counterions; however, the reason why the NH_4^+ salt but not the enH_2^{2+} salt exhibits this band is not clear but may be simply associated with the fact that each salt has a different crystal structure.

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The Structure of Heptakis(*tert*-butyl isocyanide)molybdenum(II) Hexafluorophosphate, a Seven-Coordinate Complex with C_{2v} Monocapped Trigonal Prismatic Geometry[1]

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Abstract: The structure of heptakis(*tert*-butyl isocyanide)molybdenum(II) hexafluorophosphate has been determined in a single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic system. Refinement was carried out in the nonstandard space group $F2/m$ having a = 25.220 (10) Å, b = 11.665 (5) Å, c = 38.013 (17) Å, β = 90.42 (3)°, and Z = 4. The geometry of the seven-coordinate molybdenum(II) cation is that of a distorted capped trigonal prism of approximate C_{2v} symmetry. Deviations of the structure from idealized geometry (typified by the $[NbF_7]^{2-}$ ion) result largely from inequivalencies in the Mo–C bond lengths. These occur in three classes, viz., the Mo–C bond of the unique, capping ligand, 2.171 (9) Å, the four Mo–C bonds to the capped face, average 2.133 (7) Å, and the two Mo–C bonds opposite the capped face, 2.051 (7) Å. The structure bears many similarities to that of the related $[(t\text{-}C_4H_9NC)_6MoI]^+$ cation, in which the iodide ligand occupies the capped face of the trigonal prism. The stereochemistry of the C_{2v} monocapped trigonal prism is defined in terms of polyhedral shape parameters.

The number of structurally well-characterized seven-coordinate transition metal complexes has increased dramatically in the past several years.[3,4] Compounds containing only monodentate ligands are still rare,[5,6] however, and X-ray structural information about monomers with seven identical ligands is available only for $[ZrF_7]^{3-}$,[7] $[NbF_7]^{2-}$,[8] and $[V(CN)_7]^{4-}$.[9] Compounds of the last kind are interesting because they permit an analysis of the factors influencing the choice of geometry for a seven-coordinate complex in the absence of stereochemical constraints imposed by multidentate, chelating ligands. The paucity of X-ray structural data for discrete ML_7 complexes has recently been noted.[10]

During a study of the alkylation of silver octacyanomolybdate(IV),[2] a number of cationic molybdenum(II) isocyanide complexes were isolated, including $[Mo(CNR)_6I]^+$[11] and $[Mo(CNR)_7]^{2+}$,[12] where R = CH_3 or $t\text{-}C_4H_9$. These compounds, as well as $[Mo(CNR)_6X]^+$[13] and $Mo(CNR)_5X_2$, X = Cl or Br,[14] have also been obtained by halogen oxidation of molybdenum hexacarbonyl, a route that has long been known to produce seven-coordinate molybdenum(II) compounds.[15] The existence of X-ray quality crystals of $[Mo(CNR)_7]^{2+}$ and $[Mo(CNR)_6X]^+$, X = Cl, Br, or I, salts afforded an excellent opportunity to investigate the effects of charge, ligand size, and even crystal packing forces on the geometry of seven-coordinate d^4 mo lybdenum(II) complexes. The iodohexakis(*tert*-butyl isocyanide)molybdenum(II) cation has already been shown to have the C_{2v} monocapped trigonal prismatic structure, with the iodide ligand on the capped face.[11] A structural study of the isomorphous bromide analog is currently in progress. The present paper reports the structure of the parent dication, $[(t\text{-}C_4H_9NC)_7Mo]^{2+}$, in which the molybdenum coordination geometry is also that of a capped trigonal prism.

Experimental Procedures and Results

Collection and Reduction of Data. The compound was prepared as previously described[12] and recrystallized from a mixture of ethanol and ether. A parallelpiped crystal, suitable for X-ray diffraction studies, was selected and mounted on the end of a glass fiber. Precession and Weissenberg photographs indicate that the crystals belong to the monoclinic system. The observed systematic absences (hkl for $h + k$ odd) require the space group to be $C2/m\text{-}C^3{}_{2h}$, $C2\text{-}C^3{}_2$, or $Cm\text{-}C^3{}_s$. The cell constants obtained by least-squares refinement of the setting angles (procedure of Busing and Levy[16]) of 12 independent reflections are a = 25.220 (10) Å, b = 11.665 (5) Å, c = 22.733 (10) Å, and β = 56.73 (3)°. These measurements were made on a Picker FACS-I-DOS four-circle diffractometer at 22° utilizing Mo Kα_1 radiation with an assumed wavelength of 0.7093 Å. The calculated density of 1.150 g/cm^3 for four molecules per cell agrees well with the experimental value of 1.16 (2) g/cm^3 obtained by neutral buoyancy in a methyl bromide–ether solution.

Diffraction data were collected on a crystal with faces (001), $(00\bar{1})$, (110), $(\bar{1}\bar{1}0)$, $(\bar{1}10)$, and $(1\bar{1}0)$; the distances between parallel faces were 0.020, 0.021, and 0.016 cm, respectively. The crystal was mounted approximately along the a^* axis, and data were collected using graphite monochromatized Mo Kα radiation. A takeoff angle of 2.20° was employed with a 2θ scan range from 1° below to 1° above the calculated positions of Kα_1 and Kα_2, respectively. The scan rate was 1°/min, and 20-sec stationary background counts were taken at the upper and lower limits of the scan range. Three standard reflections, well separated in reciprocal space, were measured after every 100 data points in order to monitor crystal and instrument stability. In no case did any standard deviate by more than ±2% of its average value for the entire run.

A single form of the data $\{h,k,\pm l\}$ was collected out to a value of 2θ (Mo Kα) of 50°, above which there were few reflections with intensities greater than background. Data reduction was carried out as previously described,[17] with the value of ϵ in the expression for $\sigma(I)$ being chosen as 0.04. Owing to the low linear absorption coefficient, 3.61 cm^{-1}, for Mo radiation and the size of the crystal, no correction for absorption effects was made. A test calculation using ORABS[18] showed the transmission factors to vary from 0.937 to 0.954. Of the approximately 4700 original data (independent reflections), 3014 were found to have intensities greater than three times their standard deviations, and these were used in the solution and final refinement of the structure.

Determination and Refinement of the Structure. Examination of a three-dimensional Patterson function revealed the positions of the molybdenum, a single phosphorus, and a single carbon atom. Assuming the space group to be the centrosymmetric $C2/m$, several cycles of least-squares refinement were run with the three atoms assigned isotropic thermal parameters. All least-squares refinements in this work were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and weights, w, being taken as $4F_o{}^2/\sigma^2(F_o{}^2)$.[17] In all calculations of F_c the atomic scattering factors were taken from Hanson, Herman, Lea, and Skillman.[19] The effects of anomalous dispersion for the molybdenum and phosphorus atoms were also included in the calculations of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer and Liberman.[20] A difference Fourier map revealed several atoms of the isocyanide ligands and portions of the two hexafluorophosphate groups. Subsequent least-squares analysis and examination of difference Fourier maps revealed the coordinates of all non-hydrogen atoms. At this stage of refinement, with all atoms assigned isotropic thermal parameters and assuming the centrosymmetric space group $C2/m$, the usual agreement factors

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$$

were 0.108 and 0.145, respectively. Examination of the thermal parameters of the *tert*-butyl portion of the isocyanide ligands and the fluorine atoms of the hexafluorophosphate groups suggested either that the space group choice was incorrect or that large thermal vibrations existed, since there were many values of B greater than 10 Å^2. Refinement in the acentric space group $C2$ did little to reduce these large values. Since significant deviations in equivalent bond lengths in the cation were observed, as well as large correlation coefficients for those parameters related by the mirror of the centric group, refinement was therefore continued in the centrosymmetric group (refinement in Cm was not attempted since this space group would require doubling the number of parameters without removing the constraint of the mirror plane). Because of the small value of the lattice parameter β in $C2/m$, the hkl indices and atomic coordinates were transformed to the more suitable, although nonstandard, space group $F2/m$. The derived new cell parameters are a = 25.220 (10) Å, b = 11.665 (5) Å, c = 38.013 (17) Å, and β = 90.42 (3)°. All subsequent refinements were carried out in this system, and the final lists of coordinates and structure factors refer to the space group $F2/m$.

After several additional cycles of least-squares refinement, during which all atoms were assigned variable anisotropic thermal parameters, the values of R_1 and R_2 were 0.063 and 0.080. The parameters were refined in two blocks. In the first, the positional and thermal parameters of the two hexafluorophosphate groups, the molybdenum atom, and the *tert*-butyl isocyanide ligand situated on the mirror plane were refined. The second block varied the parameters of the molybdenum atom and remaining ligands. A test calculation showed the refinement to be unaffected by this choice of blocking. A total of 280 parameters were refined.

A subsequent difference Fourier map revealed several areas of residual electron density in the vicinity of the *tert*-butyl groups. As would be expected from consideration of the large thermal vibrations observed for the carbon atoms of these groups, location of the hydrogen atoms was difficult. An attempt at refinement of the most reasonable hydrogen positions resulted in very unsatisfactory geometry, and no further attempt was made to locate or refine the hydrogen atoms. A final cycle of least-squares refinement, in which no parameter shift was greater than 0.20 times its estimated standard deviation, resulted in values of 0.060 and 0.073 for R_1 and R_2, and refinement was considered to have converged. Examination of the values of $w(|F_o| - |F_c|)^2$ showed a dependence on sin θ with unusually large values in the region $2\theta < 15°$. This anomaly may be attributed to the absence of hydrogen atom contributions to the calculated structure factors and possibly to inadequacies in the thermal model for the *tert*-butyl and hexafluorophosphate groups which exhibit large vibrational amplitudes. For these reasons, no compensating weighting scheme was applied. The error on an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, was estimated to be 2.09. A final difference Fourier map revealed no peak with electron density greater than 0.53 e/Å^3, as compared to an average peak for carbon of 2.5–3.5 e/Å^3.

The positional and thermal parameters derived from the last cycle of least-squares refinement and their associated standard deviations as estimated from the inverse matrix are presented in Table I. The molecular geometry is summarized in Tables II–IV. A compilation of observed and calculated structure factor amplitudes is available.[21]

Discussion

The crystal structure consists of seven-coordinate $[(t\text{-}C_4H_9NC)_7Mo]^{2+}$ cations and hexafluorophosphate anions. The unit cell packing shows no unusual features, all interatomic distances between ions being normal van der Waals contacts. Although the crystallographically required site symmetry of the cations is only C_m, the actual dimensions (Table III) are close to those of an idealized C_{2v} capped trigonal prism. As shown in Figure 1, the trigonal prism is defined by the carbon atoms C21, C31, and C41 and the symmetry related (primed) atoms, with carbon C11 at the capped site.

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

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.14857 (3)	0.0	0.12628 (2)	11.1 (1)	57.8 (7)	5.20 (6)	0,0	−0.79 (6)	0.0
P1	0.4441 (1)	0.5	0.18023 (7)	21.0 (6)	86.6 (29)	9.1 (3)	0.0	−0.1 (3)	0.0
P2	0.3732 (1)	0.0	0.0330 (1)	22.7 (7)	143 (5)	13.4 (4)	0.0	−3.3 (4)	0.0
F11	0.4725 (4)	0.5	0.2169 (2)	62 (3)	242 (12)	18 (1)	0.0	−19 (1)	0.0
F12	0.3901 (3)	0,5	0.2009 (2)	36 (2)	312 (15)	22 (1)	0.0	11 (1)	0.0
F13	0.4111 (3)	0,5	0.1449 (2)	55 (2)	236 (12)	15.0 (9)	0.0	−12 (1)	0.0
F14	0.4423 (3)	0.3668 (5)	0.1811 (2)	68 (2)	102 (6)	24,9 (8)	5 (3)	−5 (1)	−1 (2)
F15	0.4954 (3)	0.5	0.1600 (3)	31 (2)	357 (18)	35 (2)	0.0	20 (1)	0.0
F21	0.4293 (3)	0.0	0.0180 (3)	31 (2)	410 (20)	25 (1)	0.0	5 (1)	0.0
F22	0.3974 (3)	0.0	0.0714 (2)	46 (2)	355 (17)	17 (1)	0.0	−9 (1)	0.0
F23	0.3176 (3)	0.0	0.0480 (3)	23 (2)	561 (27)	23 (1)	0.0	1 (1)	0.0
F24	0.3503 (4)	0.0	−0,0045 (2)	45 (2)	492 (22)	14.2 (9)	0.0	−8 (1)	0.0
F25	0.3742 (4)	0.1303 (7)	0.0327 (2)	96 (3)	157 (9)	38 (1)	22 (4)	6 (2)	8 (3)
C11	0.1685 (4)	0.0	0.0709 (3)	16 (2)	127 (11)	7.2 (8)	0.0	−2 (1)	0.0
N12	0.1744 (3)	0.0	0.0413 (2)	24 (2)	199 (13)	6.7 (8)	0.0	−0 (1)	0.0
C13	0.1807 (6)	0.0	0.0028 (3)	34 (4)	394 (34)	5 (1)	0.0	0 (2)	0.0
C14	0.2124 (5)	0.1025 (14)	−0.0057 (3)	62 (4)	461 (28)	18 (1)	−36 (8)	3 (2)	55 (5)
C15	0.1271 (6)	0,0	−0.0129 (4)	31 (4)	815 (63)	10 (1)	0.0	−9 (2)	0.0
C21	0.2136 (3)	0.1155 (6)	0.1305 (2)	16 (1)	89 (7)	7.8 (6)	−3 (3)	−0.5 (7)	−3 (2)
N22	0.2497 (2)	0.1736 (5)	0.1329 (2)	20 (1)	110 (7)	11.0 (6)	−17 (3)	−0.7 (7)	−3 (2)
C23	0.2961 (3)	0.2475 (8)	0.1378 (2)	23 (2)	129 (9)	16 (1)	−30 (4)	2 (1)	−9 (3)
C24	0.3427 (4)	0.1673 (11)	0.1484 (3)	21 (2)	224 (16)	34 (2)	−8 (5)	−8 (2)	−7 (4)
C25	0.2838 (4)	0.3264 (10)	0.1688 (3)	39 (3)	226 (15)	22 (1)	−52 (5)	9 (1)	−40 (4)
C26	0.3071 (5)	0.3089 (11)	0.1034 (3)	56 (3)	291 (19)	16 (1)	−73 (7)	4 (2)	13 (4)
C31	0.0897 (3)	0.1163 (6)	0.1070 (2)	19 (1)	69 (7)	8.5 (6)	5 (3)	−2.6 (7)	0 (2)
N32	0.0584 (2)	0.1765 (5)	0.0953 (2)	23 (1)	80 (6)	11.6 (6)	11 (2)	−2.2 (7)	3 (2)
C33	0.0171 (3)	0.2508 (7)	0.0802 (2)	24 (2)	111 (9)	15.3 (9)	21 (3)	−5 (1)	13 (2)
C34	−0.0281 (4)	0.1740 (10)	0.0680 (4)	38 (3)	179 (14)	37 (2)	4 (5)	−24 (2)	5 (4)
C35	0.0419 (5)	0.3174 (11)	0.0506 (3)	54 (3)	268 (18)	23 (1)	38 (6)	5 (2)	55 (4)
C36	−0.0051 (4)	0.3238 (10)	0.1108 (3)	52 (3)	207 (14)	18 (1)	68 (6)	1 (1)	−1 (3)
C41	0.1306 (3)	0.1027 (7)	0.1683 (2)	21 (1)	129 (9)	8.1 (7)	4 (3)	−0.9 (8)	12 (2)
N42	0.1208 (3)	0.1653 (7)	0.1913 (2)	29 (2)	173 (9)	11.6 (6)	−1 (3)	1.0 (8)	−17 (2)
C43	0.1056 (4)	0.2462 (10)	0.2200 (3)	37 (2)	196 (13)	12.7 (9)	−4 (5)	5 (1)	−33 (3)
C44	0.1546 (4)	0.3148 (11)	0.2309 (3)	40 (3)	313 (20)	24 (2)	−35 (6)	4 (2)	−58 (5)
C45	0.0580 (5)	0.3168 (11)	0.2065 (3)	46 (3)	243 (18)	26 (2)	53 (6)	−4 (2)	−31 (4)
C46	0.0858 (5)	0.1705 (11)	0.2504 (3)	70 (4)	243 (17)	13 (1)	−21 (7)	13 (2)	−19 (4)

[a] Atoms are labeled as indicated in Figure 1 or according to the label of the attached atom; thus F11 is bonded to P1, F21 to P2, etc. [b] Standard deviations, in parentheses, occur in the last significant digit for each parameter. [c] Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Values reported are $\times 10^4$.

Table II. Dimensions of the Mo—C≡N—C_4H_9 Chains[a]

Bond	Distance, Å	Angle	Deg
Mo–C11	2.171 (9)	Mo–C11–N12	174.2 (7)
Mo–C21	2.127 (7)	Mo–C21–N22	177.2 (6)
Mo–C31	2.138 (7)	Mo–C31–N32	177.3 (6)
Mo–C41	2.051 (7)	Mo–C41–N42	176.9 (8)
C11–N12	1.134 (11)	C11–N12–C13	178.5 (11)
C21–N22	1.140 (7)	C21–N22–C23	177.1 (7)
C31–N32	1.143 (7)	C31–N32–C33	178 (1)
C41–N42	1.165 (8)	C41–N42–C43	177.2 (8)
N12–C13	1.466 (14)	Around Min	105.9 (8)
N22–C23	1.464 (9)	C13 Max	114.3 (8)
N32–C33	1.470 (8)	Mean N–C–C	106.7
N42–C43	1.49 (1)	Mean C–C–C	112.3
C13–C14	1.48 (1)	Around Min	106.3 (7)
C13–C15	1.47 (2)	C23 Max	114.8 (9)
C23–C24	1.55 (1)	Mean N–C–C	107.2
C23–C25	1.53 (1)	Mean C–C–C	111.6
C23–C26	1.52 (1)	Around Min	106.2 (9)
C33–C34	1.52 (1)	C33 Max	115.6 (9)
C33–C35	1.51 (1)	Mean N–C–C	107.2
C33–C36	1.55 (1)	Mean C–C–C	111.6
C43–C44	1.53 (1)	Around Min	105.9 (9)
C43–C45	1.54 (1)	C43 Max	116 (1)
C43–C46	1.54 (1)	Mean N–C–C	107.2
		Mean C–C–C	111.5

[a] See footnotes *a* and *b*, Table I.

Table III. Dimensions of the Coordination Polyhedron[a]

Edge	Length, A	Type[b]	Angle	Deg
C11–C21	2.861 (9)	*a*	C11–Mo–C21	83.7 (3)
C11–C31	2.778 (11)	*a*	C11–Mo–C31	80.3 (3)
Mean *a*	2.823		Mean *a*	82.0
C21–C31	3.244 (9)	*t*	C21–Mo–C31	99.0 (2)
C21–C21′	2.695 (14)	*r*	C21–Mo–C21′	78.6 (4)
C31–C31′	2.714 (14)	*r*	C31–Mo–C31′	78.8 (4)
Mean *r*	2.705		Mean *r*	78.7
C21–C41	2.551 (10)	*p*	C21–Mo–C41	75.2 (3)
C31–C41	2.551 (10)	*p*	C31–Mo–C41	75.0 (3)
Mean *p*	2.551		Mean *p*	75.1
C41–C41′	2.396 (16)	*c*	C41–Mo–C41′	71.5 (4)

Other angles	Deg
C11–Mo–C41	144.2 (2)
C21–Mo–C31′	164.0 (2)
C21–Mo–C41′	119.0 (3)
C31–Mo–C41′	118.8 (3)

[a] See footnotes *a* and *b*, Table I. [b] See Figure 2 for nomenclature.

In a recent discussion of idealized polyhedra for the various coordination numbers, the dihedral angles δ' between faces[22] on the C_{2v} capped trigonal prism were calculated to be 0° along the diagonals on the two uncapped rectangular faces, and 41.5° between the triangular face of the prism and the adjacent triangle formed by the ligand on the capped face.[10] In the case of the $[(t\text{-}C_4H_9NC)_7Mo]^{2+}$ cation, the δ' values on the uncapped rectangular faces are required by symmetry to be 0°, and the third value was computed to be 40.3 ± 0.4°. These results are in good accord with theoretical expectations,[10] and provide an unambiguous confirmation of the assigned coordination polyhedron. Since the value of 41.5° calculated for the third δ' angle applies rigorously only to a C_{2v} capped trigonal prismatic

Table IV. Dimensions of the Hexafluorophosphate Groups[a]

Bond	Length, Å	F–P–F angles (deg)	
P1–F11	1.563 (8)	Around P1	
P1–F12	1.574 (8)	Min	87.0 (5)
P1–F13	1.572 (7)	Max	93.7 (6)
P1–F14	1.556 (5)	Min	175.3 (6)
P1–F15	1.510 (8)	Max	179.3 (8)
Mean	1.555		
P2–F21	1.529 (9)	Around P2	
P2–F22	1.578 (8)	Min	89.0 (4)
P2–F23	1.520 (8)	Max	91.0 (4)
P2–F24	1.533 (8)	Min	178.0 (9)
P2–F25	1.520 (8)	Max	179.8 (2.8)
Mean	1.536		

[a] The atom labeling is defined by this table. Standard deviations are in parentheses.

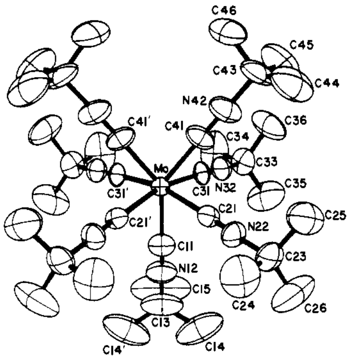

Figure 1. Structure and labeling scheme for the $[(t\text{-}C_4H_9NC)_7Mo]^{2+}$ cation showing the 40% probability thermal elipsoids.

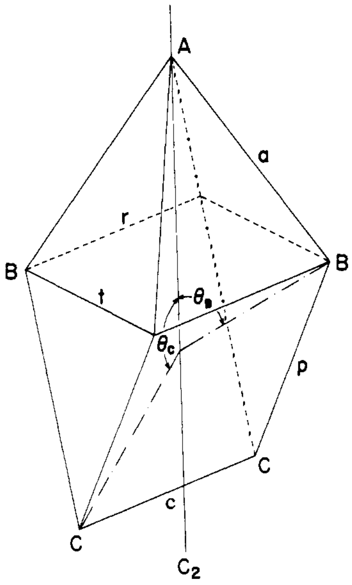

Figure 2. The C_{2v} capped trigonal prism showing the edge and angle labels. The shape of the polyhedron is specified by the parameter ratios a/c, r/c, t/c, and p/c. The position of the metal atom on the C_2 axis can be fixed by θ_B.

complex having (inter alia[10]) seven identical metal-ligand bond lengths, it can in principle deviate substantially from that value if the bond to the ligand on the capped face were shortened or elongated. In the complex $[(t\text{-}C_4H_9NC)_6MoI]^+$ cation, for example, the nonzero δ' angle is 36.7°, a direct consequence of the Mo-I bond length of 2.862 (Å).[5] It is therefore of interest to define and examine the complete set of shape parameters for the C_{2v} monocapped trigonal prismatic geometry.

Figure 2 displays the C_{2v} capped trigonal prism and defines a set of shape parameters. The three ligand sites not related by symmetry are designated A, B, and C, with angles θ_B and θ_C between the principal C_2 axis and the metal-ligand bonds to the B and C sites, respectively. There are four apical (a) edges, two edges on the nearly rectangular (r) faces, two on the triangular (t) faces, four others that define the prism (p), and a unique edge (c) connecting the C ligands. The shape of a capped trigonal prism ($mm2$) is specified by four parameters, e.g., the edge length ratios a/c, r/c, t/c, and p/c. If the location of the metal atom on the C_2 axis is desired, a fifth parameter such as θ_B can be specified.

In Table V are summarized the shape parameters determined for (i) the idealized C_{2v} monocapped trigonal prismatic geometry calculated[23] for a "hard sphere model" (HSM) based on a choice of 6.0 for the exponent in the potential $E = \sum_{i \neq j} r_{ij}^{-n}$, (ii) the heptafluoroniobate(V) ion,[8] (iii) the present structure, $[(t\text{-}C_4H_9NC)_7Mo]^{2+}$, and (iv) the structurally similar $[(t\text{-}C_4H_9NC)_6MoI]^+$ ion.[5] The shape parameters of the heptafluoroniobate(V) ion correspond closely to those calculated for the hard sphere model. Examination of the results for the heptakis(*tert*-butyl isocyanide)molybdenum(II) cation, however, reveals some deviations from the hard sphere parameters. The differences arise primarily because the Mo-C bond lengths occur in three distinct sets, viz., 2.171 (9) Å for the unique, capping ligand in site A, (average) 2.133 (7) Å for the four Mo-C bonds to the capped face (B site), and (average) 2.051 (7) Å for the two Mo-C bonds (in site C) defining the edge opposite the capped face. The relative variations in the polyhedron edge lengths of the $[(t\text{-}C_4H_9NC)_7Mo]^{2+}$ cation are nearly the same as those expected from the hard sphere model. In particular, the edge lengths increase as $c < p < r < a < t$, with the interchange of the positions of a and r being the only difference from the order observed for the HSM or the $[NbF_7]^{2-}$ ion. This difference reflects the lengthening of the Mo-C bond involving the capping ligand. In the extreme case of the $[(t\text{-}C_4H_9NC)_6MoI]^+$ cation, the a edge length is the largest, owing to the Mo-I bond length of 2.862 Å. The angular shape parameters θ_B and θ_C for all three structures are quite comparable, indicating the relative constancy of the metal atom position in the body of the trigonal prism.

The pattern of Mo-C bond lengths in heptakis(*tert*-butyl isocyanide)molybdenum(II) and iodohexakis(*tert*-butyl isocyanide)molybdenum(II) is identical, with $r_A > r_B > r_C$. It therefore appears that the two isocyanide ligands on the c edge of the trigonal prism are most strongly bonded to the molybdenum atom. The long Mo-C distance in $[(t\text{-}C_4H_9NC)_7Mo]^{2+}$ corresponds to the most weakly bonded, capping ligand, which is readily replaced by halide according to eq 1. The existence of eq 1, which has been observed spectroscopically,[24] makes it difficult to isolate pure samples of $[Mo(CNR)_7]X_2$ salts when X is halide and R = *tert*-butyl. The possible influence of nonbonded intraligand steric interactions on the Mo-C bond distances is currently being evaluated through X-ray structural studies of the cations $[Mo(CNR)_6X]^+$, X = Cl, Br, and I.

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

The triangular edges (t) of the capped trigonal prism are larger than the rectangular (r) edges in all four structures listed in Table V. This feature is expected because of the greater interligand repulsions on the triangular faces of the prism compared to the rectangular ones, and similar results have been reported for other monocapped trigonal prismatic

Table V. Shape Parameters for Selected C_{2v} Capped Trigonal Prismatic Structures[a]

Parameter[b]	Hard sphere model[c]	$[NbF_7]^{2-}$	$[(t\text{-}C_4H_9NC)_7Mo]^{2+}$	$[(t\text{-}C_4H_9NC)_6MoI]^+$
r_A	1.0	1.945 (1.000)	2.171 (1.027)	2.862
r_B	1.0	1.935 (0.995)	2.133 (1.008)	2.115 (1.014)
r_C	1.0	1.962 (1.009)	2.051 (0.970)	2.055 (0.986)
θ_B	79.4°	78.6°	82.0°	81.5°
θ_C	143.3°	143.0°	144.2°	145.1°
a	1.2775	2,458 (1.264)	2.820 (1.333)	3.295
r	1.2975	2.527 (1.300)	2.705 (1.279)	2.867 (1.375)
t	1.4769	2.829 (1.455)	3.244 (1.534)	3.038 (1.457)
p	1.2327	2.413 (1.241)	2.551 (1.206)	2.526 (1.211)
c	1.1950	2.357 (1.212)	2.396 (1.133)	2.356 (1.130)
a/c	1.0690	1.0429	1.1770	1.3986
r/c	1.0858	1.0721	1.1290	1.2169
t/c	1.2359	1.2003	1.3539	1.2895
p/c	1.0315	1.0238	1.0647	1.0722
Ref	23	8	This work	5

[a] Shape parameter lengths (in Å) are normalized to the mean metal–ligand bond length except for the iodohexakis(*tert*-butyl isocyanide)-molybdenum(II) ion, in which the normalization was carried out exclusive of the Mo–I bond length. The normalized values are in parentheses. [b] Defined in Figure 2. In all cases the crystallographic site symmetry was lower than *mm*2, and average values were computed. [c] A value of 6.0 was used for the Born exponent.

structures.[25] The difference between the t and r edge lengths and the t/r ratio in $[(t\text{-}C_4H_9NC)_6MoI]^+$ are both less than in the parent heptacoordinate dication. The origin of this effect is not entirely obvious, but perhaps the presence of the large iodide ion on the capping face reduces the effect of interligand repulsions between the B and C sites on the triangular faces. Preliminary X-ray results for the $[(t\text{-}C_4H_9NC)_6MoBr]^+$ analog[26] support this interpretation, the average t and r edge lengths being 3.09 (2) and 2.81 (2) Å, respectively, intermediate between the values for $[MoL_7]^{2+}$ and $[MoL_6I]^+$, L = *tert*-butyl isocyanide (Table V).

Other features of the structure (Tables II-IV) are normal. The dimensions of the isocyanide chains compare favorably with related parameters for $[Mo(CN)_4(CNCH_3)_4]$[2] and $[(t\text{-}C_4H_9NC)_6MoI]^+$.[5] The methyl carbon atoms of the *tert*-butyl groups have large thermal parameters, as found for the iodo complex.[5] The largest are associated with the *tert*-butyl group confined by space group symmetry to lie on a mirror plane (Figure 1, atoms C13, C14, C14′, and C15). The C-C bond lengths reported in Table II for these atoms have not been corrected for thermal motion and are therefore slightly shorter than expected for a saturated hydrocarbon moiety. The largest of the three principal axes of the thermal ellipsoids associated with each methyl carbon atom of the *tert*-butyl groups is nearly perpendicular to the C-C bond axis, consistent with torsional vibrational motion about the N-C bonds (Figure 1). Vibrational motion associated with the two hexafluorophosphate groups is also rather high, but the dimensions of these anions (Table IV) are regular. They both have crystallographically required *Cm* site symmetry, with P-F distances again slightly shorter than expected,[27] being uncorrected for thermal motion. The final difference Fourier map showed evidence for a slight degree of rotational disorder for both the *tert*-butyl and hexafluorophosphate groups, judging by the appearance of a small amount of electron density (<0.5 e/Å^3) between the fluorine atom or carbon atom peak positions. The PF_6^- ion is more ordered in the present crystal then is often the case, however.[27]

Conclusions

The C_{2v} capped trigonal prism is the preferred geometry for seven-coordinate $[MoL_7]^{2+}$ and $[MoL_6X]^+$ complexes with L = *tert*-butyl isocyanide and X = halide. The two ligands on the c edge (Figure 2) of the coordination polyhedron are bonded most strongly to the molybdenum atom. The capping ligand appears to be the most weakly bonded one, the chemical manifestation of which is preferential substitution at this site by halide ion (iodide, bromide) in $[MoL_6X]^+$ complexes. The chemical, kinetic, and fluxional properties of these and related seven-coordinate complexes containing only monodentate ligands are under investigation.

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Supplementary Material Available. A table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2697.

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Organonitrogen Derivatives of Metal Carbonyls. VIII. Reactions of Metal Carbonyl Anions with α-Chloroenamines[1-3]

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Abstract: Reactions of the α-chloroenamines, $(CH_3)_2C{=}C(NR_2)Cl$ (R = CH_3 or 2R = $-(CH_2)_5-$), with various metal carbonyl anions provide routes to diverse types of transition metal complexes in which the $(CH_3)_2C{=}C(NR_2)-$ unit may be bonded to the metal as a C-monohapto vinyl, CC- or CN-dihapto cyclic acyl, CC- or CN-dihapto keteneimmonium, or 2-azabutadiene ligand. Reactions of $NaRe(CO)_5$ with $(CH_3)_2C{=}C(NR_2)Cl$ give the pale yellow CC-dihapto cyclic acyl derivatives $R_2NCC(CH_3)_2CORe(CO)_4$ which isomerize to the yellow monohapto vinyl derivatives $(CH_3)_2C{=}C(NR_2)Re(CO)_5$ upon heating in hexane. Reaction of $NaW(CO)_3C_5H_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ gives the yellow CC-dihapto cyclic acyl derivative $(CH_3)_2NCC(CH_3)_2COW(CO)_2C_5H_5$ which undergoes decarbonylation to the CN-dihapto keteneimmonium derivative $[(CH_3)_2C{=}C{=}N(CH_3)_2]W(CO)_2C_5H_5$ upon heating in boiling hexane or methylcyclohexane. Reactions of $NaMo(CO)_3C_5H_5$ with $(CH_3)_2C{=}C(NR_2)Cl$ at room temperature give the yellow CN-dihapto keteneimmonium derivatives $[(CH_3)_2C{=}C{=}NR_2]Mo(CO)_2C_5H_5$. These molybdenum complexes are protonated with hexafluorophosphoric acid in propionic anhydride to give the corresponding 1-azaallyl derivatives $[(CH_3)_2CCHNR_2Mo(CO)_2C_5H_5][PF_6]$. Deprotonation of these 1-azaallyl derivatives with aqueous ammonia gives the corresponding CC-dihapto keteneimmonium derivatives $[R_2N{=}C{=}C(CH_3)_2]Mo(CO)_2C_5H_5$ as unstable yellow solids. Reaction of $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mo(CO)_2C_5H_5$ with iodine at room temperature results in complete decarbonylation to give black $[(CH_3)_2C{=}C{=}N(CH_3)_2]MoI_2C_5H_5$. Reactions of $NaCo(CO)_4$ with $(CH_3)_2C{=}C(NR_2)Cl$ give the air-sensitive yellow volatile liquid CC-dihapto keteneimmonium derivatives $[(CH_3)_2N{=}C{=}C(CH_3)_2]Co(CO)_3$. Reactions of $NaMn(CO)_5$ with $(CH_3)_2C{=}C(NR_2)Cl$ give the relatively air-stable yellow crystalline CN-dihapto cyclic acyl derivatives, $(CH_3)_2C{=}C(NR_2)COMn(CO)_4$, which undergo double decarbonylation upon ultraviolet irradiation or heating to give the corresponding volatile yellow crystalline 2-azabutadiene derivatives $[(CH_3)_2C{=}CHN(CH_3){=}CH_2]Mn(CO)_3$ (from R = CH_3) and $[(CH_3)_2C{=}CHNC_5H_9]Mn(CO)_3$ (from 2R = $-(CH_2)_5-$). Reaction of $(CH_3)_2C{=}C[N(CH_3)_2]COMn(CO)_4$ with $Fe_2(CO)_9$ in boiling hexane results in a single decarbonylation to give the yellow liquid CN-dihapto keteneimmonium derivative $[(CH_3)_2C{=}C{=}N(CH_3)_2]Mn(CO)_4$. Reaction of $NaFe(CO)_2C_5H_5$ with $(CH_3)_2C{=}C[N(CH_3)_2]Cl$ gives the brown air-sensitive liquid monohapto vinyl derivative $(CH_3)_2C{=}C[N(CH_3)_2]Fe(CO)_2C_5H_5$ which appears to undergo thermal isomerization to the corresponding CC-dihapto cyclic acyl derivative. The structures of these new compounds can be deduced from their infrared ν(CO), ^1H NMR, and carbon-13 NMR spectra.

Vinylic halides are normally too unreactive toward nucleophiles to use effectively for the synthesis of vinylmetal derivatives by reactions with metal carbonyl anions. Thus vinyl halides give less than ~5% yields of $CH_2{=}CHFe(CO)_2C_5H_5$ upon reaction with the extremely nucleophilic[5] $NaFe(CO)_2C_5H_5$[6] and apparently do not react with alkali metal derivatives of significantly less nucleophilic metal carbonyl anions to give the corresponding vinylmetal derivatives.

The extremely low reactivity of the halogen in vinyl halides toward nucleophiles can be increased drastically by appropriate substituents on the carbon–carbon double bonds. Thus the polycyanovinyl halides $(NC)_2C{=}C(X)Cl$ (X = H, Cl, CN, etc.) are extremely reactive toward nucleophiles[7] and react with metal carbonyl anions to form extensive series of polycyanovinyl transition metal derivatives in generally good yields.[8]

Another class of vinylic halides which are extremely reactive toward nucleophiles are the α-chloroenamines, I.[9] The high reactivity of these chloroenamines toward nucleophiles arises from the stability of the keteneimmonium cations, II, formed by halide loss. Reactions of α-chloroenamines with metal carbonyl anions were of interest because of the possibility of giving either metal complexes of the keteneimmonium cations II with either the carbon–carbon or the carbon–nitrogen double bond bonded to a transition metal (i.e., CC-dihapto or CN-dihapto derivatives, respectively) or novel cyclic acyl derivatives similar to the reported[10] compounds III and IV obtained by reactions of 2-chloroethyldimethylamine and 2-chloromethylpyridine with appropriate metal carbonyl anions.

This paper reports the details of our studies on reactions of the α-chloroenamines, I (R = CH_3 or 2R = $-(CH_2)_5-$), with metal carbonyl anions. This work has resulted not only