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# Synthesis and Characterization of Seven-Coordinate Molybdenum(II) and Tungsten(II) Isocyanide Complexes[1]

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The synthesis of the seven-coordinate $[\text{ML}_7]^{2+}$ and $[\text{ML}_6\text{X}]^+$ cations, where M = Mo or W, L = alkyl (usually *tert*-butyl) isocyanide, and X = Cl, Br, or I, is described. These complexes are best prepared by oxidative addition of the metal hexacarbonyl with halogen in the presence of the isocyanide ligand, although other routes are available. The X-ray crystal structure analysis of $[(t\text{-C}_4\text{H}_9\text{NC})_6\text{MoBr}]\text{Br}$ is presented. This complex, like the iodide analogue described previously, has a $C_{2v}$ capped trigonal-prismatic structure with the bromide ion as the capping ligand. All six molybdenum and tungsten $[\text{ML}_6\text{X}]\text{X}$ salts are isomorphous and presumably have this structure. The familiar pattern of metal–ligand bond lengths is observed. There are two short Mo–C distances, 2.05 Å, involving the two isocyanide ligands on the unique edge, four longer Mo–C distances, 2.12 Å, involving the four isocyanide ligands on the quadrilateral, capped face, and a molybdenum–bromine bond of 2.673 (2) Å. Solution conductivity data confirm electrolytic behavior expected for heptacoordinate cations $[\text{MoL}_7]^{2+}$ and $[\text{MoL}_6\text{I}]^+$. Temperature-dependent proton and $^{13}$C NMR spectral results suggest fluxional structures. Infrared (solids) and solution electronic spectral bands are reported.

Although numerous seven-coordinate transition metal complexes have been prepared and structurally characterized,[3] relatively few of these contain only monodentate ligands. Apart from heptafluorides, the class of geometrically characterized $\text{ML}_7$ complexes is limited to $[\text{V(CN)}_7]^{4-}$,[4] $[\text{Mo(CN)}_7]^{5-}$,[5] and $[\text{Mo(CNR)}_7]^{2+}$, R = *tert*-butyl.[6] The last of these has a $C_{2v}$ capped trigonal-prismatic structure, as does the related $[\text{Mo(CNR)}_6\text{I}]^+$ complex in which iodide is the capping ligand.[7] Compounds of general formula $\text{Mo(CNR)}_5\text{X}_2$ have also been reported,[8] but their structures are unknown.

The $[\text{Mo(CNR)}_7]^{2+}$ and $[\text{Mo(CNR)}_6\text{X}]^+$ complexes provide an opportunity to examine the effects of charge and ligand steric factors on the geometry of seven-coordinate species in the absence of any constraints imposed by chelating ligands. Structural information of this kind is important to test the predictions of theoretical discussions of the bonding in seven-coordination.[9] The present paper provides geometric data for bromohexakis(*tert*-butyl isocyanide)molybdenum(II) bromide, which is isomorphous with the iodide analogue. Moreover, since the original synthesis of $[\text{Mo(CNR)}_6\text{I}]^+$ was serendipitous and difficult to reproduce,[7] a more rational approach was devised.[10] Here we report further improvement of the synthetic method and preparative details for the complete series of complexes $[\text{M(CNR)}_7]^{2+}$ and $[\text{M(CNR)}_6\text{X}]^+$, where M = Mo or W, X = Cl, Br, or I, and R = alkyl, generally *tert*-butyl. Analogous aryl isocyanide complexes $[\text{M(CNPh)}_6\text{Cl}]^+$, M = Mo or W, may be obtained by irradiation of $[\text{M(CNPh)}_6]$ in chloroform.[11] The reductive coupling of isocyanide ligands in $[\text{Mo(CNR)}_6\text{I}]^+$ and related cations to form $[\text{Mo(CNR)}_4(\text{RHN}{=}\text{C}{=}\text{C}{=}\text{NHR})\text{X}]^+$ has been briefly described[2] and will be reported in detail elsewhere.[12]

## Experimental Procedure

**Synthetic Work.** All complexes were prepared and stored under an atmosphere of dinitrogen using anhydrous solvents. Methyl isocyanide and *tert*-butyl isocyanide were prepared by standard methods[13] and purified by distillation prior to use. Potassium octacyanomolybdate(IV) dihydrate was synthesized by a literature procedure.[14] Other starting materials were commercially available. Microchemical analyses were preformed by Galbraith Laboratories, Knoxville, Tenn.

**Heptakis(alkyl isocyanide)molybdenum(II) and -tungsten(II) Salts.** $[(\text{CH}_3\text{NC})_7\text{Mo}]\text{I}_2$**.** A mixture containing 2 mmol (0.528 g) of mo-

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lybdenum hexacarbonyl, 2 mmol (0.508 g) of iodine, an excess (21 mmol, 0.861 g) of methyl isocyanide, and 40 mL of methanol was heated to reflux for 5 h. The resultant bright yellow-brown solution was cooled to room temperature, and 150 mL of diethyl ether was added. The mixture was allowed to stand for several hours at 0 °C. Yellow, micalike crystals formed and were recrystallized from methanol–ether. The yield of pure product was ~0.45 g (35% based on Mo). Anal. Calcd for $C_{14}H_{21}N_7MoI_2$: C, 26.4; H, 3.32; N, 15.4; I, 39.8. Found: C, 26.3; H, 3.18; N, 15.2; I, 39.6. IR (KBr pellet): 3021 (vw), 2965 (w), 2921 (w), 2848 (vw), 2223 (sh), 2157 (vs, br), 2100 (sh), 1730 (vw, br), 1490 (w), 1447 (m), 1435 (sh), 1420 (sh), 1402 (s), 740 (vw, br), 690 (m), 500 (m, br) $cm^{-1}$.

**$[(CH_3NC)_7Mo](PF_6)_2$.** This compound was prepared by dissolving the iodide salt in methanol and adding to this solution an equivalent amount of $NaPF_6$, dissolved in a small amount of methanol. After the mixture stood for several hours at 0 °C, yellow crystals of the product were separated by filtration. Anal. Calcd for $C_{14}H_{21}N_7MoP_2F_{12}$: C, 25.0; H, 3.14; N, 14.6; Mo, 14.3; P, 9.20. Found: C, 24.9; H, 3.20; N, 14.5; Mo, 14.0; P, 9.01.

**$[(t\text{-}C_4H_9NC)_7Mo](PF_6)_2$.** This complex was prepared in a manner similar to that reported for the methyl derivative. For reasons discussed later, it was not possible to isolate a pure iodide salt. A solution containing 0.672 g (4 mmol) of $NaPF_6$ in 40 mL of methanol was, therefore, added to the yellow-brown solution. After the mixture stood for a couple of hours at 0 °C, yellow crystals of product formed. The yield was ~0.8 g or 40% based on Mo. Anal. Calcd for $C_{35}H_{63}N_7MoP_2F_{12}$: C, 43.4; H, 6.56; N, 10.1; P, 6.40; F, 23.6. Found: C, 43.5; H, 6.43; N, 10.0; P, 6.98; F, 22.4. IR (KBr pellet): 3020 (sh), 2988 (m), 2943 (w) 2880 (sh), 2212 (sh), 2138 (vs, br), 2055 (sh), 1730 (vw, br), 1474 (sh), 1459 (m), 1399 (vw), 1392 (sh), 1371 (m), 1281 (m), 1193 (s), 865 (sh), 843 (sh), 832 (vs), 692 (vw), 555 (m), 536 (w), 455 (w, br) $cm^{-1}$.

**$[(t\text{-}C_4H_9NC)_7Mo](I_5)_2$.** In the absence of direct light, an ice-cooled solution of 4.97 g (10 mmol) of $K_4Mo(CN)_8{\cdot}2H_2O$ and 1.95 g (30 mmol) of KCN in 80 mL of water was added slowly to an ice-cooled solution of 13.0 g (76.5 mmol) of $AgNO_3$ in 25 mL of water. The resulting precipitate was filtered, washed with water until the filtrate showed a negative silver ion test, methanol, and ethyl ether, and then dried in vacuo over $P_2O_5$. The precipitated mixture of AgCN and $Ag_4Mo(CN)_8$ was then suspended with stirring in 50 mL of chloroform in a 250-mL round-bottomed flask covered with aluminum foil to which 100 g of *tert*-butyl isocyanide was slowly added. The mixture was stirred for about 24 h and filtered. The filtrate was left to evaporate slowly in the air in a 250-mL Erlenmeyer flask. After 2 weeks, dark brown crystals were collected, washed twice with cold methanol to remove the resultant oil, and dried after a final washing with ethyl ether. The yield was 2.8 g (15% based on molybdenum). Anal. Calcd for $C_{35}H_{63}N_7MoI_{10}$: C, 21.6; H, 3.26. Found: C, 21.3; H, 3.12. IR (KBr pellet): 3031 (vw), 2987 (m), 2928 (w, br), 2856 (sh), 2195 (w), 2144 (vs), 2129 (sh), 2055 (sh), 1732 (w, br), 1491 (vw), 1469 (vw), 1452 (w), 1393 (vw), 1365 (vw), 1226 (w), 1192 (m), 750 (sh), 743 (w), 689 (w), 528 (m) $cm^{-1}$.

**$[(t\text{-}C_4H_9NC)_7Mo](I_3)_2$.** Recrystallization of the above compound four times from hot methanol yielded dark red crystals of product. Anal. Calcd for $C_{35}H_{63}N_7MoI_6$: C, 29.2; H, 4.41; N, 6.81; I, 52.9. Found: C, 29.4; H, 4.43; N, 6.56; I, 51.5. IR (KBr pellet): 2981 (m), 2931 (w, br), 2210 (s), 2143 (vs), 2055 (sh), 1729 (vw, br), 1448 (w), 1366 (m), 1230 (m), 1193 (s), 690 (w), 534 (m), 455 (vw) $cm^{-1}$.

**$[(t\text{-}C_4H_9NC)_7W](PF_6)_2$.** A 1.5-g (2-mmol) portion of $[(t\text{-}C_4H_9NC)_6WCl]Cl$, prepared as described below, was stirred in 20 mL of methanol in the presence of 0.5 g (6 mmol) of *tert*-butyl isocyanide for 30 min. A solution of 2 g (12 mmol) of $NaPF_6$ in 20 mL of methanol was then added. After the mixture stood at 0 °C overnight, a yellow precipitate formed which was filtered, washed with diethyl ether, and recrystallized from methylene chloride and diethyl ether. The yield was 80% (1.7 g) based on tungsten. Anal. Calcd for $C_{35}H_{63}N_7WP_2F_{12}$: C, 39.8; H, 6.02; N, 9.29. Found: C, 40.0; H, 5.89; N, 9.04. IR (Nujol mull): 2145 (vs, br), 2085 (sh), 1245 (m), 1205 (vs, br), 890 (sh), 865 (vs, br), 780 (w), 720 (w), 567 (s), 547 (s) $cm^{-1}$.

**Halohexakis(alkyl isocyanide)molybdenum(II) and -tungsten(II) Salts. $[(t\text{-}C_4H_9NC)_6MoCl]Cl$.** Chlorine gas was slowly introduced into a stirred suspension of 4 mmol of molybdenum hexacarbonyl in 20 mL of benzene until about 80% of the solid was dissolved yielding a brownish yellow solution. A 2-g (24 mmol) portion of *tert*-butyl isocyanide was added to the mixture, followed by 40 mL of benzene. The mixture was then filtered and 1 g more of *tert*-butyl isocyanide was added to the greenish yellow filtrate. After the mixture was stirred for 2 days, a yellow precipitate was filtered, washed with benzene and diethyl ether, and recrystallized from acetone and ether. The yield was 40% (1.1 g, based on molybdenum). Anal. Calcd for $C_{30}H_{54}N_6MoCl_2$: C, 54.1; H, 8.18; N, 12.6; Cl, 10.7. Found C, 54.0; H, 8.38; N, 12.2; Cl, 11.1. IR (Nujol mull): 2209 (sh), 2149 (vs, br), 2079 (sh), 1242 (m), 1201 (s), 541 (s), 476 (w), 436 (w) $cm^{-1}$.

**$[(t\text{-}C_4H_9NC)_6MoBr]Br$.** Bromine (0.64 g, 4 mmol) was added dropwise over a period of 10 min to a stirred suspension of 1.06 g (4 mmol) of molybdenum hexacarbonyl in 20 mL of benzene. The subsequent additions of *tert*-butyl isocyanide, workup, and product purification steps were identical with those described above for the chloride analogue. The yield was 30% based on molybdenum. Anal. Calcd for $C_{30}H_{54}N_6MoBr_2$: C, 47.8; H, 7.21; N, 11.1; Br, 21.2. Found: C, 47.9; H, 7.29; N, 10.8; Br, 20.5. IR (Nujol mull): 2205 (sh), 2140 (vs, br), 2075 (sh), 1245 (sh), 1190 (vs), 965 (m), 540 (s) $cm^{-1}$.

**$[(t\text{-}C_4H_9NC)_6MoI]I$. Method A.** About 2.6 g of $[(t\text{-}C_4H_9NC)_7Mo](I_5)_2$, prepared as described above, was dissolved in 75 mL of methylene chloride, washed twice with an equal volume of a saturated aqueous solution of sodium thiosulfate and three times with water, and then dried with $MgSO_4$. The dried solution was filtered, mixed with 400 mL of ethyl ether, and allowed to stand overnight at 0 °C. The yield of orange crystals was 0.93 g (82% based on molybdenum). Anal. Calcd for a monohydrate $C_{30}H_{56}N_6MoI_2O$: C, 41.6; H, 6.51; N, 9.70; Mo, 11.1; I, 29.3; O, 1.85. Found: C, 41.2; H, 6.21; N, 9.85; Mo, 10.7; I, 28.9; O, 1.46. IR (KBr pellet): 3430 (m, br), 3029 (vw), 2984 (m), 2937 (w), 2875 (vw), 2177 (sh), 2119 (vs), 2047 (sh), 1734 (vw), 1625 (w), 1453 (w), 1394 (vw), 1368 (s), 1230 (m), 1188 (s), 687 (vw), 524 (m), 450 (vw, br) $cm^{-1}$.

**Method B.** A 1.3-g portion of $[(t\text{-}C_4H_9NC)_6MoCl]Cl$ or 1.5 g of $[(t\text{-}C_4H_9NC)_6MoBr]Br$ was refluxed with 5 g of NaI in 60 mL of methanol for 6 h. After removal of the solvent under reduced pressure, the product was extracted into methylene chloride and precipitated by addition of diethyl ether. Recrystallization from methanol and diethyl ether yielded 80% of orange crystals. Anal. Found: C, 41.7; H, 6.37; N, 9.43. IR (Nujol mull): 2123 (vs, br), 1240 (w), 1200 (s, br), 540 (s) $cm^{-1}$.

**$[(t\text{-}C_4H_9NC)_6WCl]Cl$.** This compound was prepared in 30% yield from 4 mmol of tungsten hexacarbonyl in a manner identical with that reported for the synthesis of the molybdenum analogue. Anal. Calcd for a monohydrate $C_{30}H_{56}N_6WCl_2O$: C, 46.7; H, 7.32; N, 10.9. Found: C, 46.1; H, 6.74; N, 10.5. IR (Nujol mull): 2129 (vs, br), 2079 (sh), 1243 (m), 1203 (s), 541 (m) $cm^{-1}$.

**$[(t\text{-}C_4H_9NC)_6WBr]Br$.** A procedure similar to that described for the molybdenum analogue was used to prepare this compound in 35% yield from 4 mmol of $W(CO)_6$. Recrystallization was achieved by slow vapor diffusion of diethyl ether into a solution of 2:1 (v/v) acetone–benzene. Anal. Calcd for a monohydrate $C_{30}H_{56}N_6WBr_2O$: C, 41.9; H, 6.56; N, 9.77. Found: C, 41.9; H, 6.62; N, 9.42. IR (Nujol mull): 2137 (vs, br), 1233 (sh), 1198 (s), 538 (s) $cm^{-1}$.

**$[(t\text{-}C_4H_9NC)_6WI]I$.** A solution of 1.5 g of $[(t\text{-}C_4H_9NC)_6WCl]Cl$ and 5 g of NaI in methanol was refluxed for 12 h. The rest of the procedure was the same as that described for the molybdenum analogue. The yield was 70% based on tungsten. Anal. Calcd for $C_{30}H_{54}N_6WI_2$: C, 38.5; H, 5.81; N, 8.97. Found: C, 38.2; H, 5.70; N, 8.70. IR (Nujol mull): 2130 (vs, br), 1240 (sh), 1195 (s), 535 (s) $cm^{-1}$.

**Physical Measurements.** Infrared spectra were recorded on a Jasco IRA-1 or a Perkin-Elmer Model 621 spectrophotometer calibrated with polystyrene film to an accuracy of ±5 $cm^{-1}$. Solids were examined as KBr pellets or as Nujol mulls spread between CsI plates. Electronic spectra were recorded on a Cary Model 14 or Model 118C spectrophotometer using 1-cm path length matched quartz cells. Conductivities were determined at a constant temperature of 25 °C with an Industrial Instruments Inc. Model RC 16B2 conductance bridge. The nitromethane solvent was dried and distilled prior to use. Proton NMR spectra were measured on a Varian A-60A spectrometer at ambient probe temperature. Variable-temperature $^{13}C$ NMR spectra were obtained with a JEOL PS-100 high-resolution spectrometer using pulsed Fourier transform techniques and proton noise decoupling. Cell constants and the space group for the series of complexes $[(t\text{-}C_4H_9NC)_6MX]X$ (M = Mo, W; X = Cl, Br, I) were determined with a Weissenberg camera. The film was not calibrated.

**Collection and Reduction of X-ray Data for $[(t\text{-}C_4H_9NC)_6MoBr]Br$.** Approximate unit cell parameters and the space group of a pale orange

**Table I.** Experimental Details of the X-ray Diffraction Study of $[(t\text{-}C_4H_9NC)_6MoBr]Br$

(A) Crystal Parameters[a] at 23 °C

$a = 16.395\ (10)$ Å
$b = 22.005\ (13)$ Å
$c = 22.075\ (13)$ Å
$V = 7964.04$ Å$^3$
mol wt 754.6
space group *Cmca*
$Z = 8$
$\rho(\text{calcd}) = 1.258$ g/cm$^3$
$\rho(\text{obsd})^b = 1.263\ (1)$ g/cm$^3$

(B) Measurement of Intensity Data

instrument: Picker FACS-I-DOS diffractometer
radiation: graphite-monochromatized Mo K$\alpha$ ($\lambda_{\alpha_1}$ 0.709 30 Å)
attenuator: used for counts >10 000/s
takeoff angle: 2.0°
detector aperture: 6.35 mm × 6.35 mm
crystal–detector dist: 33 cm
scan mode: coupled $\theta$(crystal)–$2\theta$(counter)
scan rate: 1°/min
scan range: $2.0 < 2\theta < 50°$
scan length: from $2\theta(K\alpha_1) - 0.85°$ to $2\theta(K\alpha_2) + 0.85°$
bgd measurements: stationary crystal, stationary counter, 20-s counts at each end of $2\theta$ scan range
standards: three reflcns $(\bar{2},10,0)$, $(\bar{6},2,0)$, $(\bar{2},0,8)$ measd every 97 data
no. of reflcns collected: 4854 ($-h,+k,\pm l$ at $2\theta \leqslant 20°$ and $-h,+k,+l$ at $2\theta > 20°$)

(C) Reduction of Intensity Data[c]

convrsn to $F_o^2$ and $\sigma(F_o^2)$: correction for bgd, attenuators, and Lorentz–polarization of monochromatized X radiation in the usual manner[d,e] with $\epsilon = 0.05$
absorption correction:[f] $\mu = 22.8$ cm$^{-1}$; transmission factors varied between 0.68 and 0.73
averaging:[g] done over two or more equivalent forms; agreement factor $R_{av} = 0.0133$
scaling: Wilson's method;[h] $\overline{B} = 2.76$ Å$^2$
obsd data: 2425 unique reflcns for which $F_o^2 > 2\sigma(F_o^2)$

[a] From a least-squares fit to the setting angles of 18 reflections. [b] By suspension in $CCl_4$–*n*-heptane solutions. [c] Programs for an IBM 360/91 computer used in this work are described in J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens, and S. J. Lippard, *Inorg. Chem.*, **15**, 1155 (1976). [d] B. G. Segal and S. J. Lippard, *ibid.*, **13**, 822 (1974). [e] J. T. Gill and S. J. Lippard, *ibid.*, **14**, 751 (1975). [f] Absorption corrections were carried out using a local version of ORABS, the Wehe–Busing–Levy program, adapted to the Picker FACS geometry. [g] Using AVERAGE by J. T. Gill, $R_{av} = \Sigma_{i=1}{}^N \Sigma_{j=1}{}^n |\overline{F_i^2} - F_{ij}| / \Sigma_{i=1}{}^N \overline{F_i^2}$. [h] A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

crystal were determined with precession and Weissenberg cameras using nickel-filtered Cu K$\bar{\alpha}$ radiation (λ 1.5418 Å). The compound was found to be isomorphous with the iodide analogue,[7] crystallizing in either the centrosymmetric, orthorhombic space group *Cmca* ($D_{2h}{}^{18}$; No. 64)[15a] or in acentric *Aba*2 ($C_{2v}{}^{17}$; No. 41).[15b]

Using an automated four-circle diffractometer, data were collected on a rectangular prism with faces (100) and ($\bar{1}$00) 0.45 mm apart, (010) and (0$\bar{1}$0) 0.15 mm apart, and (001) and (00$\bar{1}$) 0.17 mm apart. The crystal mounting axis was parallel to $a^*$, offset by 4° from the spindle axis for data collection. Details of data collection and reduction are given in Table I.

**Determination and Refinement of the Structure.** The starting coordinates of the anion and of the inner core atoms ($MoC_6Br$) of the cation were those of the isomorphous $[(t\text{-}C_4H_9NC)_6MoI]I$ analogue,[7] with the appropriate transformation ($x' = z$; $y' = y$; $z' = x$) to refine in *Cmca*. The iodide complex had been refined in *Acam*. After several cycles of isotropic refinement, a difference Fourier map revealed some of the terminal carbon atoms of the *tert*-butyl groups to be disordered. These were introduced into the structure factor calculation and refined. Two *tert*-butyl groups lying on mirror planes were treated as ordered and refined anisotropically with full weight. For the remaining two ligands, six disordered carbon atoms representing two orientations were refined isotropically with half-weight. All other atoms were assigned anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Owing to the disorder, no attempt was made to locate hydrogen atoms. Least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$, converged at final values of 0.064 and 0.080 for the residuals $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, respectively. A total of 186 variable parameters were used to fit 2425 data having $F_o^2 > 2\sigma(F_o^2)$. In the final refinement cycle, no parameter shift exceeded 0.3 times its estimated standard deviation. Atomic scattering factors and anomalous dispersion contributions from molybdenum and bromine were taken from ref 16. The error on an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, was 2.025 and an examination of the function $w\Delta^2$ for data sectioned according to $|F_o|$ and $(\sin\theta)/\lambda$ showed the weighting scheme to be satisfactory.

A final difference Fourier map revealed residual electron density (maximum value 1.5 e/Å$^3$) at $0.43 < x < 0.57$, $-0.04 < y < 0.04$, $-0.03 < z < 0.03$, a loosely packed region of the unit cell containing a channel formed by the *tert*-butyl terminal carbon atoms and capped by two bromide ions at $x = \pm 0.23$, $y = z = 0$. Similar results were observed in the structure determination of the isomorphous iodide complex.[7] Since the magnitude and positional maxima of the residual electron density depends on the parameters varied in the least-squares refinement, e.g., which terminal carbon atoms were allowed to refine anisotropically, its existence is probably due to an incomplete or improper model for the terminal carbon atoms. There may also be some residual water in the channel, a possibility discussed below. All other electron density on the difference maps was less than 0.8 e/Å$^3$.

Atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the final cycle of least-squares refinement, are given in Table II. Table III summarizes interatomic distances and angles. A listing of observed and calculated structure factor amplitudes and the root-mean-square amplitudes of thermal vibration are available as Tables S1 and S2 (supplementary material). The coordination geometry of the $[(t\text{-}C_4H_9NC)_6MoBr]^+$ cation is depicted in Figure 1. Figure 2 displays a packing diagram showing the channel formed by the *tert*-butyl groups.

## Results and Discussion

**Syntheses.** The alkylation[17] of silver octacyanomolybdate to form yellow $Mo(CN)_4(CNR)_4$ compounds, eq 1, was

$$Ag_4[Mo(CN)_8] + 4RX \rightarrow Mo(CN)_4(CNR)_4 + 4AgX \qquad (1)$$

$$R = CH_3, C_2H_5, n\text{-}C_3H_7, i\text{-}C_3H_7, t\text{-}C_4H_9, \text{etc.}$$

observed in one instance[18] to lead to the formation of a small crop of red-orange crystals shown by X-ray crystallography[7] to be $[(t\text{-}C_4H_9NC)_6MoI]I$. Although reduction to divalent molybdenum was tentatively suggested to proceed according to eq 2, the failure to reproduce the synthesis of iodo-

$$Ag_4[Mo(CN)_8] + 6RI \rightarrow [Mo(CNR)_6I]I + 2AgCN + 2AgI + I_2 \qquad (2)$$

hexakis(*tert*-butyl isocyanide)molybdenum(II) iodide by this route led to an alternative explanation. In particular, it seemed possible that a cyanide ion contaminant in the silver octacyanomolybdate(IV) became alkylated and that the resulting excess isocyanide served as the reducing agent. To test this hypothesis, a 3:1 mixture of AgCN and $Ag_4[Mo(CN)_8]$ was treated with an excess of *tert*-butyl iodide to produce dark brown-violet crystals of a material analyzing as $[(t\text{-}C_4H_9NC)_7Mo](I_5)_2$. Several recrystallizations from hot methanol gave the triiodide salt. When the pentaiodide compound was dissolved in methylene chloride, washed with aqueous thiosulfate, and the resulting solution treated with ethyl ether at 0 °C, reasonable quantities of $[(t\text{-}C_4H_9NC)_6MoI]I{\cdot}H_2O$ were isolated. Since an alternative synthesis of this complex was independently developed, no attempt was made to identify the organic by-products of the alkylation–reduction reaction.

A more satisfactory route to complexes of the type $[Mo(CNR)_6X]^+$ and $[Mo(CNR)_7]^{2+}$ involves oxidative addition of molybdenum hexacarbonyl with halogen in the presence of the isocyanide ligand. The compounds $[(RNC)_7Mo]Y_2$ (R = $CH_3$, Y = $PF_6$, I; R = $t\text{-}C_4H_9$, Y = $PF_6$) were prepared according to eq 3, followed by metathesis to obtain the

$$Mo(CO)_6 + I_2 + 7RNC \rightarrow [(RNC)_7Mo]I_2 + 6CO \qquad (3)$$

hexafluorophosphate salts. In this reaction substitution of all

**Table II.** Final Positional and Thermal Parameters of the Atoms[a,b]

| atom | $x$ | $y$ | $z$ | $\beta_{11}$[c] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo | 0.0 | 0.28804 (4) | 0.28018 (4) | 2.74 (4) | 1.25 (2) | 1.21 (2) | 0.0 | 0.0 | 0.12 (2) |
| Br1 | 0.0 | 0.20216 (6) | 0.19452 (6) | 6.10 (8) | 1.98 (3) | 1.98 (3) | 0.0 | 0.0 | −0.58 (3) |
| Br2 | 0.2302 (1) | 0.0 | 0.0 | 6.87 (1) | 3.26 (5) | 2.89 (4) | 0.0 | 0.0 | 0.50 (3) |
| C1 | 0.0 | 0.3796 (5) | 0.2974 (5) | 4.0 (6) | 1.2 (3) | 2.3 (3) | 0.0 | 0.0 | −0.1 (2) |
| N1 | 0.0 | 0.4308 (5) | 0.3070 (5) | 5.7 (7) | 2.0 (3) | 2.9 (3) | 0.0 | 0.0 | −0.3 (3) |
| C11 | 0.0 | 0.4968 (5) | 0.3189 (8) | 5.1 (7) | 1.0 (3) | 4.1 (5) | 0.0 | 0.0 | −0.7 (3) |
| C2 | 0.0 | 0.3044 (6) | 0.3715 (6) | 4.2 (6) | 2.2 (3) | 1.5 (3) | 0.0 | 0.0 | −0.0 (3) |
| N2 | 0.0 | 0.3138 (5) | 0.4228 (5) | 6.6 (7) | 3.0 (3) | 1.6 (3) | 0.0 | 0.0 | −0.2 (2) |
| C21 | 0.0 | 0.3223 (8) | 0.4887 (6) | 4.8 (7) | 4.3 (5) | 1.1 (3) | 0.0 | 0.0 | −0.6 (3) |
| C3 | 0.0941 (5) | 0.3241 (4) | 0.2251 (4) | 3.9 (4) | 1.9 (2) | 1.5 (2) | −0.3 (2) | 0.4 (2) | −0.0 (2) |
| N3 | 0.1396 (5) | 0.3459 (3) | 0.1910 (3) | 4.1 (4) | 2.1 (2) | 2.1 (2) | −0.4 (2) | 0.6 (2) | 0.2 (2) |
| C31 | 0.1820 (5) | 0.3785 (4) | 0.1421 (4) | 3.8 (4) | 2.0 (2) | 2.1 (2) | −0.1 (3) | 1.0 (3) | 0.1 (2) |
| C4 | 0.0942 (5) | 0.2331 (4) | 0.3158 (4) | 2.8 (4) | 1.8 (2) | 1.8 (2) | 0.2 (2) | −0.3 (2) | 0.1 (2) |
| N4 | 0.1402 (5) | 0.1996 (3) | 0.3366 (3) | 3.9 (4) | 2.3 (2) | 2.3 (2) | 0.7 (2) | −0.4 (2) | −0.0 (2) |
| C41 | 0.1911 (7) | 0.1536 (5) | 0.3678 (5) | 7.3 (7) | 2.9 (3) | 3.2 (3) | 2.3 (4) | −2.4 (4) | −0.7 (2) |
| C111 | 0.0 | 0.5236 (9) | 0.2604 (13) | 60.7 (76) | 1.7 (5) | 5.3 (9) | 0.0 | 0.0 | −0.2 (6) |
| C112 | 0.0796 (13) | 0.5177 (7) | 0.3380 (13) | 11.2 (13) | 3.6 (5) | 18.5 (16) | 0.3 (6) | −8.8 (12) | −2.8 (7) |
| C211 | 0.0 | 0.2617 (14) | 0.5151 (9) | 57.0 (72) | 5.5 (10) | 1.7 (6) | 0.0 | 0.0 | 0.5 (6) |
| C212 | 0.0798 (14) | 0.3419 (15) | 0.5087 (9) | 12.7 (15) | 18.9 (18) | 5.0 (6) | −8.2 (13) | 0.6 (7) | −4.6 (8) |

| atom | $x$ | $y$ | $z$ | $B$[d] | atom | $x$ | $y$ | $z$ | $B$[d] |
|---|---|---|---|---|---|---|---|---|---|
| C311 | 0.2364 (18) | 0.4279 (12) | 0.1702 (12) | 8.3 (6) | C411 | 0.2283 (17) | 0.1775 (12) | 0.4220 (12) | 7.2 (6) |
| C312 | 0.1678 (13) | 0.4452 (9) | 0.1521 (9) | 5.4 (5) | C412 | 0.2863 (15) | 0.1699 (11) | 0.3433 (11) | 6.9 (6) |
| C313 | 0.2301 (20) | 0.3331 (14) | 0.1062 (14) | 10.1 (8) | C413 | 0.2277 (19) | 0.1111 (14) | 0.3263 (13) | 8.7 (7) |
| C314 | 0.2728 (13) | 0.3642 (10) | 0.1479 (10) | 6.0 (5) | C414 | 0.1731 (17) | 0.0964 (12) | 0.3418 (12) | 7.2 (6) |
| C315 | 0.1471 (14) | 0.3580 (10) | 0.0840 (10) | 5.9 (5) | C415 | 0.1161 (19) | 0.1052 (13) | 0.4051 (14) | 10.0 (8) |
| C316 | 0.1176 (19) | 0.4109 (13) | 0.1013 (13) | 9.1 (7) | C416 | 0.1838 (16) | 0.1622 (11) | 0.4339 (11) | 6.0 (5) |

[a] Atoms are labeled as indicated in Figure 1. The labeling of terminal methyl carbon atoms is as described in ref 7. Their disorder is discussed in the text. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic ellipsoid is given in the text. Values for $\beta$ are × $10^3$. [d] $B$ is the isotropic thermal parameter, in Å$^2$.

the carbonyl ligands is facilitated by oxidation of the molybdenum atom. A mixed carbonyl–isocyanide molybdenum(0) intermediate is more likely than a binary molybdenum iodide since the latter is known to produce oxotetrakis(alkyl isocyanide)molybdenum(IV) complexes under the reaction conditions.[19] Decrease of the solution conductivity (see below) with time of $[(\mathrm{RNC})_7\mathrm{Mo}]\mathrm{I}_2$ complexes together with the fact that the *tert*-butyl derivative could only be isolated as a mixture of $[(t\text{-}\mathrm{C_4H_9NC})_7\mathrm{Mo}]\mathrm{I}_2$ and $[(t\text{-}\mathrm{C_4H_9})_6\mathrm{MoI}]\mathrm{I}$ suggests the existence of the equilibrium shown in eq 4. The structural results[6,7] for the two cations show that the capping isocyanide ligand is replaced by iodide in eq 4.

$$[(\mathrm{RNC})_7\mathrm{Mo}]\mathrm{I}_2 \rightleftharpoons [(\mathrm{RNC})_6\mathrm{MoI}]\mathrm{I} + \mathrm{RNC} \qquad (4)$$

The general synthetic method used to prepare halohexakis(*tert*-butyl isocyanide)molybdenum(II) and the tungsten(II) analogues is outlined in eq 5 and 6 ($\mathrm{R} = t\text{-}\mathrm{C_4H_9}$;

$$\mathrm{M(CO)_6} \xrightarrow{\mathrm{X_2}} \mathrm{M(CO)_4X_2} \xrightarrow{\mathrm{RNC}} [(\mathrm{RNC})_6\mathrm{MX}]\mathrm{X} \qquad (5)$$

$$[(\mathrm{RNC})_6\mathrm{MX}]\mathrm{X} \xrightarrow{\mathrm{I^-}} [(\mathrm{RNC})_6\mathrm{MI}]\mathrm{I} \qquad (6)$$

M = Mo, W; X = Cl, Br). Use of benzene rather than methanol as the solvent avoided formation of the $[(\mathrm{RNC})_4\mathrm{MoXO}]^+$ oxo ions. The parent tungsten complex $[(t\text{-}\mathrm{C_4H_9NC})_7\mathrm{W}]^{2+}$ was obtained according to eq 7. In the

$$[(\mathrm{RNC})_6\mathrm{WX}]\mathrm{X} \xrightarrow[\mathrm{PF_6^-}]{\mathrm{RNC}} [(\mathrm{RNC})_7\mathrm{W}](\mathrm{PF_6})_2 \qquad (7)$$

case of the larger $[(\mathrm{RNC})_6\mathrm{MX}]^+$ complexes, where M = W and/or X = I, some of the analytical data suggest the presence of as much as one water molecule of crystallization. The crystal lattice of these complexes has space to accommodate residual water (see ref 7 and discussion below). A procedure analogous to that of eq 5 was used to obtain $\mathrm{Mo(CNR)_5X_2}$ complexes (R = cyclohexyl, X = Br; R = *p*-tolyl, X = Br, Cl),[8] a stoichiometry never observed in the present study.

**Description of the $[(t\text{-}\mathrm{C_4H_9NC})_6\mathrm{MoBr}]\mathrm{Br}$ Structure.** The geometry of the $[(t\text{-}\mathrm{C_4H_9NC})_6\mathrm{MoBr}]^+$ cation is that of a capped trigonal prism with the bromide ion occupying the capping position (Figure 1). As with the isomorphous, isostructural iodide analogue, the cation has a crystallographically required mirror plane containing the *c* edge (Figure 3) of the prism. Perusal of the interatomic distances and angles (Table III), however, reveals the virtual symmetry to be $C_{2v}$. Calculation of the (unnormalized[20]) $\delta'$ angles[21] confirms the choice of a capped trigonal prism as the closest idealized coordination polyhedron. These results, together with a list of normalized shape parameters (Figure 3) for several related capped trigonal-prismatic structures, are summarized in Table IV.

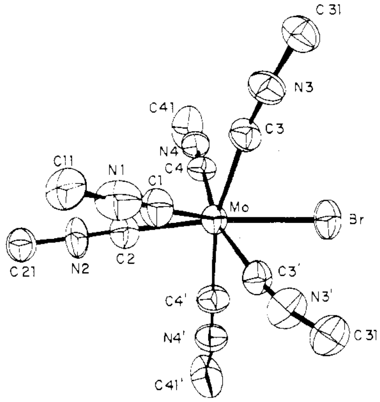

**Figure 1.** Geometry of the bromohexakis(*tert*-butyl isocyanide)molybdenum(II) cation omitting the terminal methyl carbon atoms and showing the atom labeling scheme and 40% probability thermal ellipsoids. The primed atoms are related to the unprimed ones by a crystallographic mirror plane.

Table IV provides an opportunity to examine the stereochemistry of the structurally analogous cations $\mathrm{MoL_7}^{2+}$, $\mathrm{MoL_6Br}^+$, and $\mathrm{MoL_6I}^+$, where L is *tert*-butyl isocyanide. The pattern of Mo–C bond lengths, $r_\mathrm{A} > r_\mathrm{B} > r_\mathrm{C}$, is identical among the three complexes and reflects the greater metal–ligand bond strength to the isocyanide groups on the unique ($c$) edge of

**Table III.** Molecular Geometry of the $[(t\text{-}C_4H_9NC)_6MoBr]^+$ Cation[a,b]

Bond Distances, Å

| | | | |
|---|---|---|---|
| Mo–Br1 | 2.673 (2) | C2–N2 | 1.153 (15) |
| Mo–C1 | 2.051 (12) | C3–N3 | 1.162 (10) |
| Mo–C2 | 2.047 (13) | C4–N4 | 1.150 (10) |
| Mo–C3 | 2.119 (9) | N1–C11 | 1.476 (15) |
| Mo–C4 | 2.113 (9) | N2–C21 | 1.466 (17) |
| C1–N1 | 1.146 (14) | N3–C31 | 1.471 (11) |
| | | N4–C41 | 1.482 (12) |

Interbond Angles, Deg

| | | | |
|---|---|---|---|
| Br1–Mo–C1 | 145.7 (3) | C4–Mo–C4′ | 93.9 (4) |
| Br1–Mo–C2 | 145.1 (4) | C3–Mo–C4′ | 163.8 (3) |
| Br1–Mo–C3 | 81.9 (2) | N1–C1–Mo | 179.9 (11) |
| Br1–Mo–C4 | 81.9 (2) | N2–C2–Mo | 179.8 (12) |
| C1–Mo–C2 | 69.2 (5) | N3–C3–Mo | 173.2 (8) |
| C1–Mo–C3 | 74.8 (3) | N4–C4–Mo | 174.0 (7) |
| C1–Mo–C4 | 119.5 (3) | C11–N1–C1 | 179.7 (29) |
| C2–Mo–C3 | 120.0 (3) | C21–N2–C2 | 177.0 (15) |
| C2–Mo–C4 | 74.6 (3) | C31–N3–C3 | 168.2 (9) |
| C3–Mo–C4 | 84.0 (3) | C41–N4–C4 | 173.0 (10) |
| C3–Mo–C3′ | 93.4 (5) | | |

| central atom | C–C dist, Å | | N–C–C angle, deg | |
|---|---|---|---|---|
| | group A | group B | group A | group B |
| C11 | 1.44 (2, 3)[c] | | 106 (4,5) | |
| C21 | 1.46 (1, 2) | | 109 (3, 4) | |
| C31 | 1.52 (2, 4) | 1.52 (5, 9) | 108 (1, 2) | 108 (1, 2) |
| C41[d] | 1.52 (14, 25) | 1.57 (22, 40) | 109 (5, 9) | 110 (2, 3) |

Nonbonded Contacts along Polyhedral Edges

| edge | length Å | type[e] |
|---|---|---|
| Br1–C3 | 3.168 (9) | *a* |
| Br1–C4 | 3.165 (8) | *a* |
| Mean *a* | 3.167 | |
| C3–C4 | 2.832 (12) | *r* |
| C3–C3′ | 3.086 (18) | *t* |
| C4–C4′ | 3.089 (17) | *t* |
| Mean *t* | 3.088 | |
| C1–C3 | 2.535 (13) | *p* |
| C2–C4 | 2.521 (13) | *p* |
| Mean *p* | 2.528 | |
| C1–C2 | 2.326 (17) | |

[a] See footnotes *a* and *b*, Table II. [b] Reported values have not been corrected for thermal motion. [c] Numbers in parentheses are ± standard deviations from the mean and range of values, respectively, in the last significant figures. Groups A and B for C31 and C41 as central atoms are disordered as described in the text. [d] The poor geometry observed for this group reveals that, although crudely accounting for the electron density in this region of the unit cell, the disordered model employed is not chemically significant. [e] See Figure 3 for nomenclature.

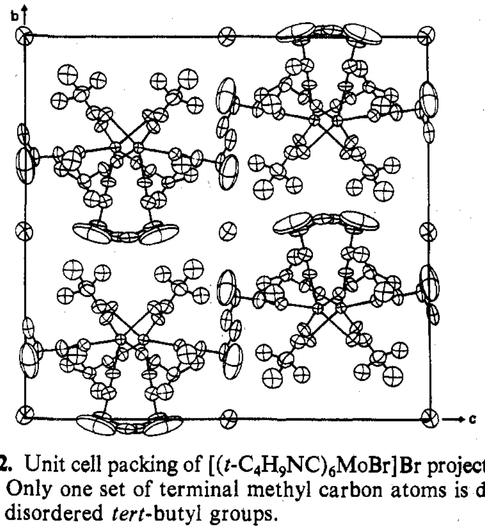

**Figure 2.** Unit cell packing of $[(t\text{-}C_4H_9NC)_6MoBr]Br$ projected down [100]. Only one set of terminal methyl carbon atoms is displayed for the disordered *tert*-butyl groups.

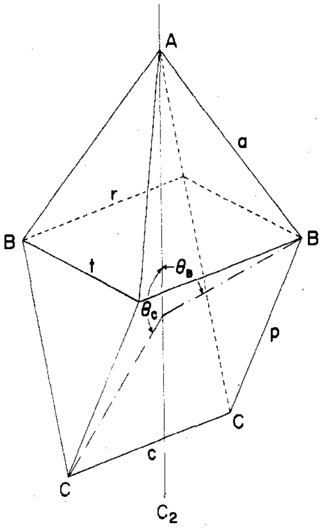

**Figure 3.** The $C_{2v}$ capped trigonal prism showing edge and angle labels (reproduced from ref 6).

**Table IV.** Normalized Shape Parameters for Related Capped Trigonal-Prismatic Structures[a]

| parameter[b] | hard-sphere model[c] | $[(t\text{-}C_4H_9\text{-}NC)_7Mo]^{2+}$ | $[(t\text{-}C_4H_9NC)_6MoX]^+$ | |
|---|---|---|---|---|
| | | | X = Br | X = I |
| $r_A$, | 1.0 | 1.027 | | |
| $r_B$, | 1.0 | 1.008 | 1.016 | 1.014 |
| $r_C$, | 1.0 | 0.970 | 0.984 | 0.986 |
| $\theta_B$, deg | 79.4 | 82.0 | 81.9 | 81.5 |
| $\theta_C$, deg | 143.3 | 144.2 | 145.4 | 145.1 |
| *a*, | 1.2775 | 1.333 | | |
| *r*, | 1.2975 | 1.279 | 1.360 | 1.375 |
| *t*, | 1.4769 | 1.534 | 1.483 | 1.457 |
| *p*, | 1.2327 | 1.206 | 1.214 | 1.211 |
| *c*, | 1.1950 | 1.133 | 1.117 | 1.130 |
| *a*/*c* | 1.0690 | 1.1770 | 1 3616 | 1.3986 |
| *r*/*c* | 1.0858 | 1.1290 | 1.2175 | 1.2169 |
| *t*/*c* | 1.2359 | 1.3539 | 1.3276 | 1.2895 |
| *p*/*c* | 1.0315 | 1.0647 | 1.0868 | 1.0722 |
| $\delta_1'$, deg | 41.5 | 40.3 | 39.5 | 36.7 |
| $\delta_2'$, deg | 0.0 | 0.0 | 1.09 | 0.07 |
| $\delta_3'$, deg | 0.0 | 0.0 | 1.11 | 0.07 |
| ref | 22 | 6 | this work | 7 |

[a] Shape parameter lengths are normalized to the mean metal–ligand bond length except for the last two entries in which the normalization was carried out exclusive of the Mo–X bond length. [b] Defined in Figure 3 or, in the case of the δ′ angles, in ref 21. [c] A value of 6.0 was used for the Born exponent

the capped trigonal prism, Figure 3. An analysis of intramolecular nonbonded interactions among the methyl groups of the *tert*-butyl residues indicates that the observed Mo–C bond length variation is not the result of steric factors. For example, shortening $r_B$ to 0.945 in $MoL_7^{2+}$ without changing any angles reduces the shortest $CH_3\cdots CH_3$ contact across the *a*, *r*, and *t* edges from 4.5 to 4.3 Å, both well above the sum of the van der Waals radii for two methyl groups, 4 Å. The short and presumably strong bonds to the ligands on the unique (*c*) edge found in the X-ray structure of these three different capped trigonal-prismatic $d^4$ complexes are not in accord with the expectations of a molecular orbital analysis which predicted that the bonds to the quadrilateral face ligands would be strongest.[9]

Other variations of the shape parameters listed in Table IV follow the trends noted previously.[7] In most respects the geometry of the bromide structure is intermediate between those of the iodide analogue and the parent $MoL_7^{2+}$ cation but is closer to that of the former. The $MoL_6$ moiety involving the four B- and two C-type ligands is structurally similar

**Table V.** Molar Conductivity and $^{13}C$ NMR Spectral Results for Selected Complexes

| compound | $\Lambda_M$,[a] $\Omega^{-1}$ $cm^2$ $mol^{-1}$ | chem shift[b] | | | $T$, °C |
|---|---|---|---|---|---|
| | | C*NR | CN*C*R$_3$ | CNC(*C*H$_3$)$_3$ | |
| $[(CH_3NC)_7Mo]I_2$ | 176.2 | | | | |
| $[(CH_3NC)_7Mo](PF_6)_2$[c] | | 153.7[d] | 33.9 | | ambient |
| | | 152.1 | 31.1 | | −70 |
| $[(t\text{-}C_4H_9NC)_7Mo](PF_6)_2$ | 183.8 | | | | |
| $[(t\text{-}C_4H_9NC)_7Mo](I_3)_2$ | 178.2 | | | | |
| $[(t\text{-}C_4H_9NC)_6MoI]I$[e] | 80.1 | *f* | 57.3 | 30.2 | ambient |
| | | 157.3 | 56.9 | 30.0 | −32 |

[a] In nitromethane solution, $10^{-3}$ M concentration, 25 °C. [b] Ppm downfield from tetramethylsilane. [c] In acetone-$d_6$. The complex was also investigated down to −135 °C in a mixture (80/20) of Freon 22 and $CD_2Cl_2$ with no noticeable changes. [d] Sharpens considerably with decreasing temperature. [e] In $CDCl_3$. Here the $^{13}C$ peak of the solvent was used as the standard and the results converted to the $Me_4Si$ scale. [f] Not observed.

among all three complexes, being little affected by the size and type of the capping ligand or by the overall charge on the complex.

The geometry of the isocyanide ligands, except for the disordered terminal carbon atoms, is normal. The approximate model used to account for the electron density of the disordered *tert*-butyl groups lying off the mirror plane has six half-occupancy methyl carbon atoms distributed evenly in a circular fashion about the C≡N—C bond axis. For the ligands lying on the mirror plane, the difference Fourier maps showed that it would be difficult to refine two independent sets of $C(CH_3)_3$ groups, and attempts to do so were unsuccessful. The most satisfactory model is that reported in the Experimental Section. The inner coordination geometry was unaffected by the mode of refinement of the *tert*-butyl groups.

The crystal packing projected along [100], Figure 2, further reveals the disorder of the anisotropically refined *tert*-butyl groups lying on the mirror plane. It is also evident from this figure that the uncoordinated bromide anions reside in channels defined by the terminal methyl groups of the isocyanide ligands. For example, there are two bromide ions situated at $x = \pm 0.23$, $y = z = 0.5$ (Figure 2). The electron density found in this channel on the final difference Fourier maps in both this structure determination and that of the isomorphous iodide analogue could be the consequence of improper phasing of the disordered *tert*-butyl groups, of residual water, or of both. All six compounds, $[(t\text{-}C_4H_9NC)_6MX]X$, M = Mo or W, X = Cl, Br, or I, are isomorphous and, presumably, isostructural. The molybdenum–iodide derivative prepared using aqueous thiosulfate was found analytically to be a monohydrate. Analytical data for others in the class also suggest partial hydration. The presence of water in the lattice was not usually obvious from the infrared spectra. When peaks did appear at ~3600 $cm^{-1}$, repeated infrared measurements over a period of several months showed the compounds to lose water slowly when stored in a desiccator. Since the lattice can accommodate water, it seems likely that all the $[(t\text{-}C_4H_9NC)_6MX]X$ salts will be hydrated to a slight extent unless special precautions are taken to dry all solvents rigorously.

**Solution Properties.** Limited conductivity measurements were made on $[L_7Mo]^{2+}$ and $[L_6MoI]^+$ complexes in nitromethane solution over a concentration range. The data were fit to the approximate law shown in eq 8,[23] where $\Lambda_e$ is the

$$\Lambda_e = \Lambda_0 - Bc^{1/2} \tag{8}$$

equivalent conductance, $c$ the equivalent concentration, and $\Lambda_0$ the limiting value of $\Lambda_e$ at infinite dilution. The measured values of $\Lambda_e$ were initially plotted against $c^{1/2}$ and the linear portion was extrapolated to zero concentration to obtain $\Lambda_0$ as the intercept. The function $(\Lambda_0 - \Lambda_e)$ was then plotted against $c^{1/2}$ to obtain the straight lines shown in Figure 4. The values of $\Lambda_0$, as well as $\Lambda_M$ (Table V), are in good agreement with literature results[23,24] for 1:2 and 1:1 electrolytes corresponding to $[L_7Mo]X_2$ and $[L_6MoI]X$ complexes, respectively.

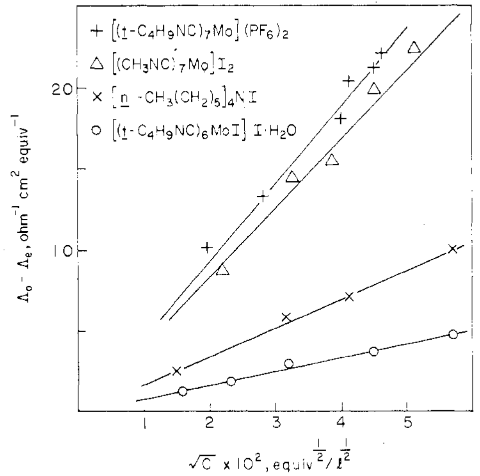

**Figure 4.** Conductivity plots for selected nitromethane solutions of seven-coordinate molybdenum(II) complexes; data for tetra-*n*-hexylammonium iodide are included for comparison.

The conductivity results thus clearly suggest the presence of seven-coordinate molybdenum(II) cations in solution. The slope ($B$) of the conductivity plot for the $[(t\text{-}C_4H_9NC)_6MoI]I\cdot H_2O$ complex is lower than the average predicted value (cf. $n$-Hex$_4$NI, Figure 4), which might reflect ion-pair formation in this concentration range. An attempt to measure the $[(RNC)_7Mo]I_2$ complexes revealed a decrease in conductivity with time implying the occurrence of reaction 4, as mentioned above. This equilibrium does not affect the conductivity of $[(t\text{-}C_4H_9NC)_6MoI]I\cdot H_2O$ in the absence of free isocyanide ligand needed to form the $[(RNC)_7Mo]^{2+}$ cation.

The proton NMR spectra of all eight *tert*-butyl isocyanide complexes exhibit a single sharp peak at ambient temperature in $CDCl_3$ with $\delta$ = 1.55 ppm for $[L_6MoX]^+$, 1.53 ppm for $[L_6WX]^+$, 1.62 ppm for $(MoL_7)^{2+}$, and 1.59 ppm for $(WL_7)^{2+}$. In an attempt to investigate the possible fluxional behavior of these complexes, low-temperature $^{13}C$ NMR spectra of two molybdenum complexes were recorded (Table V). No splitting of the resonances down to −32 °C for the iodohexakis(*tert*-butyl isocyanide)molybdenum(II) cation and down to −135 °C for the heptakis(methyl isocyanide)molybdenum(II) cation was noticed. These preliminary results imply fluxional behavior irrespective of the solution geometry since no heptacoordinate complex can have symmetry-equivalent ligands. Intermolecular exchange of isocyanide ligands does not occur in these and related complexes, as will be described elsewhere.[12] Stereochemical nonrigidity in seven-coordinate compounds has been previously observed.[25] Here, as before,[26] the $^{13}C$ resonance of the isocyanide carbon atom bonded to the metal sharpens with decreasing temperature owing to its relatively long relaxation time.[27]

Electronic spectral data for the eight *tert*-butyl isocyanide complexes dissolved in methanol are summarized in Table VI.

**Table VI.** Summary of Electronic Spectral Bands for $[(t\text{-}C_4H_9NC)_6MY]Z_n$ Compounds[a]

| M | Y | Z | n | λ, nm ($\epsilon_{max}$, $M^{-1}$ $cm^{-1}$ × $10^{-3}$) | | |
|---|---|---|---|---|---|---|
| Mo | Cl | Cl | 1 | 404 (2.01) | 278 (26.2) | 235 (38.5) |
| Mo | Br | Br | 1 | 407 (1.55) | 279 (14.3) | 240 (21.1) |
| Mo | I | I | 1 | 406 (4.07) | 275[b] (21.9) | 240 (24.4) |
| Mo | L[c] | $PF_6$ | 2 | 413 (1.05) | 275 (26.3) | 248 (33.9) |
| W | Cl | Cl | 1 | ~400[d] (1.39) | 285 (26.0) | 244 (36.1) |
| W | Br | Br | 1 | ~400[d] (1.96) | 286 (22.7) | 244 (36.2) |
| W | I | I | 1 | 414 (1.40) | 287[b] (24.3) | 243 (39.8) |
| W | L[c] | $PF_6$ | 2 | 376 (6.17) | 287 (30.5) | 249 (43.1) |

[a] Methanol solutions at ambient temperature. [b] Shoulder. [c] L = $t\text{-}C_4H_9NC$. [d] Broad envelope consisting of at least two peaks at ~390 and ~405 nm.

The energy levels of the d orbitals in these complexes may be deduced from simple crystal field arguments to be $a_1(x^2 - y^2) < b_2(yz) < b_1(xz) < a_1(z^2) < a_2(xy)$, where the $z$ axis is taken along the $C_2$ axis of the capped trigonal prism and the projection of the $x$ axis bisects the $t$ edge (Figure 3). Molecular orbital calculations deduce the identical level ordering.[9] The $b_2(yz) \rightarrow a_1(z^2)$ transition would be the lowest energy allowed band to which we tentatively assign the absorption ~400 nm in all the compounds. This band has more than one component in the tungsten–halo complexes, and a halide to tungsten charge-transfer transition is a possible source of the extra feature. More detailed spectral data at lower temperatures and on single crystals will be required to assign the bands definitively. The absence of systematic trends with variation of the capping ligand and metal atom was disappointing. The 235–245-nm band appearing in the spectrum of all complexes (Table VI) might be a L → M charge-transfer band. A similar transition was given this assignment for isocyanide complexes of chromium(0) and molybdenum(0).[28]

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**Registry No.** $[(CH_3CN)_7Mo]I_2$, 41982-04-1; $[(CN_3CN)_7Mo](PF_6)_2$, 66632-84-6; $[(t\text{-}C_4H_9NC)_7Mo](PF_6)_2$, 56086-00-1; $[(t\text{-}C_4H_9NC)_7Mo](I_5)_2$, 66652-51-5; $[(t\text{-}C_4H_9NC)_7Mo](I_3)_2$, 41982-06-3; $[(t\text{-}C_4H_9NC)_7W](PF_6)_2$, 66687-57-8; $[(t\text{-}C_4H_9NC)_6MoCl]Cl$, 66652-50-4; $[(t\text{-}C_4H_9NC)_6MoBr]Br$, 66674-70-2; $[(t\text{-}C_4H_9NC)_6MoI]I$, 66700-89-8; $[(t\text{-}C_4H_9NC)_6WCl]Cl$, 66687-55-6; $[(t\text{-}C_4H_9NC)_6WBr]Br$, 66652-49-1; $[(t\text{-}C_4H_9NC)_6WI]I$, 66652-48-0.

**Supplementary Material Available:** Tables S1 and S2 listing structure factor amplitudes and root-mean-square amplitudes of vibration (15 pages). Ordering information is given on any current masthead page.

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