichloride) and also strong bands at 1720 and 1650 cm^{-1}. The 1650-cm^{-1} band is attributed to the C=N stretch of *tert*-butyl isocyanide dichloride. A C–Cl stretch was also observed at 850 cm^{-1}. The mass spectrum revealed at least two compounds. The more volatile component (C.I., methane) gave rise to a *m/e* 197 peak, and the less volatile component gave rise to a *m/e* 154 peak. This second peak corresponds to *tert*-butyl isocyanide dichloride, *M*$_r$ 153. The spectrum shows A + 2 and A + 4 peaks (which are, respectively, ~65% and ~10% of the parent height) characteristic of two chlorine atoms. Peaks at *m/e* 138, 118, and 98 might correspond to loss of methane, HCl and isobutylene, respectively.

Results and Discussion

Synthesis of Seven-Coordinate Isocyanide Complexes of Mo(II) and W(II). Oxidation of M(CNR)$_3$(CO)$_3$ (M = Mo or W, R = alkyl; M = Mo, R = aryl) with mild oxidants such as iodobenzene dichloride or iodine is a convenient and versatile route to seven-coordinate complexes of Mo(II) and W(II) containing halogen, carbonyl, and isocyanide ligands. These compounds may be isolated directly or converted in the presence of additional isocyanide to halohexakis(isocyanide)metal(II) cations or heptakis(isocyanide)metal(II) dications (Mo or W) in good yield (Figure 1).

The oxidation potential of mixed isocyanide–carbonyl–metal(0) compounds (Mo or W) decreases with increasing isocyanide substitution.[21] This phenomenon facilitates the direct oxidation of M(CNR)$_3$(CO)$_3$ complexes with a weak oxidant such as iodine, which only slowly oxidizes the corresponding M(CO)$_6$ compounds. In aromatic or alcoholic solvents at room temperature this oxidation is essentially instantaneous and occurs with concomitant loss of carbon monoxide. In the absence of free isocyanide ligand, the complexes [M(CNR)$_3$(CO)$_2$I$_2$] (M = Mo or W; R = *tert*-butyl) are the only products that are isolated. When free isocyanide is present the remaining carbonyl ligands are replaced, ultimately producing the heptakis(isocyanide)metal(II) dication or the halohexakis(isocyanide)metal(II) cation. The stoichiometry of the final product depends on the particular isocyanide ligand and the reaction conditions employed. The possible intermediates along the reaction path are shown in Figure 1.

A number of the species shown in the figure have been previously reported, including W(CN-*t*-C$_4$H$_9$)$_3$(CO)$_2$I$_2$,[10] Mo(CN-c-C$_6$H$_{11}$)$_5$Br$_2$,[22] and many examples of [M-(CNR)$_6$X]$^+$ [5a,c,6] and [M(CNR)$_7$]$^{2+}$ [5,7-9] (M = Mo and W). Two additional mixed halo–carbonyl–isocyanide complexes, [Mo(CN-*t*-C$_4$H$_9$)$_3$(CO)$_2$I$_2$] and [W(CN-*t*-C$_4$H$_9$)$_4$-(CO)I$_2$], have been isolated in this work. Examples of each stoichiometry except M(CNR)$_5$I$_2$ and [M(CNR)$_5$(CO)I]I have been crystallographically characterized.[4,5b,6-8,10,13] Only one of the mixed iodo–isocyanide–carbonyl complexes isolated so far is ionic, and this situation occurs only when the d^4 metal center is surrounded by six excellent σ donors (five isocyanides and 1 iodide).[35] The instantaneous gas evolution observed upon oxidation of M(CNR)$_3$(CO)$_3$, and again when free isocyanide is added, attests to the weakness of the M(II)–CO bond. Loss of carbon monoxide is irreversible under the reaction conditions employed here. The inability of carbon monoxide to stabilize electron-deficient metal complexes is well-known.[23] The final products (Figure 1), [M(CNR)$_6$X]$^+$ and [M(CNR)$_7$]$^{2+}$, may be interconverted when R = alkyl.[5,24] The interconversion proceeds through a dissociative mechanism, eq 1.[25] Support for a 6-coordinate intermediate is found in the

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[24] The [Mo(CNaryl)$_7$]$^{2+}$ complexes have only recently been prepared by Walton and co-workers (private communication) and structurally characterized by us.[18]

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$$[\mathrm{M(CNR)_6X}]^+ \underset{\pm \mathrm{X}^-}{\rightleftharpoons} \text{“}[\mathrm{M(CNR)_6}]^{2+}\text{”} \underset{\pm \mathrm{CNR}}{\rightleftharpoons} [\mathrm{M(CNR)_7}]^{2+} \tag{1}$$

recent work of Walton and co-workers who have characterized both the 6- and 7-coordinate homoleptic alkyl isocyanide complexes of isoelectronic Cr(II).[26] A number of 6-coordinate complexes of Mo(II) containing a variety of ligands have also been isolated,[27,28] some of which exhibit reversible carbon monoxide binding.[28] Moreover, a dissociative pathway seems more likely than an associative one on the basis of electron counting[29] (16-electron complexes are more common than 20-electron complexes) and steric crowding (an 8-coordinate intermediate would be considerably more crowded than a 6-coordinate intermediate) considerations.

In the course of synthesizing $[\mathrm{M(CNR)_6X}]^+$ or $[\mathrm{M(CNR)_7}]^{2+}$ complexes, uncoordinated isocyanide and coordinating anions may be present. Consequently, the equilibrium between the two complexes (eq 1) must be taken into account if pure compounds are to be obtained. The heptakis(alkyl isocyanide)metal(II) dications may be isolated by precipitation from solution containing excess isocyanide with a noncoordinating anion such as $\mathrm{PF_6^-}$. The iodohexakis(alkyl isocyanide)metal(II) cations may be purified by chromatography when only a small amount of the heptakis(alkyl isocyanide)metal(II) dication is present. The efficiency of the separation decreases rapidly for complexes containing alkyl groups larger than *tert*-butyl, however. When larger quantities of the undesired dication are present, it is more practical to convert $[\mathrm{M(CNR)_7}](\mathrm{X})_2$ back to $[\mathrm{M(CNR)_6X}]\mathrm{X}$. This conversion is achieved simply by dissolving the mixture in an alcohol, allowing time for equilibrium to occur, and removing the liberated isocyanide with the solvent. Since the shift to $[\mathrm{M(CNR)_6X}]^+$ is driven by removal of uncoordinated isocyanide, the solvent must have a boiling point near that of the free isocyanide to ensure its complete removal with solvent. A very substantial photochemical rate enhancement[20] of this reaction was observed when a deoxygenated solution of the two compounds was photolyzed by a Pyrex-jacketed 450-Watt medium-pressure mercury Hanovia lamp. The acceleration is most likely due to photochemical generation of the hexacoordinate intermediate shown in eq 1. It may be possible to detect the octahedral d^4 intermediate by ESR or IR spectroscopy. Dihalopentakis(alkyl isocyanide)metal(II) species reported by other workers[22] have never been observed by us, even upon prolonged (more than 48 h) photolysis of halohexakis(alkyl isocyanide)metal(II) halide complexes. The equilibrium (2) must

$$\mathrm{M(CNR)_5X_2} + \mathrm{CNR} \rightleftharpoons [\mathrm{M(CNR)_6X}]\mathrm{X} \tag{2}$$

strongly favor the halohexakis(alkyl isocyanide)metal(II) cations. Evidently, very careful control of the stoichiometry of the reactants must be employed to obtain $\mathrm{M(CNR)_5X_2}$ species.

Oxidations of $\mathrm{M(CNR)_3(CO)_3}$ (M = Mo or W, R = alkyl) using iodobenzene dichloride appear to parallel those of iodine. No attempt has been made to isolate mixed chloride–carbonyl–isocyanide–metal(II) species, however. If the oxidation of $\mathrm{M(CN\text{-}}t\text{-}\mathrm{C_4H_9)_3(CO)_3}$ with iodobenzene dichloride is carried out in toluene, $[\mathrm{M(CNR)_6Cl}]\mathrm{Cl}$ will precipitate as it forms, preventing further reaction to produce $[\mathrm{M(CNR)_7}]^{2+}$. This useful modification is limited to complexes such as chlorohexakis(*tert*-butyl isocyanide)metal(II) chloride (Mo or W) where the $[\mathrm{M(CNR)_6X}]^+$ formed is insoluble in the isocyanide/toluene solution but the intermediate mixed halide–carbonyl–isocyanide complexes are soluble.

Unlike iodine, iodobenzene dichloride readily oxidizes $\mathrm{Mo(CO)_6}$ in toluene with concomitant loss of carbon monoxide. If isocyanide is added to this solution a brown tar forms and $[\mathrm{Mo(CNR)_6Cl}]\mathrm{Cl}$ is formed in 30% yield or less. In the absence of $\mathrm{Mo(CO)_6}$, however, iodobenzene dichloride smoothly oxidizes *tert*-butyl isocyanide in benzene or chlorinated hydrocarbons without formation of polymer. A minor product, *tert*-butyl isocyanide dichloride, was identified by its mass spectrum. The major product, *tert*-butyl isocyanate, was identified by comparison of its spectra to reported infrared and $^1\mathrm{H}$ NMR spectra.[30] It probably arises from hydrolysis of *tert*-butyl isocyanide dichloride by atmospheric moisture. Isocyanide dichlorides have been prepared previously by the oxidation of alkyl isocyanides with chlorine gas in chlorinated hydrocarbons at 0 °C.[31] The present results indicate that oxidation products of $\mathrm{Mo(CO)_6}$ are responsible for the formation of the brown tar and lower yields obtained in the previous synthesis[5b] of chlorohexakis(*tert*-butyl isocyanide)metal(II) chloride (Mo and W). Until recently,[7c] $[\mathrm{M(CNR)_6Cl}]\mathrm{Cl}$ (M = Mo, W) was a required intermediate in the synthesis of the other halohexakis(isocyanide)metal(II) cations. Polymerization of isocyanide is avoided when $\mathrm{Mo(CNR)_3(CO)_3}$ species are oxidized with iodobenzene dichloride in the presence of free isocyanide.

The reagent iodobenzene dichloride[15] has, in laboratory applications, several advantages over chlorine. Its properties parallel those of the halogens. It may be weighed out and, if it is kept cold and protected from moisture, it will remain stable for months. It must be handled with care, however, because it is corrosive.

The general utility of the synthetic procedures described in this work hinges on the availability of the $\mathrm{M(CNR)_3(CO)_3}$ (M = Mo and W; R = alkyl and aryl) compounds. Pure $\mathrm{M(CNR)_3(CO)_3}$ complexes are conveniently prepared by displacement of cycloheptatriene[16a] by isocyanide from (cycloheptatriene)tricarbonylmetal(0). More recently they have been prepared under mild conditions directly from $\mathrm{M(CO)_6}$ by using a Co(II) catalyst.[16b] The $\mathrm{M(CNR)_3(CO)_3}$ complexes are air stable as long as they are protected from light. In some cases it is not necessary to isolate and purify the $\mathrm{M(CNR)_3(CO)_3}$ species. This situation arises when the particular isocyanide is stable up to 120 °C as is the case when R = *tert*-butyl or cyclohexyl isocyanide. Here $\mathrm{M(CNR)_3(CO)_3}$ may be prepared in situ from the corresponding hexacarbonyl by refluxing the product in 6–10 equiv of neat isocyanide. The product contains a mixture of $\mathrm{M(CNR)}_x\mathrm{(CO)}_{6-x}$ compounds, $1 \leq x \leq 3$, with $x = 3$ predominating. All of these compounds are oxidized by iodobenzene dichloride or iodine. The procedure is suitable for the synthesis of the halohexakis(alkyl isocyanide)metal(II) cations and heptakis(alkyl isocyanide)metal(II) dications. Upon oxidation, the final product is

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Table I. Proton Magnetic Resonance Spectra, Selected IR Spectral Bands, and Electronic Spectral Bands of $[M(CNR)_6X]^+$ and $[M(CNR)_7]^{2+}$ Cations

compound	^1H NMR bands, δ [a]	IR bands, cm^{-1} [b]	electronic spectrum[c] λ, nm (ϵ_{max}, M^{-1} cm^{-1} $\times$ 10^{-3})
$[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$	1.55 (s)	2114 (s), 2045 (sh)	380 (1.73), 278 (sh), 265 (sh), 244 (36.2)
$[Mo(CN\text{-}t\text{-}C_4H_9)_6Cl]Cl$	1.55 (s)	2149 (s), 2130 (sh)	404 (1.10), 276 (20.7), 237 (25.6)
$[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$	1.55 (s)	2114 (s)	408 (1.24), 276 (24.3), 240 (sh), 219 (52.5)
$[Mo(CN\text{-}t\text{-}C_4H_9)_6I](PF_6)$		2120 (s)	411 (1.36), 274 (24.0), 234 (33.2), 218 (35.5)
$[Mo(CNCH_3)_6I](BF_4)$	3.65 (s)	2155 (s)	412 (1.3), 270 (16.9), 252 (sh), 222 (28.2)
$[Mo(CN\text{-}c\text{-}C_6H_{11})_6I]I$	1.3–2.1 (m) 4.15 (m)	2130 (s)	414 (1.24), 278 (23.1), 246 (sh), 219 (49.0)
$[Mo(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$	1.62 (s)	2138 (s)	413 (1.5), 275 (26.3), 248 (33.9)
$[Mo(CN\text{-}c\text{-}C_6H_{11})_7](PF_6)_2$	1.3–2.2 (m) 4.34 (m)	2143 (s)	411 (1.3), 285 (sh), 257 (38.6)
$[W(CN\text{-}t\text{-}C_4H_9)_6(CN)]H_2PO_4$	1.56 (s)	2101 (s), 2045 (sh)	
$[W(CN\text{-}t\text{-}C_4H_9)_6I]I$	1.53 (s)	2110 (s)	415 (1.54), 285 (sh), 243 (38.5), 209 (36.2)
$[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$	1.60 (s)	2145 (s)	417 (1.49), 280 (32.6), 253 (46.1)
$[Mo(CNC_6H_4\text{-}p\text{-}Cl)_6I]I$[d]	7.64 (d) 7.41 (d) $J = 8.8$ Hz		447 (sh), 337 (51.3), 323 (sh), 244 (94.4)
$[Mo(CNC_6H_4Cl)_6I](PF_6)$		2115 (s)	
$[Mo(CNC_6H_4\text{-}p\text{-}CH_3)_6I](PF_6)$	7.38 (d) 7.23 (d) $J = 8.8$ Hz	2130 (s)	452 (sh), 334 (sh), 300 (32.2), 255 (sh), 238 (65.1), 229 (67.3)
$[Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2]$	1.55 (s)	2210 (s), 2173 (s), 2155 (s), 1995 (s), 1935 (s)	402 (sh), 348 (2.24), 272 (sh), 222 (45.0)
$[Mo(CN\text{-}t\text{-}C_4H_9)_5(CO)I]I$	1.52 (s)	2093 (s), 2046 (s), 1911 (s)	
$[W(CN\text{-}t\text{-}C_4H_9)_4(CO)I_2]$	1.53 (s)	2155 (s), 1905 (s)	
$[Mo(CN\text{-}t\text{-}C_4H_9)SnCl_3](PF_6)$	1.58 (s)	2200 (s), 2170 (s), 2109 (vs)	498 (0.53), 344 (sh), 312 (sh), 266 (sh), 256 (48.8)

[a] In $CDCl_3$. Chemical shifts are relative to Me_4Si. s = singlet; d = doublet; m = multiplet. [b] KBr pellet. s = strong, sh = shoulder, v = very. [c] In methanol. [d] Electronic spectrum in CH_2Cl_2. sh = shoulder.

determined by the number of equivalents of isocyanide used. This procedure may be carried out in a single flask with inexpensive starting materials and makes efficient use of the isocyanide ligand.

The coordinated halide in the halohexakis(alkyl isocyanide)metal(II) cation is selectively replaced by both charged and uncharged ligands.[5b,12] Cyanide ion readily displaces iodide at room temperature to produce $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)]^+$ which is isolated as the hexafluorophosphate salt. Similarly, the trichlorostannate ligand of $[Mo(SnCl_3)(CN\text{-}t\text{-}C_4H_9)_6]^+$ is readily replaced by an alkyl isocyanide to produce $[MoL_7]^{2+}$.

Dealkylation of Heptakis(*tert*-butyl isocyanide)metal(II) Dications. The $[M(CNR)_6(CN)]^+$ complexes described above have also been prepared via a novel dealkylation reaction of a coordinated *tert*-butyl isocyanide. When heptakis(*tert*-butyl isocyanide)molybdenum(II) is refluxed in ethanol for 3 or more days, it is converted to cyanohexakis(*tert*-butyl isocyanide)molybdenum(II) hexafluorophosphate. The progress of this reaction was monitored by ^1H NMR spectroscopy where a new singlet (δ 1.54 in $CDCl_3$) corresponding to $[M(CN\text{-}t\text{-}C_4H_9)_6(CN)]^+$ gradually appeared. This reaction most likely involves solvolysis of the *tert*-butyl moiety where $[M(CN\text{-}t\text{-}C_4H_9)_6(CN)]^+$ acts as the leaving group (eq 3). Products

$$[(RNC)_6M{-}C{\equiv}N{-}C(CH_3)_3]^{2+} \overset{\Delta}{\rightleftharpoons} [(RNC)_6MC{\equiv}N]^+ + C(CH_3)_3^+ \quad (3)$$

corresponding to further dealkylation have not been observed, probably because the reduced overall charge of the complex reduces the rate of dealkylation. The final organic products, presumed to be *tert*-butyl alcohol or isobutylene, have not been isolated. Considerable precedence exists in the literature for this type of reaction, however, with more traditional leaving groups.[32] Dealkylation of coordinated *tert*-butyl isocyanide has been reported to occur when $[Pt(CN\text{-}t\text{-}Bu)_4]^{2+}$ is dissolved in methanol at 25 °C,[33] but the reported product, $Pt(CN\text{-}t\text{-}Bu)_2(CN)_2$, was not extensively characterized. Cleavage of the nitrogen–alkyl bond of a coordinated isocyanide is also required in the reported transalkylation by substituted benzyl halides of cyanopentakis(benzyl isocyanide)iron(II) bromide.[34] Finally, the mass spectra of compounds of the general formula $M(CN\text{-}t\text{-}C_4H_9)_x(CO)_{6-x}$ (x = 1–3; M = Cr, Mo, or W) contain prominent ions due to loss of a *tert*-butyl group.[21,35] This reaction has not been generally recognized, but it may be relatively common among cationic isocyanide complexes when the isocyanide alkyl group can form a stable carbonium ion.

Spectroscopic Properties. Electronic spectra taken in methanol are collected in Table I. All complexes containing alkyl isocyanides exhibit three characteristic bands at ~420–380 ($\epsilon \sim 10^3$), ~287–274 (sh), and ~257–235 nm ($\epsilon \sim 4 \times 10^4$).[36] The lowest energy band at 420 to 380 nm has been tentatively assigned to the $b_2(yz) \rightarrow a_1(z^2)$ transition.[5b] This assignment is consistent with the observed photochemical ligand labilization observed in these compounds when they are irradiated with visible

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(36) Although a band at 376 nm was previously reported for $[W(CN\text{-}t\text{-}Bu)_7](PF_6)_2$,[5b] we find that this complex has its low energy absorption maximum at 417 nm, in near agreement with other workers.[7c] Since $[Mo(CN\text{-}t\text{-}Bu)_6(CN)]^+$ has its absorption maximum at 380 nm (Table I), the previously reported spectrum was probably taken on a sample of $[W(CN\text{-}t\text{-}Bu)_7]^{2+}$ that had undergone the dealkylation reaction described in the text.

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light. The absorption bands at 274–287 and 235–257 nm are assigned as charge transfer bands ($\epsilon \sim 4 \times 10^4$). An additional band at 209–222 nm ($\epsilon \sim 4 \times 10^4$) is observed in all complexes containing a coordinated iodide ligand regardless of the nature of the counterion. The large value of the extinction coefficient tends to rule out the possibility of an iodide impurity in these compounds. The iodohexakis(aryl isocyanide) complexes show a set of bands that are red shifted from the positions of their alkyl analogues (Table I).

Table I also summarizes the ^{1}H NMR spectral data and major CN infrared stretching frequencies. The chemical shifts agree reasonably well with previously published data in the case of known compounds and are consistent with their fluxionality in solution.[5b,c] The chemical shift of the protons of coordinated *tert*-butyl isocyanide is quite insensitive to its coordination environment. The chemical shift of protons on the carbon atom α to the isocyanide nitrogen atom is somewhat more sensitive to the coordination environment; however, only a few examples have been characterized. The infrared spectral properties of the known compounds are consistent with the values reported in the literature.

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Registry No. $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$, 78656-70-9; $[Mo(CN\text{-}t\text{-}C_4H_9)_6Cl]Cl$, 66652-50-4; $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]I$, 66700-89-8; $[Mo(CN\text{-}t\text{-}C_4H_9)_6I](PF_6)$, 79516-88-4; $[Mo(CNCH_3)_6I](BF_4)$, 79466-85-6; $[Mo(CN\text{-}c\text{-}C_6H_{11})_6I]I$, 79466-86-7; $[Mo(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$, 41982-05-2; $[Mo(CN\text{-}c\text{-}C_6H_{11})_7](PF_6)_2$, 72155-82-9; $[W(CN\text{-}t\text{-}C_4H_9)_6CN](H_2PO_4)$, 79466-88-9; $[W(CN\text{-}t\text{-}C_4H_9)_6I]I$, 66652-48-0; $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$, 66687-57-8; $[Mo(CNC_6H_4\text{-}p\text{-}Cl)_6I]I$, 79466-89-0; $[Mo(CNC_6H_4\text{-}p\text{-}Cl)_6I](PF_6)$, 79466-91-4; $[Mo(CNC_6H_4\text{-}p\text{-}CH_3)_6I](PF_6)$, 79466-93-6; $[Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_2I_2]$, 79466-94-7; $[Mo(CN\text{-}t\text{-}C_4H_9)_5(CO)I]I$, 79466-95-8; $[W(CN\text{-}t\text{-}C_4H_9)_4(CO)I_2]$, 79466-96-9; $[Mo(CN\text{-}t\text{-}C_4H_9)_6SnCl_3](PF_6)$, 79466-98-1; $[Mo(CN\text{-}t\text{-}C_4H_9)_7](BPh_4)_2$, 76945-59-0; $[Mo(CN\text{-}c\text{-}C_6H_{11})_7]I_2$, 79466-99-2; $Mo(CNCH_3)_3(CO)_3$, 79516-89-5; $Mo(CO)_6$, 13939-06-5; $Mo(CN\text{-}t\text{-}C_4H_9)_3(CO)_3$, 79516-90-8; $W(CN\text{-}t\text{-}C_4H_9)_3(CO)_3$, 70095-01-1; $Mo(CNC_6H_4\text{-}p\text{-}Cl)_3(CO)_3$, 79516-91-9; $Mo(CNC_6H_4\text{-}p\text{-}CH_3)_3(CO)_3$, 79516-92-0; $Mo(CN\text{-}c\text{-}C_6H_{11})_3(CO)_3$, 31473-80-0; $W(CO)_6$, 14040-11-0.

Synthesis and Characterization of Tungsten Oxo Neopentylidene Complexes[1]

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Tantalum complexes of the type $Ta(CHCMe_3)X_3(PR_3)_2$ (X = Cl or Br) react with $W(O)(OCMe_3)_4$ to give $[Ta(OCMe_3)_4X]_2$ and $W(O)(CHCMe_3)X_2(PR_3)_2$. In $W(O)(CHCMe_3)X_2(PR_3)_2$ the phosphine ligands are trans and the oxo and neopentylidene ligands are cis to one another. Five-coordinate complexes can be prepared by scavenging one phosphine ligand with $PdCl_2(PhCN)_2$. Addition of 1 or 2 equiv of $AlCl_3$ to $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ in dichloromethane yields mono- and dicationic complexes, respectively. If $AlMe_3$ is added to $W(O)(CHCMe_3)Cl_2(PEt_3)_2$ unstable $[W(O)(CHCMe_3)(CH_3)(PEt_3)_2]^+(AlMe_2Cl_2^-)$ is formed, which on treatment with TMEDA yields $W(O)(CHCMe_3)(CH_3)(Cl)(TMEDA)$. Attempts to prepare cationic complexes with BF_4^- or PF_6^- counterions yielded fluoride complexes. Complexes containing *tert*-butoxide ligands in place of halides have been prepared by several routes. *tert*-Butoxide complexes containing phosphine ligands are relatively unstable toward decomposition to give phosphine oxide. Phosphine-free, unstable $[W(O)(CHCMe_3)(OCMe_3)_2]_2$ and other phosphine-free complexes such as $W(O)(CHCMe_3)Cl_2(TMEDA)$ and $W(O)(CHCMe_3)(S_2CNMe_2)_2$ have also been prepared. In none of these complexes is the $W{=}C_\alpha{-}C_\beta$ angle in the neopentylidene ligand large, as judged by the relatively high values for J_{CH_α} (115–130 Hz).

Introduction

Neopentylidene complexes of niobium and tantalum of several different types can be made readily by α hydrogen atom abstraction.[2] We had evidence that these principles extend to tungsten,[3] but, unfortunately, the necessary tungsten(VI) alkyl complexes are rare.[4] Therefore we had to turn to alternative methods to make tungsten(VI) neopentylidene complexes. We chose to attempt to transfer a neopentylidene ligand from tantalum to tungsten since tantalum alkylidene complexes are related to phosphorus ylides[2] and since we had been able to transfer a benzylidene or ethylidene ligand from phosphorus to tantalum.[5] The result was a route to what may be the most important type of group 6 alkylidene complex, that containing a second π-type ligand, in this case, an oxo ligand. Oxo alkylidene complexes are probably an important type of olefin metathesis catalyst,[6,7] and they have also led directly to the discovery of tungsten alkylidyne complexes which will metathesize acetylenes.[8] Here we

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