

of the crypt cations allows more interpenetration of what would be the nonmetal layers in CdI_2 .

The isolation of the pentastannide ion is also a pleasant surprise, the red Sn_5^{4-} anion having been the only species identified by Zintl² in ammonia solutions of the tin alloys and more recently verified in the solid state.^{7,9} A yellow-brown color like that of Sn_5^{2-} was observed in liquid ammonia solutions by Kraus and Kurtz.³¹

Acknowledgment. Dr. Don J. Merryman conducted the first exploratory synthesis reactions which led to the isolation of good crystals of the two phases reported here. The structural investigations were greatly aided by the ready advice and council of Professor R. A. Jacobson on a greater than usual number of crystallographic problems.

Registry No. $(\text{cryptNa}^+)_2\text{Pb}_5^{2-}$, 58862-91-2; $(\text{cryptNa}^+)_2\text{Sn}_5^{2-}$, 61665-35-8.

Supplementary Material Available: Listings of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Dicarbonyl(η -cyclopentadienyl)(2-propanoneoximato-*O,N*)molybdenum, a Complex Containing a Novel Chelating Oximato Ligand

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A crystallographic study has shown the product of the reaction of 2-bromo-2-nitrosopropane with $\text{NaMo}(\text{C}_5\text{H}_5)(\text{CO})_3$ to contain an oximato ligand bound in a novel chelating fashion. Crystals of the title compound are orthorhombic, of space group $Pna2_1$, with $a = 7.745$ (11) Å, $b = 12.810$ (18) Å, $c = 11.301$ (16) Å, and $Z = 4$. The structure determination was based upon 865 independent nonzero reflection data; full-matrix least-squares refinement converged to a final conventional R factor of 0.053. The monomeric molecules contain a molybdenum atom bound to an η -cyclopentadienyl ring, two carbonyl groups, and a bidentate $(\text{CH}_3)_2\text{C}=\text{NO}$ ligand. The 2-propanoneoximato group is bound in chelating fashion with Mo-N and Mo-O bond lengths of 2.089 (12) and 2.139 (12) Å, respectively. The molecular structure is rationalized on the basis of a bonding model in which the oximato ligand occupies two coordination sites of a seven-coordinate metal atom. The N-O bond distance of 1.336 (27) Å and the N-C distance of 1.253 (18) Å are close to the values expected for a single and a double bond, respectively. The pertinence of the structural results to the chemistry of metal-nitroso and metal-nitrosyl systems is discussed.

Introduction

In a recent study of the reactions of metal carbonylate anions with 2-bromo-2-nitrosopropane, King and Douglas obtained several types of products.¹ These included metal complexes containing dimethyl ketimine and isopropyliden-amido ligands, as well as two compounds believed to contain a novel $(\text{CH}_3)_2\text{CNO}$ ligand. One of these latter two complexes, a bis(tricarbonyliron) species, was formulated as containing a 2-propanoneoximato group linking the iron atoms through a diatomic Fe-N-O-Fe bridge. This structure was recently confirmed by a crystallographic study² and a second example of a bis(tricarbonyliron) complex containing an identical bridging group has subsequently appeared.³ A less

straightforward structural problem was presented by the mononuclear molybdenum complex $[(\text{CH}_3)_2\text{CNO}]\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2$, obtained by the reaction of 2-bromo-2-nitrosopropane with $\text{NaMo}(\text{C}_5\text{H}_5)(\text{CO})_3$. At least four possible modes for the binding of the $(\text{CH}_3)_2\text{CNO}$ ligand to the metal atom were considered, including binding through C and N, C and O, and N and O or via a delocalized π system involving C, N, and O. Spectroscopic data provided no basis for clear distinction among these four possibilities.¹ We have now completed a crystal structure analysis of the molybdenum complex because of the novelty of the proposed structures and because of our continuing interest in metal complexes derived from azo and nitroso ligands.

Table I. Crystal Data and Experimental Parameters

A. Crystal Data			
Formula	MoC ₁₀ H ₁₁ NO ₃	Z	4
Formula wt	289.14	Density (obsd)	1.61 (5) g cm ⁻³
a	7.745 (11) Å	Density (calcd)	1.713 g cm ⁻³
b	12.810 (18) Å	Space group	<i>Pna</i> 2 ₁
c	11.301 (16) Å	μ (Mo K α)	11.4 cm ⁻¹
V	1121.2 Å ³		
B. Experimental Parameters			
Radiation	Mo K α , λ (K α ₁)	Scan range	-0.50 + 0.66°
	0.709 30 Å,		in 2 θ from
	0.003 in Nb Filter		K α ₁ peak
Temp	22 °C	Background	20-s fixed
Receiving	5 mm square, 30	counting	counts, each
aperture	cm from crystal		end of scan
Takeoff	1.5°	2 θ (max)	55°
angle		Data	1297
Scan rate	1°/min in 2 θ	collected	
		Data with	865
		$F_o^2 >$	
		$3\sigma(F_o^2)$	

Experimental Section

Data Collection and Reduction. A sample of [(CH₃)₂CNO]-Mo(C₅H₅)(CO)₂ was provided by Professor R. B. King. Suitable single crystals could be obtained by recrystallization from hexane. Preliminary precession photographs revealed orthorhombic symmetry with systematic absences $0kl, k + l \neq 2n$, and $h0l, h \neq 2n$. These absences are consistent with the space groups *Pna*2₁ and *Pnma* (with *b* and *c* axes interchanged). Cell parameters were obtained by least-squares refinement⁴ of the setting angles of 15 reflections which had been accurately centered on a Picker four-angle x-ray diffractometer. Owing to the limited amount of sample available, the observed (floatation in aqueous ZnBr₂ solution) density could only be roughly determined. With *Z* = 4, the centrosymmetric space group *Pnma* would require a molecular mirror plane or center of symmetry in an ordered structure. Since none of the probable molecular structures could accommodate either of these symmetry elements, space group *Pna*2₁ was initially assumed. This choice was subsequently confirmed by the successful solution of the structure. Crystal data are tabulated in part A of Table I.

Intensity data were collected from a purple crystal of dimensions 0.20 × 0.12 × 0.12 mm mounted on a glass fiber approximately parallel to the *c** direction. Bounding planes belonged to the {001}, {010}, and {110} forms. Narrow-source, open-counter ω scans through several strong reflections yielded well-formed peaks with an average full width at half-maximum of 0.14°. Intensity data were collected on a Picker automatic diffractometer by use of procedures previously described.⁵ Experimental parameters specific to this data set are summarized in part B of Table I. Copper foil attenuators were used to bring the two reflections for which counting rates exceeded ~10 000 counts/s into the linear range of the counting system. Three standard reflections were measured at regular intervals throughout data collection. These standards showed only random variations, with maximum deviations less than 2% from their average values. The intensity data were processed according to previously described methods.⁵ The *p* factor in the expression for the standard deviation of the observed intensities was assigned a value of 0.05. A trial calculation showed that transmission factors ranged only from 0.83 to 0.89; hence no absorption correction was applied.

Solution and Refinement of the Structure. Solution of the structure was carried out by heavy-atom Patterson and difference Fourier methods. Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms, based upon all data with $F_o^2 \geq 3\sigma(F_o^2)$, yielded discrepancy factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.143$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.178$. Further refinement, with anisotropic temperature factors assigned to the Mo, N, and O atoms gave $R_1 = 0.094$ and $R_2 = 0.118$. In the final refinement, all nonhydrogen atoms were treated anisotropically. A difference Fourier map prior to the final cycle of refinement showed no peaks greater than 1.0 e/Å³, with the exception of two peaks of 1.2 e/Å³ immediately adjacent to the Mo atom. This map showed no convincing evidence for peaks attributable to hydrogen atoms; hence these atoms were not included in the final refinement. Convergence of this refinement was achieved with $R_1 = 0.053$ and $R_2 = 0.071$. In the last cycle, the

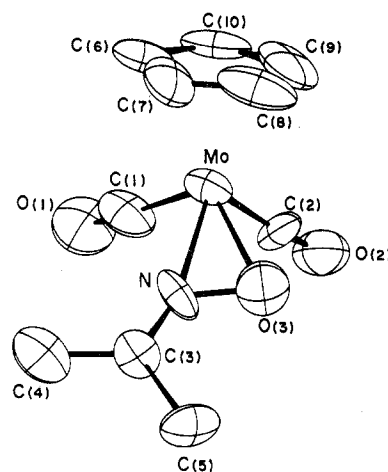


Figure 1. View of the molecular structure of [(CH₃)₂CNO]-Mo(C₅H₅)(CO)₂. Thermal ellipsoids are drawn at the 50% probability level.

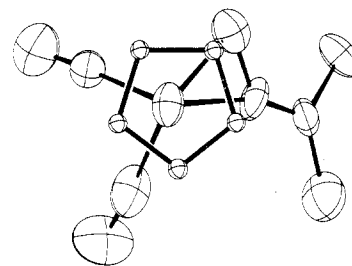


Figure 2. Alternative view of the structure, projected perpendicular to the plane of the five-membered ring. Thermal parameters of the cyclopentadienyl carbon atoms have been reduced for clarity.

largest parameter shift was less than one-third of its standard deviation. The origin of the polar space group *Pna*2₁ was established by fixing the *z* coordinate of the molybdenum atom at 0.2. The structure of opposite polarity to that initially chosen was refined by changing the sign of *l* for all reflection data. This refinement yielded only small parameter shifts (largest *z*-coordinate shift 1.5 σ) and no significant change in *R* factor ($R_2 = 0.07063$ for the original model and 0.07056 for the alternative model). In view of the small differences between the results of these two refinements and the lack of any objective basis for choosing between them, all results are reported in terms of the first model.

Throughout the least-squares refinement, the weights of the observed structure amplitudes were taken as $w = 4F_o^2 / \sigma^2(F_o^2)$ and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The final standard deviation of an observation of unit weight was 1.9. Calculation of structure factors for data with $F_o^2 \leq 3\sigma(F_o^2)$ showed only four reflections with $|F_c^2 - F_o^2| > 3\sigma(F_o^2)$. Scattering factors for all atoms, including anomalous terms for the Mo atom, were taken from ref 6.

Final atomic positional and thermal parameters are listed in Table II. Intramolecular distances and angles are tabulated in Table III. Information concerning selected molecular planes is given in Table IV. A table of observed and calculated structure factors and a listing of principal amplitudes of thermal motion are available.⁷

Description of the Structure and Discussion

Two views of the molecular structure of dicarbonyl(η -cyclopentadienyl)(2-propanoneoximato-*O,N*)molybdenum are shown in Figures 1 and 2. The discrete mononuclear molecules contain a molybdenum atom bound to an η -cyclopentadienyl ring, two carbonyl groups, and a bidentate (CH₃)₂C=NO ligand. This is one of the four structural alternatives considered by King and Douglas.¹ The novel aspect of this structure is the three-membered Mo-N-O ring formed by the chelating 2-propanoneoximato ligand. Such three-membered M-N-O metallocycles have previously been found only in bi- and trinuclear complexes of nitrosobenzenes, in which the nitroso moiety also interacts with a second metal

Table II. Atomic Positional and Thermal Parameters for $[(\text{CH}_3)_2\text{CNO}]\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	-0.017 54 (12) ^a	0.027 08 (7)	0.2	125.1 (19) ^b	38.2 (6)	105.3 (12)	5.1 (10)	-16.5 (35)	-8.8 (20)
O(1)	0.299 8 (22)	0.020 2 (15)	0.0375 (16)	170 (30)	150 (17)	154 (19)	75 (18)	20 (17)	5 (14)
O(2)	0.288 0 (22)	0.085 3 (10)	0.3593 (15)	280 (39)	67 (10)	127 (17)	9 (17)	-49 (19)	2 (11)
O(3)	-0.067 3 (18)	-0.098 5 (9)	0.3199 (13)	256 (30)	64 (9)	109 (14)	-33 (13)	19 (16)	12 (9)
N	-0.040 7 (13)	-0.135 1 (9)	0.2108 (23)	127 (18)	56 (7)	107 (17)	-10 (9)	11 (21)	-50 (15)
C(1)	0.179 9 (31)	0.017 6 (17)	0.0947 (26)	123 (39)	83 (17)	160 (28)	20 (23)	-31 (28)	-26 (18)
C(2)	0.175 1 (30)	0.059 2 (15)	0.3021 (18)	198 (43)	50 (12)	61 (16)	-7 (20)	-30 (21)	20 (12)
C(3)	-0.039 9 (18)	-0.229 8 (10)	0.1831 (22)	127 (21)	46 (8)	89 (24)	-32 (11)	17 (22)	0 (11)
C(4)	-0.001 2 (28)	-0.259 7 (20)	0.0572 (19)	265 (45)	76 (14)	142 (24)	6 (19)	16 (26)	-20 (16)
C(5)	-0.063 6 (27)	-0.308 2 (16)	0.2857 (21)	217 (39)	62 (13)	151 (25)	0 (18)	-7 (26)	32 (14)
C(6)	-0.166 0 (21)	0.121 5 (13)	0.0571 (18)	128 (30)	46 (11)	151 (26)	30 (14)	13 (21)	9 (13)
C(7)	-0.288 1 (29)	0.060 7 (19)	0.1105 (22)	179 (42)	100 (18)	128 (27)	65 (22)	12 (26)	-22 (17)
C(8)	-0.306 0 (24)	0.086 4 (17)	0.2302 (31)	107 (26)	67 (13)	291 (56)	32 (15)	-17 (36)	3 (22)
C(9)	-0.188 4 (30)	0.165 0 (22)	0.2545 (24)	223 (48)	106 (23)	178 (29)	118 (29)	-20 (35)	-42 (20)
C(10)	-0.101 3 (25)	0.187 2 (14)	0.1454 (25)	145 (35)	36 (10)	206 (32)	32 (17)	-38 (28)	20 (13)

^a Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. ^b The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Tabulated β values have been multiplied by 10^4 .

Table III. Bond Distances (Å) and Angles (deg)

A. Distances			
Mo-N	2.089 (12)	N-C(3)	1.253 (18)
Mo-O(3)	2.139 (12)	C(1)-O(1)	1.132 (27)
Mo-C(1)	1.942 (28)	C(2)-O(2)	1.138 (23)
Mo-C(2)	1.930 (21)	C(3)-C(4)	1.503 (30)
Mo-C(6)	2.322 (18)	C(3)-C(5)	1.545 (29)
Mo-C(7)	2.366 (23)	C(6)-C(7)	1.366 (29)
Mo-C(8)	2.384 (19)	C(6)-C(10)	1.399 (27)
Mo-C(9)	2.291 (19)	C(7)-C(8)	1.398 (36)
Mo-C(10)	2.238 (17)	C(8)-C(9)	1.385 (30)
N-O(3)	1.336 (27)	C(9)-C(10)	1.434 (29)

B. Angles

N-Mo-O(3)	36.8 (8)	Mo-C(1)-O(1)	173.9 (24)
N-Mo-C(1)	92.3 (8)	Mo-C(2)-O(2)	175.0 (17)
N-Mo-C(2)	104.1 (8)	N-C(3)-C(4)	118.9 (23)
O(3)-Mo-C(1)	118.9 (8)	N-C(3)-C(5)	116.2 (25)
O(3)-Mo-C(2)	85.5 (7)	C(4)-C(3)-C(5)	124.7 (16)
C(1)-Mo-C(2)	76.7 (7)	C(7)-C(6)-C(10)	106.0 (19)
Mo-N-O(3)	73.6 (7)	C(6)-C(7)-C(8)	111.2 (23)
Mo-N-C(3)	161.4 (24)	C(7)-C(8)-C(9)	107.3 (25)
O(3)-N-C(3)	124.9 (24)	C(8)-C(9)-C(10)	106.5 (21)
Mo-O(3)-N	69.6 (9)	C(9)-C(10)-C(6)	109.0 (17)

Table IV. Least-Squares Planes

1. $-0.6960x + 0.6810y - 0.2227z = 1.8042$	
C(6) ^a	0.003 ^b
C(7)	-0.006
C(8)	0.007
Mo*	-1.988
2. $-0.9840x + 0.0150y - 0.1778z = -0.1400$	
O	-0.009
N	0.000
C(3)	0.032
C(4)	-0.016
C(5)	-0.008
Mo*	-0.123

^a All atoms listed were given unit weights in the calculation of the least-squares plane, except those marked with an asterisk, which were given zero weight. ^b Tabulated figures are distances, in Å, from the least-squares plane.

atom through a M-N-M bridge.^{8,9} Bidentate O,N-bonded 2-propanoneoximate ligands are found in two binuclear iron carbonyl complexes, but in each case they form diatomic bridges with an Fe-N-O-Fe linkage.^{2,3} Most frequently, oximate groups bind through nitrogen only, with the oxygen atom often involved in hydrogen bonds, as in metal complexes of dimethylglyoxime and related ligands.¹⁰ The lack of opportunities for hydrogen bonding in the present case may contribute to the preference for a chelating structure.

The coordination geometry about the molybdenum atom is related to the seven-coordinate configuration observed for many $(\eta\text{-C}_5\text{H}_5)\text{ML}_4$ species, where the cyclopentadienyl group is viewed as occupying three coordination sites.¹⁶ The principal feature of the metal coordination sphere which weighs in favor

Table V. Comparison of the Coordination Geometries of $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{L}$ Complexes, with L = $(\text{CH}_3)_2\text{CNO}$ and CH_3SCH_2

	L = $(\text{CH}_3)_2\text{CNO}$	L = CH_3SCH_2
C(1)-Mo-C(2) ^a	76.7 (7)	77.5 (4)
C(1)-Mo-O(3)	118.9 (8)	114.0 (4)
C(2)-Mo-O(3)	85.5 (7)	78.5 (4)
C(1)-Mo-N	92.3 (8)	89.9 (3)
C(2)-Mo-N	104.1 (8)	109.3 (3)
N-Mo-O(3)	36.8 (8)	44.4 (3)

^a Atom numbering is that defined for the $(\text{CH}_3)_2\text{CNO}$ complex; in the CH_3SCH_2 derivative these atoms are replaced by the stereochemically equivalent atoms; i.e., O(3) is replaced by the methylene carbon atom, N by S, etc.

of this description over one based upon a six-coordinate $(\eta\text{-C}_5\text{H}_5)\text{ML}_3$ model (with the $(\text{CH}_3)_2\text{CNO}$ ligand occupying a single coordination site) is the C(1)-Mo-C(2) angle of 76.7 (7)°. This is a typical value for heptacoordinate metal carbonyl derivatives but is significantly smaller than the angles of near 90° found in related hexacoordinate complexes. The same reasoning was employed by deGill and Dahl for $(\text{CH}_3\text{SCH}_2)\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2$, which has a structure very similar to that of $[(\text{CH}_3)_2\text{CNO}]\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2$.¹⁷ The coordination geometries of these two molecules are compared in Table V. From the tabulated data, the close similarity of the two structures is evident; the differences in bond angles may be attributed to the longer Mo-S, Mo-C, and C-S distances in the organosulfur complex in comparison to the Mo-N, Mo-O, and N-O distances we observe.

The C-N and N-O distances in the chelating $(\text{CH}_3)_2\text{CNO}$ ligand are consistent with the description of these bonds as a double bond and a single bond, respectively. Thus, the N-O bond distance of 1.336 (27) Å is significantly longer than the double-bond N=O distance of 1.209 (3) Å observed in $(\text{C}_6\text{H}_5\text{NO})_2\text{PdCl}_2$ ¹⁸ and close to the value of 1.36 Å predicted for the length of a single N-O bond on the basis of covalent radii.¹⁹ Likewise the C-N distance of 1.253 (8) Å is a reasonable double-bond value. These distances are equal within experimental error to the N-O and C=N distances reported for the bridging $(\text{CH}_3)_2\text{CNO}$ ligand in two binuclear iron carbonyl derivatives.^{2,3} They also do not differ greatly from the analogous distances observed in dimethylglyoximate-metal complexes, although some such complexes display C=N and N-O distances slightly longer than those we observe.¹⁰ A long N-O bond of 1.40 (1) Å has also been found in the bridged dimeric bis[tricarbonyl(3-chloro-2-methylnitrosobenzene)iron].⁸ On the basis of bond lengths, there appears to be no need in the present case to postulate a π -allyl type of electron delocalization as was suggested for

the organosulfur ligand in $(\text{CH}_3\text{SCH}_2)\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2$.¹⁷ In spite of the similarities in bond distances between the bridging $(\text{CH}_3)_2\text{CNO}$ ligand in $[(\text{CH}_3)_2\text{CNO}][(\text{CH}_3)_2\text{C}-\text{N}]\text{Fe}_2(\text{CO})_6$ and the chelating group in $[(\text{CH}_3)_2\text{CNO}]\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2$, significant differences in bond angles for these two groups are observed. The O-N-C and C-C-C angles in the bridging oximato ligand are 115.1 (5) and 117.7 (5)°, respectively,² while in the chelating group these angles increase to 124.9 (24) and 124.7 (16)°. No bond angle data are available for the other $(\text{CH}_3)_2\text{CNO}$ -bridged binuclear iron carbonyl derivative.³

Although there is no structurally documented precedent for the chelating $(\text{CH}_3)_2\text{CNO}$ group found here, a number of cases are known in which other ligands fulfill a stereochemically similar role. Representative examples of metal complexes containing three-membered metallocycles in which at least one of the ring members is not a carbon atom include the closely related CO_2 and CS_2 complexes $\text{Ni}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_{11})_3)_2$ ²⁰ and $\text{Pt}(\text{CS}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_2$,²¹ manganese²² and molybdenum²³ complexes containing a chelating thiocarboxamido ligand, and the phenylhydrazinemolybdenum derivative $(\eta^2\text{-H}_2\text{NNHC}_6\text{H}_5)\text{Mo}(\text{C}_5\text{H}_5)(\text{NO})\text{I}$.²⁴ No single simple description of the bonding within the metallocyclic ring is adequate for all of these complexes. In the case of the phenylhydrazinemolybdenum complex, the reasonable choice is a σ -bonded model, with a N-N single bond and the nitrogen atoms essentially sp^3 hybridized. On the other hand, a significant degree of olefinlike π interaction is indicated for the binding of CO_2 in $\text{Ni}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_{11})_3)_2$. This conclusion is based upon the P-Ni-P angle of 120° and the coordinated C-O distance of 1.22 (2) Å, only 0.06 Å longer than in free CO_2 and much closer to the expected double-bond value than to a single-bond distance. In other cases (e.g., the platinum-carbon disulfide adduct and the two thiocarboxamido complexes mentioned above) no objective choice between these two extreme descriptions is possible and an intermediate picture is required. For reasons discussed above, we view the $(\text{CH}_3)_2\text{CNO}$ -Mo interaction observed in the present case as best represented by a model closer to the σ -bonding limit than to the π -bonding extreme.

Other portions of the structure display no unexpected features. The carbon atoms of the cyclopentadienyl ring are closely coplanar; the ring C-C distances do not differ significantly and have a mean value of 1.396 Å. The thermal motions of the cyclopentadienyl carbon atoms, and indeed of the entire molecule, are rather large and may in part be responsible for the relatively low precision of the light-atom coordinates. The Mo-C(cyclopentadienyl) distances show some apparently significant variations, though this also may be a consequence of thermal motion.

Although this is the first crystallographically documented example of a mononuclear metal complex containing a chelating RNO ligand, similar three-membered M-N-O groupings have been proposed in several palladium complexes derived from di-*tert*-butylnitroxide²⁵ and also in a series of nitrosobenzene derivatives of Ni, Pd, and Pt.²⁶ In some members of the latter series of complexes, the coordinated nitrosobenzene has been shown to undergo N-O bond cleavage followed by further chemical reactions including transfer of an oxygen atom or a phenylnitrene group, either to a coordinated ligand or to an added reactant.²⁶ Metal-nitroso complexes have also been suggested as possible intermediates in the reduction of alkyl-nitro compounds by iron carbonyls.³ The diversity of the chemical reactions of nitroso compounds with transition metal systems is further underscored by the variety of types of ligands which have been obtained from such reactions. Those which have been confirmed crystallographically include N-bonded nitrosoarenes,¹⁸ (N + O)-bonded bridging nitrosoarenes,^{8,9} chelating and bridging bidentate

oximato ligands,^{2,3} and a bridging isopropylidenamido group.² Other proposed ligands include chelating²⁶ and O-bonded²⁷ nitrosoarenes and a dimethyl ketimine group.¹

Many of these products of the reactions of transition metal systems with C-nitroso compounds not only are of interest in themselves but also may be pertinent to the understanding of the reactions of metal-bound nitrosyl groups. Thus, for example, metal-coordinated nitrosoarenes have been prepared by the reaction of a coordinated nitrosyl group with aromatic amines.²⁸ Also, an intermediate of stoichiometry $\text{ReO}(\text{C}_6\text{H}_5)_3(\text{CH}_3\text{NO})$ has recently been characterized in the reaction of $\text{ReO}(\text{CH}_3)_4$ with NO.²⁹ This intermediate is believed to have either a bridging or a chelating RNO ligand and to undergo NO bond cleavage and elimination of CH_2N : to yield $\text{ReO}_2(\text{CH}_3)_3$, the ultimate product.

A final point of interest is the recent development of an improved route for the preparation of $[(\text{CH}_3)_2\text{CNO}]\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2$ and related complexes.³⁰ This route is based upon the structural results which show the $(\text{CH}_3)_2\text{CNO}$ ligand to be bound as an oximato group. It employs oxime precursors as starting materials, thus avoiding use of the unstable 2-bromo-2-nitrosopropane.

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Registry No. $[(\text{CH}_3)_2\text{CNO}]\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2$, 61491-36-9.

Supplementary Material Available: A listing of structure factor amplitudes and a table of principal amplitudes of thermal motion (8 pages). Ordering information is given on any current masthead page.

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