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THE PREPARATION AND SPECTROSCOPIC PROPERTIES OF SOME MOLYBDENUM CARBONYL DERIVATIVES OF AMMONIA AND PHOSPHINE

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SUMMARY

The compounds *cis*-$(PH_3)_2Mo(CO)_4$, *cis*-$(PH_3)_3Mo(CO)_3$, *cis*-$(NH_3)_2Mo(CO)_4$ and *cis*-$(NH_3)_3Mo(CO)_3$ have been prepared from cycloheptatrienemolybdenum tricarbonyl and norbornadienemolybdenum tetracarbonyl. The IR spectra of these compounds and of their ^2H and ^{15}N analogues have been recorded and assignments made. The NMR spectra are reported and the values of $J(P{-}P')$ and $J(^{15}N{-}H)$ have been obtained.

INTRODUCTION

When the present study was started there were few references in the literature to the use of phosphine, PH_3, as a ligand in transition metal complexes[1,2]. Phosphine reacted with vanadium hexacarbonyl to give $[V(CO)_4PH_2]_2$ in which two vanadium atoms were bridged by two PH_2 groups. Although there are several reports of metal carbonyl compounds containing ammonia, there has been little study of their spectra to confirm their structures[3,4].

It was decided, therefore, to investigate the reactions between phosphine/ammonia and cycloheptatrienemolybdenum tricarbonyl/norbornadienemolybdenum tetracarbonyl. Both of these complexes are known to react with substituted phosphines and amines by losing the hydrocarbon ligand[5,6].

Several recent reports have shown that phosphine can act as a unidentate, terminal ligand in transition metal carbonyl complexes[7-9].

Phosphine reacted with a pentane solution of norbornadienemolybdenum tetracarbonyl to produce, in high yield, a white crystalline solid, whose analysis and spectra showed it to be *cis*-$(PH_3)_2Mo(CO)_4$ (ref. 9), containing varying, but small traces of $(PH_3)Mo(CO)_5$ in some preparations. This impurity, which arose from small traces of $Mo(CO)_6$ in the sublimed nor-$C_7H_8Mo(CO)_4$, was identified by preparing genuine $(PH_3)Mo(CO)_5$ by Fisher's UV method and comparing spectra.

With cycloheptatrienemolybdenum tricarbonyl, phosphine gave a pale brown solid which was unstable under nitrogen or high vacuum. This instability prevented accurate analysis, but its method of preparation and IR spectrum strongly suggested that the compound was *cis*-$(PH_3)_3Mo(CO)_3$.

In a similar manner, the corresponding ammonia complexes were prepared.

cis-$(NH_3)_2Mo(CO)_4$ was a yellow solid which was slightly air sensitive, and insoluble in all common solvents except acetone, in which it decomposed rapidly at a very low temperature (−60°). The compound was fairly soluble in liquid ammonia, at −60°, without decomposition. cis-$(NH_3)_3Mo(CO)_3$ was a pale yellow solid which was air sensitive and insoluble in all common solvents.

Further confirmation of the similarity of the corresponding phosphine and ammonia compounds has been provided by their ready interconversion, in the presence of excess of the other ligand, and by their similarity in other simple chemical reactions[10].

NMR SPECTRA

1. *cis-$(PH_3)_2Mo(CO)_4$*

This compound gave a complex ^1H spectrum as expected for an $X_3AA'X'_3$ spin system similar to the ^{19}F spectrum of the equivalent compound cis-$(PF_3)_2$-$Mo(CO)_4$ where $J(P–P') = 55.5$ Hz[11]. The PMR spectrum of $(PH_3)_2Mo(CO)_4$, in acetone, consisted of a doublet, each half of which contained three lines. Also visible were the weak lines of a doublet due to the $PH_3Mo(CO)_5$ impurity. Analysis of the complex spectrum, using theoretical treatments available[12,13], gave the values shown in Table 1. In benzene, the spectrum (at 100 MHz rather than 60 MHz) gave slightly different parameters. The ^{31}P spectrum gave only the four most intense lines, for the acetone solution, which agreed with those predicted theoretically using the treatment of Anet[12] (to within 1 Hz).

TABLE 1

NMR PARAMETERS OF $(PH_3)_2Mo(CO)_4$

Parameter	In acetone	In benzene
τ^a	6.3	7.61
$J(P–H)^b$	319.2	314.0
$J(P–H')^b$	10.5	10.75
$J(P–P')^b$	20.3	24.8

^{a} In ppm with respect to TMS. ^{b} In Hz.

2. *cis-$(PH_3)_3Mo(CO)_3$*

The low solubility of this compound only allowed the detection of the strongest four lines (a doublet of doublets), in the ^1H spectrum which should be that of an X_3-$AA'A''X'_3X''_3$ spin system. The only parameters obtainable therefore from a weak solution in dioxane (the best solvent found) were $J(P–H) = 313.2$ Hz, $\tau = 6.41$ ppm. The splitting between the smaller doublets was 10 Hz.

3. *cis-$(NH_3)_2Mo(CO)_4$*

The ^1H NMR was recorded at −60° in liquid ammonia. A single, broad line was observed; $\tau = 7.91$ ppm (w.r.t. NH_3 solvent).

4. *cis*-$(^{15}NH_3)_2Mo(CO)_4$

Since this compound is magnetically similar to the *cis*-$(PH_3)_2Mo(CO)_4$, an $X_3AA'X'_3$ spin system, it was hoped to find evidence for $^{15}N-^{15}N$ coupling and possibly to measure $J(N-N')$. However, in liquid ammonia at $-60°$ only two sharp lines ($\tau = 7.9$ w.r.t. NH_3) were seen suggesting that $J(N-N') = 0$ but $J(^{15}N-H) = 68$ Hz. This value for $J(^{15}N-H)$ may be compared with that for $J(N-H)$ in $^{15}NH_3$ (61.5 Hz)[14] and in $(Me_3Si)_2{}^{15}NH$ (66.5 Hz)[15]. It is of interest to compare the values of the NMR parameters of the phosphine and ammonia complexes.

The ^1H chemical shift of phosphine decreased and $J(P-H)$ increased upon co-ordination to molybdenum in the compound $(PH_3)_2Mo(CO)_4$. These changes may be compared with those observed in the series PH_2^-, PH_3, PH_4^+ where τ decreased from 11.4 to 8.3 to 3.9 ppm and $J(P-H)$ increased from 138.7 to 183.0 to 546 Hz respectively[16]. The value of $J(P-H)$ is believed to be related to the amount of "*s*-character" in the P–H bond and so increases as the co-ordination number of phosphorus increased *e.g.* co-ordination of PH_3 in $(PH_3)_2Mo(CO)_4$. Chemical shift variation is a function of several factors whose relative importance has not yet been established for free hydrides. One factor which influences the chemical shift of the phosphorus and to a lesser extent affects the protons in the complex is the contribution to the screening from the anisotropic, paramagnetic field due to the mixing of unoccupied metal orbitals and occupied, ligand orbitals.

The ammonia complexes also showed a downfield shift from free ammonia, for similar reasons to their phosphine analogues. There was, however, little change in $J(N-H)$ upon co-ordination reflecting the smaller change in the "*s*-character" of the N–H bonds (*cf.* bond angles PH_3 93°, NH_3 107°) when the nitrogen becomes tetrahedrally bonded. Further low temperature work is in progress on these systems[10].

VIBRATIONAL SPECTRA

Studies of the IR spectra of metal carbonyls have been used extensively to determine their structures, and such studies were extremely useful in the present work, where the intractability of some of the compounds limited the number of techniques available for their characterisation. Since simple ligands were used, we have attempted to use the whole spectrum in structure determination, rather than using only the carbonyl region. In order to get more complete assignments of the ligand vibrations and of the metal–phosphorus and metal–nitrogen vibrations, isotopically substituted compounds were prepared *e.g.* $(PD_3)_2Mo(CO)_4$, $(PD_3)_3Mo(CO)_3$, $(ND_3)_2Mo(CO)_4$, $(^{15}NH_3)_2Mo(CO)_4$, $(ND_3)_3Mo(CO)_3$. However, even in simple carbonyls, complete band assignment has not been possible. In the discussion which follows, the carbonyl regions will be treated separately from the rest of the spectra, in order to allow comparisons with other similar compounds.

Carbonyl vibrations

The carbonyl stretching regions of the IR spectra of the four compounds are listed in Tables 2 and 3. Since the complexes have all been prepared from *cis* intermediates, it was expected that the complexes would be *cis* isomers. The number of IR active $\nu(C-O)$ vibrations expected is: 4 for *cis*-$L_2Mo(CO)_4$; 2 for *cis*-$L_3Mo(CO)_3$. The corresponding *trans* isomers have 1 and 3 IR active bands in the same region. The

TABLE 2

IR AND RAMAN SPECTRA OF PHOSPHINE COMPLEXES OF MOLYBDENUM CARBONYL (IN CM^{-1})

$(PH_3)_2Mo(CO)_4$[b]	$(PH_3)_2Mo(CO)_4$[a]	$(PD_3)_2Mo(CO)_4$[b]	$(PD_3)_2Mo(CO)_4$[a]	$(PH_3)_2Mo(CO)_4$[c]	$(PH_3)_3Mo(CO)_3$[a]	$(PD_3)_3Mo(CO)_3$[a]	Assignment
2339 m		1690 m		2370 s	2315	1681	ν(P–H)
2036 s		2036 s		2039 s	1971.5[b]	1971.5[b]	
1946 vs		1946 vs		1915–1950 s	1892[b]	1892[b]	ν(C–O)
1932 vvs		1932 vvs					
1923 vs		1923 vs					
1022 s	1015 m	778 w	770 w	1020 m	1082 m	782 w	
1007 s	1008 m	755 m	740 m	1008 m	1056 w	770 w	
	1001 m	748 m	730 m		1016 s	745 m	δ(P–H)
	996 m	743 m			1011 s	735 s	
					1000 s	650 wv	
					908 w	640 vvw	
					888 w		
					852 w		
611 s	611 s	610 m	610 m	620 vw	620 m	618 m	δ(M–CO)
590 s	589 s	590 m	580 m	500 vw	598 m	590 m	
	543 w	580 m			590 m		
Not obs.	720 vw	Not obs.	490 vw		710 vw	520 vw	PH_3-rock
394 m	438 w	428 w	436 vw	452 vs	450 w	450 w	
379 m	392 m	390 w	420 w	414 v			
	385 m		392 m				ν(M–CO)
			385 m				
	270 m		265 m				
	218 m		219 vw (sh)		310 w	295 w	
			210 m	208 w	271 m	261 m	ν(M–P)
				199 s	228 w	225 w	
				90 w			δ(C–M–C)

[a] Nujol mull. [b] Solution in cyclohexane. [c] Raman spectrum on solid.

TABLE 3

IR SPECTRA OF AMMONIA COMPLEXES OF MOLYBDENUM CARBONYL[a] (CM^{-1})

$(NH_3)_2Mo(CO)_4$	$(ND_3)_2Mo(CO)_4$	$(^{15}NH_3)_3Mo(CO)_4$	$(NH_3)_3Mo(CO)_3$	$(ND_3)_3Mo(CO)_3$	Assignment
3370 m	2520 m	3368 m	3371 m	2518 m	
3295 m	2425 w	3295 m	3284 m	2419 w	ν(N–H)
	2400 m			2393 m	
2010 m	2015 m	2010 m			
1915 vvs	1925 vvs	1920 vvs	1880 vvs	1880 vvs	ν(C–O)
1837 vvs	1835 vvs	1835 vvs	1730 vvs	1710 vvs	
1780 vvs	1780 vvs	1783 vvs			
1600 m	1169 m	1593 m	1686 m	1171 m	
1226 m	1022 w	1219 m	1204 m	1010 w	δ(N–H)
1216 (sh)	945 m	1208 (sh)		931 m	
	940 m				
952 w	673 w				
919 w	659 w	not obs.	955 w	649 w	
845 w	625 w				NH_3-rock
591 m	587 m	581 m	615 w	545 w	δ(M–CO)
560 w	560 w	560 w	565 w		
505 vw	505 vvw	505 vvw	520 vvw	520 vvw	possibly δ(C–M–C) and ν(M–C)
487 vw	488 vvw	488 vw	503 vvw	504 vvw	
468 vw		470 vw	482 vvw	483 vvw	
398 w	400 w	400 w			
361 s	360 s	360 s	360 w	360 w	ν(M–CO)

[a] Measured on nujol mulls.

carbonyl region of a solution of $(PH_3)_2Mo(CO)_4$ showed four main bands as expected, of relative intensities medium, strong, very strong, strong, going from high to low frequency. Using the vector dipole method of Kaesz and El-Sayed[17], which predicts relative intensities $A_1''/A_1'/B_1/B_2=0/2/2/4$, the absorptions can be assigned as: 2037 (A_1''), 1946 (A_1'), 1932 (B_2), 1923 (B_1) cm^{-1}. This differs from the spectrum of this compound reported by Fischer[9], who does not report the strong band at 1932 cm^{-1} but quotes a weak absorption at 1897 cm^{-1} as the fourth band expected. An extra band, at 1960 cm^{-1}, which appeared weakly and with varying intensities, in different preparations, was shown to be the strongest band of $PH_3Mo(CO)_5$. Confirmation of this was obtained by measuring the carbonyl region of the IR spectrum of a sample of $PH_3Mo(CO)_5$ prepared from PH_3 and $Mo(CO)_6$. The spectrum showed bands at 2081 vw and 1960 vs cm^{-1} which can be assigned to A_1'' and E vibrations respectively.

The Raman spectrum of solid $(PH_3)_2Mo(CO)_4$ showed bands at 2039, ~2000 vw, ~1915–1950 (br) and 1880 cm^{-1}. The weak bands at 2000 and 1880 cm^{-1} may be assigned to the B_1 and A_1 modes of the $PH_3Mo(CO)_5$ impurity while the broad band at ~1915–1950 cm^{-1} contained the three lower frequency bands of $(PH_3)_2Mo(CO)_4$. The carbonyl region of the $(PH_3)_3Mo(CO)_3$, in cyclohexane, showed two bands as expected for a *cis*, C_{3v} isomer. The frequencies of these absorptions indicate that in this compound phosphine has similar π-bonding abilities to substituted phosphines such as $(CH_3O)_3P$. This is also reflected in the values of the force constants for the C–O bands obtained by the approximate Cotton–Kraihanzel[18] methods. These values are $k = 14.86$, $k_i = 0.41$ mdyne/Å.

The carbonyl region of $(NH_3)_2Mo(CO)_4$ has been assigned as follows: A_1'' 2010, A_1' 1837, B_1 1780, and B_2 1915 cm^{-1}. It was unfortunate that no solution data could be obtained but the evidence available suggests the *cis* configuration for this compound.

The carbonyl region of $(NH_3)_3Mo(CO)_3$ in Nujol also shows two bands indicating the presence of the *cis*, C_{3v}, isomer. The relatively low frequencies of the absorptions and Cotton–Kraihanzel force constants of 12.81 and 0.72 mdyne/Å show the expected very low π-bonding ability of ammonia even compared to other amines. In spite of the instability of the two trisubstituted complexes, it appears that only the *cis*-$L_3Mo(CO)_3$ compounds are present in the reaction products. Although ammonia appears to have such poor ligand properties in such systems it is possible to exchange phosphine by ammonia, in these complexes, at room temperature[10]. Having separated out the carbonyl stretching vibrations we now turn to the rest of the spectra. They are listed in Table 2 together with the assignments which we suggest may explain their origins. In order to arrive at more satisfactory assignments for some of these bands we have prepared and measured the spectra of $(PD_3)_2Mo(CO)_4$, $(PD_3)_3Mo(CO)_3$, $(ND_3)_2Mo(CO)_4$, $(ND_3)_2Mo(CO)_4$, $(^{15}NH_3)_2Mo(CO)_4$ which are reported in Tables 2 and 3 with the Raman spectrum of $(PH_3)_2Mo(CO)_4$. Table 4 compares the expected number of IR active vibrations for the *cis* and *trans* isomers of $L_2Mo(CO)_4$ and $L_3Mo(CO)_3$ with those described here. It will be seen that the overwhelming evidence is for the *cis* form in each case.

TABLE 4

COMPARISON OF EXPECTED AND OBSERVED BANDS IN $L_2Mo(CO)_4$ AND $L_3Mo(CO)_3$ ISOMERS

Origin	$L_2Mo(CO)_4$				$L_3Mo(CO)_3$			
	Expected		Obs. for L =		Expected		Obs. for L =	
	C_{2v}	D_{4h}	NH_3	PH_3	C_{2v}	C_{3v}	PH_3	NH_3
ν(C–O)	4	1	4	4	3	2	2	2
ν(M–C)	4	1	2	4	3	2	1	1
δ(M–CO)	6	2	2	3	5	3	3	2
ν(M–P)	2	1		2	3	2	3	

Metal–carbonyl vibrations

Values of δ(M–CO) and ν(M–CO) have been published for many compounds[19] and the values assigned here are in line with these. Deuteration studies have, however, allowed a distinction between them and the bands mainly due to the PH_3 and NH_3 parts of the molecule.

Earlier studies, especially those by Bigorgne[20], suggested that the value of ν(M–CO) increases as ν(C–O) decreases in a series of compounds. More recent work on the system $V(CO)_6^-$, $Mn(CO)_6^+$, $Re(CO)_6^+$, has suggested that this is not always the case[21]. In view of this it is not unreasonable that ν(M–CO) is so similar for the PH_3 and NH_3 complexes. Weak bands in the 500 cm^{-1} region have been tentatively assigned at C–M–C bend + ν(M–CO) combinations.

LIGAND VIBRATIONS

In both PH_3 complexes, there is a band in the 2320–2340 cm^{-1} region which can be assigned to a P–H stretching vibration. In the Raman spectrum of $(PH_3)_2$-$Mo(CO)_4$, there is a further strong band at 2371 cm^{-1} which may be assigned to the A_2 P–H stretching mode. P–H deformations were seen in the 1000 cm^{-1} region.

Upon deuteration the P–H stretch modes moved to ~1700 cm^{-1} and the deformation modes to around 750 cm^{-1}. Deuteration also allowed a tentative assignment of PH rocks.

From the ratio of $\sqrt{\mu(PD_3)}/\sqrt{\mu(PH_3)}$ the shift on deuteration should be in region of 28%. Two bands in the spectra of 270 and 220 cm^{-1} shifted by roughly the expected amount upon deuteration suggesting that they are due to ν(M–P). These values are in line with other reported values for ν(M–P) in similar complexes[17]. The observed splitting of one of these peaks upon deuteration may be due to interaction with some other mode in the deuterated compound. It is, of course, very probable that there will be considerable interaction between the vibrations in these regions *e.g.* ν(M–CO), ν(M–P) in view of their proximity in the molecule and in their frequencies.

In the spectra of the ammonia complexes, the N–H stretching vibrations were found to absorb around 3300 cm^{-1}. This value decreases to 2400–2500 cm^{-1} in the ND_3 complexes. The presence of ^{15}N rather than ^{14}N in $(NH_3)_2Mo(CO)_4$ caused little change in value of the NH stretch.

The symmetrical and antisymmetrical deformations appear around 1200 and 1600 cm^{-1} respectively and are shifted by deuteration to around 900 and 1100 cm^{-1}. The $(^{15}NH_3)_2Mo(CO)_4$ complex's deformations are shifted by 7 cm^{-1}.

Finally the NH rocks are shifted from 900 to 650 cm^{-1} in the deuterated case. These changes are all consistent with the changes in the reduced mass of the ligand and with force constant calculations and deuterations on other systems[17].

The metal–nitrogen stretch

^{15}N has been used to determine the M–N stretch in nitrodo compounds[22] and in metal amine complexes[23] with success. In spite of close study of the spectra of *cis*-$(^{15}NH_3)_2Mo(CO)_4$ no isotopic shift could be found in the region between 550–200 cm^{-1}. There was, however, a band at 190 cm^{-1} (on the limit of the IR machine) in all the ammonia complexes which could be the M–N stretch. Unfortunately no Raman data could be obtained on these compounds.

Adams[19] has outlined the dispute which has only recently been resolved over the values of ν(M–N) in metal amines. However, with other complexes *e.g.* aryl, alkyl complexes of Pd and Pt a recent paper[24] using Raman and IR data has suggested that for this type of compound the M–N stretch was below 200 cm^{-1}.

Since little spectroscopic work has been done on ammonia metal carbonyls we suggest that either the M–N is too weak to be observed in this region or it lies below 200 cm^{-1}.

EXPERIMENTAL

All manipulations were performed either under an atmosphere of dry nitrogen, or, preferably on a conventional vacuum system.

IR spectra were recorded on a Perkin–Elmer 225 spectrometer using variable path solution cells, fitted with KBr windows. CsI plates were used for mulls.

Raman spectra were obtained on the solid $(PH_3)_2Mo(CO)_4$ using a Cary Laser Raman Spectrometer with a He–Ne laser (6328 Å).

Nuclear magnetic resonance spectra were run on the Perkin–Elmer HA 60 and the Varian HA 100 spectrometers.

Analyses were performed by A. Bernhardt, Mikroanalytisches Laboratorium, Mulheim, Germany.

Cycloheptatrienemolybdenum tricarbonyl and norbornadienemolybdenum tetracarbonyl were prepared by established methods[25]. Phosphine was prepared by the pyrolysis of phosphorous acid; deutero-phosphine by the action of deuterium oxide on calcium phosphide.

Commercial ammonia was purified by fractionation and dried over potassium; deutero-ammonia was prepared by the action of a solution of potassium tert-butoxide in deuterium oxide on AnalaR ammonium chloride and dried over potassium. $^{15}NH_3$ was prepared by the action of sodium hydroxide on $^{15}NH_4Cl$.

Hydrocarbon solvents were dried over sodium. Acetone was dried over molecular sieve.

Preparation of cis-biphosphinemolybdenum tetracarbonyl

Norbornadienemolybdenum tetracarbonyl (1.9661 g, 6.55 mmoles), dissolved in pentane, reacted with phosphine (0.4815 g, 14.15 mmoles) in a sealed ampoule, when warmed to room temperature, giving a white solid product. After allowing several hours for complete reaction, the volatile products were passed into the vacuum line and fractionated. The IR spectrum indicated that they consisted of norbornadiene, pentane and phosphine (0.0181 g, 0.53 mmoles). The white solid product was crystallised from cold pentane or acetone/water mixture giving white needles of *cis*-bis(phosphine)molybdenum tetracarbonyl (1.5087 g, 5.46 mmoles, 89%). (Found: C, 17.8; H, 2.2; P, 22.0. $C_4H_6MoO_4P_2$ calcd.: C, 17.4; H, 2.2; P, 22.4%.)

Preparation of cis-triphosphinemolybdenum tricarbonyl

Phosphine (0.0815 g, 2.40 mmoles) reacted in a sealed tube over several hours with a pentane solution of cycloheptatrienemolybdenum tricarbonyl (0.1780 g, 0.654 mmoles) to form a pale brown solid. The volatile products, when fractionated, were shown by IR spectroscopy to be cycloheptatriene, pentane and phosphine (0.0233 g, 0.685 mmoles). The solid was washed with pentane to remove unreacted starting material but could not be purified further due to its instability and insolubility. The IR spectrum of the brown solid produced (0.1502 g, 0.533 mmoles, 81.5%) suggested that it was *cis*-tris(phosphine)molybdenum tricarbonyl.

Preparation of cis-diamminemolybdenum tetracarbonyl

Dry ammonia (0.0755 g, 4.5 mmoles) reacted with cyclohexane solution of norbornadienemolybdenum tetracarbonyl (0.4246 g, 1.5 mmoles), at room temperature, to give a yellow solid. The volatile products were fractionated and shown to be norbornadiene, cyclohexane and ammonia (0.0247 g, 1.45 mmoles). The solid product was obtained free of starting material, after repeatedly being washed with pentane. (Found: C, 20.02; H, 2.85; N, 11.09. $C_4H_6MoN_2O_4$ calcd.: C, 19.83; H, 2.48; N, 11.45%.)

Preparation of cis-triamminemolybdenum tricarbonyl

A solution of cycloheptatrienemolybdenum tricarbonyl (0.2789 g, 1.025 mmoles) in cyclohexane reacted immediately, at room temperature, with dry ammonia (0.0697 g, 4.10 mmoles) to give a white solid. The volatiles were shown by IR spectroscopy to be cycloheptatriene, cyclohexane and ammonia (0.0211 g, 1.24 mmoles). The white solid (0.168 g, 0.74 mmoles) was washed with pentane but could not be recrystallised because of its poor solubility. The method of preparation and its infrared spectrum suggested that it was *cis*-triamminemolybdenum tricarbonyl. (Found: C, 15.53; H, 3.90; N, 16.99. $C_3H_9MoN_3O_3$ calcd.: C, 15.59; H, 3.93; N, 18.19%.)

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