Table I. Proton Magnetic Resonance Cation Coördination Number Data for Water–HMPT–Acetone Mixtures of $ZrO(ClO_4)_2$ and $ZrO(NO_3)_2$

	Mole ratios			ZrO^{2+} coord no.		
Salt	Salt:H_2O	Salt:HMPT	H_2O:acetone	H_2O	HMPT	Total
$ZrO(ClO_4)_2$	1:10		1:10	3.6		3.6
	1:13		1:10	3.7		3.7
	1:12[a]		1:10	3.8		3.8
	1:15[a]		1:10	4.0		4.0
	1:20		1:3	3.8		3.8
	1:20		1:5	3.6		3.6
	1:20		1:10	4.1		4.1
	1:10	1:1	1:10	2.6	(1.0)[b]	(3.6)
	1:10	1:2	1:10	1.7	(2.0)[b]	(3.7)
	1:10	1:6	1:10	1.6	2.0	3.6
	1:10	1:8	1:10	1.5	2.8	4.3
		Salt:HNO_3				
$ZrO(ClO_4)_2$	1:10	1:0.2	1.5	3.5		3.5
	1:10	1:0.5	1:5	2.8		3.0
	1:10	1:1	1:5	2.4		2.4
	1:12	1:1.5	1:5	1.8		1.9
	1:13	1:2.5	1:5	1.3		1.5
	1:16	1:4	1:5	(Overlap)		
$ZrO(NO_3)_2$	1:10		1:5	1.9		1.9

[a] The solution was acidified to a 1:1 mole ratio of $HClO_4$ to salt. [b] Only one set of HMPT signals was observed (see text).

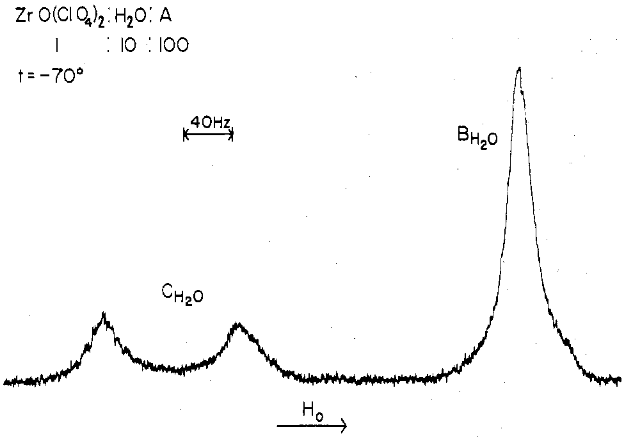

Figure 1. The water nmr spectrum of an aqueous-acetone solution of $ZrO(ClO_4)_2$, recorded on a Varian HA-100 spectrometer. The signals arising from bulk (B_{H_2O}) and coordinated (C_{H_2O}) water molecules are labeled. The mole ratios of all species also are shown.

terms of a simple monomeric ZrO^{2+} species.

In view of the propensity of zirconyl salts to form higher ionic aggregates,[3-11] polymeric species probably are present here. For example, the species generally proposed are a linear trimer, $Zr_3(OH)_4(H_2O)_{10}{}^{8+}$, and a cyclic tetramer, $Zr_4(OH)_8(H_2O)_{16}{}^{8+}$, each with bridging hydroxyl groups. The trimer is not consistent with the observation of two bound water signals of equal area but gives a hydration number of 4. The tetrameric structure[6,8] accounts for these facts if the assumption is made that only the bound water molecules are observed. Rapid proton exchange, for example, could account for the lack of a pmr signal for the hydroxyl groups.

The presence of such species also can account for the HMPT and NO_3^- solution results. The more basic HMPT was added to ascertain the structural nature of the complex which would result from the substitution of water molecules in the solvation shell of the central metal ion.[17] Although the size of the HMPT molecule prevented the replacement of more than two or three water molecules, the substitution occurred randomly as seen by the simultaneous decrease of both bound water peaks. However, the ^{31}P nmr spectra described previously show that this ligand also experiences two environments in the solvation shell. Complex formation by the nitrate ion occurs in a more interesting fashion. The selective displacement of one pair of bound water molecules by bidentate complexing proceeds quite readily. The replacement of the second set, however, is a more difficult process and it does not take place completely even at high mole ratios of NO_3^- to salt. The need to accommodate bidentate binding, the charge on the anion, and steric requirements would produce interaction at specific sites in the complex.

In general the cation hydration numbers and the nmr spectra exhibited by aqueous solutions of zirconyl perchlorate and nitrate can be interpreted most reasonably in terms of a metal ion polymer. Although a detailed structural analysis is not possible using only nmr data, they do establish the important criterion of an average of four tightly bound water molecules per metal ion. Any proposed structure based on other types of experimental data for comparable solutions must be consistent with this result.

Registry No. $ZrO(ClO_4)_2$, 15607-09-7; $ZrO(NO_3)_2$, 13826-66-9; H_2O, 7732-18-5; HMPT, 680-31-9; HNO_3, 7697-37-2; acetone, 67-64-1.

Acknowledgment. This research was supported in part by Grant No. 14-01-0001-2162 from the Office of Saline Water, Grant No. GP-9157, from the National Science Foundation, a National Institutes of Health Research Career Development Award, 1-K4-GM42334, for A. F., and a National Science Foundation instrument grant, GP-8347, for the purchase of the 100-MHz spectrometer. A Holy Cross College Faculty Fellowship to G. A. V. also is gratefully acknowledged.

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[17] C. Beguin, J. J. Delpuech, and A. Peguy, *Mol. Phys.*, 17, 317 (1969).

Contribution from the Research and Development Department,
Phillips Petroleum Company, Bartlesville, Oklahoma 74004

Reaction of Nitric Oxide with Some Halides of Molybdenum

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We have recently reported the use of the molybdenum-nitrosyl complexes $MoX_2(NO)_2L_2$ (X = Cl, Br, I; L = C_5H_5N, Ph_3P, Ph_3PO, Ph_3As) as homogeneous olefin disproportionation catalyst precursors.[1,2] In the course of these studies, it was observed that catalytic activity for a number of molybdenum compounds could be initiated or considerably enhanced by exposure to nitric oxide prior to the addition of the organoaluminum cocatalyst.[1,2] For example, a mixture of $MoOCl_3$ and $(CH_3)_3Al_2Cl_3$ in chlorobenzene failed to disproportionate 1-pentene (only slight double-bond isomerization was observed). Treatment of the $MoOCl_3$ with 25 psig of nitric oxide before the addition of $(CH_3)_3Al_2Cl_3$ resulted in a 63% conversion to disproportionation products.

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[1] E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Amer. Chem. Soc.*, 92, 528 (1970).

[2] W. B. Hughes, E. A. Zuech, E. T. Kittleman, and D. H. Kubicek, "Macromolecular Preprints, XXIIIrd IUPAC Congress," Vol. II, Boston, Mass., July 1971, p 1063.

In an effort to understand this activating effect, we have studied the reaction of nitric oxide with the molybdenum halide derivatives $MoCl_5$, $MoOCl_3$, $MoOCl_3(Ph_3PO)_2$, and $MoCl_4(Ph_3P)_2$.

Experimental Section

All reactions involving nitric oxide were conducted under an atmosphere of prepurified nitrogen in dried glass beverage bottles sealed with a perforated metal cap with neoprene rubber liner.

Infrared spectra were obtained between NaCl plates using a Perkin-Elmer Model 257 or Model 621 spectrometer.

Materials. The $MoCl_5$ (Alfa Inorganics), $MoOCl_3$ (Climax Molybdenum), and NO (Matheson) were used as received. The Ph_3P, Ph_3PO, and C_5H_5N were commercial reagent materials. The C_6H_5Cl was distilled from CaH_2. The $MoOCl_3(Ph_3PO)_2$ was prepared by the reaction of $MoOCl_3$ and Ph_3PO in ethanol[3] and the $MoCl_4(Ph_3P)_2$ from $MoCl_4(PrCN)_2$ and Ph_3P in $CHCl_3$.[4]

The new complex, $MoCl_2(NO)_2(Ph_3PO)_2$, was prepared in 90% yield by treating $[MoCl_2(NO)_2]_n$[5] with Ph_3PO in CH_2Cl_2. The green crystals had mp 250.5–252° and ν_{NO} 1775, 1655 cm^{-1} and ν_{P-O} 1150 cm^{-1} (Nujol). *Anal.* Calcd for $MoCl_2(NO)_2(Ph_3PO)_2$: C, 55.2; H, 3.9; N, 3.6. Found: C, 54.6; H, 3.9; N, 3.9.

Reaction of $MoCl_5$ with NO. A mixture of 0.54 g of $MoCl_5$ and 40 ml of C_6H_5Cl was stirred at room temperature under 30 psig of NO for 5 hr. Filtration gave 0.41 g of green solid and a yellow filtrate. The ir spectrum (Nujol) of the green solid showed two very strong bands at 1815 and 1708 cm^{-1}. A weak band was present at 746 cm^{-1} and very weak bands were at 3500, 1113, 1087, 1027, 727, 708, and 690 cm^{-1}. *Anal.* Calcd for $MoCl_2(NO)_2$: Cl, 31.3; N, 12.4. Found: Cl, 32.3; N, 11.4.

Treatment of 0.12 g of the above green solid with 0.38 g of Ph_3P in $CHCl_3$ gave 0.37 g of green solid. Recrystallization from $CHCl_3$–MeOH gave 0.12 g of $MoCl_2(NO)_2(Ph_3P)_2$ as green crystals, mp 250–255° dec. *Anal.* Calcd for $MoCl_2(NO)_2(Ph_3P)_2$: C, 57.5; H, 4.0; N, 3.7. Found: C, 57.0; H, 4.1; N, 3.8. The ir spectrum in Nujol showed ν_{NO} at 1660, 1670 and 1775, 1790 cm^{-1} and ν_{Mo-Cl} at 288 and 306 cm^{-1}. The ir spectrum in $CHCl_3$ showed ν_{NO} at 1672 and 1789 cm^{-1} and ν_{Mo-Cl} at 286 and 302 cm^{-1}.

In a similar manner, there was obtained from 0.2 g of the green solid and 0.52 g of C_5H_5N in $CHCl_3$, 0.22 g of $MoCl_2(NO)_2(C_5H_5N)_2$ as green microcrystals. *Anal.* Calcd for $MoCl_2(NO)_2(C_5H_5N)_2$: C, 31.2; H, 2.6; N, 14.6. Found: C, 30.5; H, 2.6; N, 14.2. The ir spectrum (Nujol) showed ν_{NO} at 1779, 1670, and 1645 (sh) cm^{-1}.

Reaction of $MoOCl_3$ with NO. $MoOCl_3$, 0.88 g, in 80 ml of C_6H_5Cl was stirred at room temperature for 24 hr under 30 psig of NO. Filtration gave 0.66 g of green solid and a yellow-orange filtrate. The ir spectrum (Nujol) of the green solid had two strong bands at 1814 and 1708 cm^{-1} and two very weak bands at 730 and 745 cm^{-1}.

Reaction of the green solid with Ph_3P or C_5H_5N gave materials whose ir spectra were essentially the same as those of the corresponding complexes obtained from the product of $MoCl_5$ and NO.

Reaction of $MoCl_5$ with NO and Ph_3P. $MoCl_5$, 0.54 g, in 35 ml of C_6H_5Cl was stirred at room temperature under 30 psig of NO. After 2.5 hr a solution of 1.04 g of Ph_3P in 5 ml of C_6H_5Cl was added and stirring was continued for 2.5 hr. Removal of the solvent yielded 1.52 g of light green solid. The ir spectrum (Nujol) of this material exhibited bands attributable to $MoCl_2(NO)_2(Ph_3PO)_2$ with additional bands at 1698, 1180, 1160, 1140, 1090, and 977 cm^{-1}. The ir spectrum of a sample recrystallized from $CHCl_3$–CH_3OH showed almost complete disappearance of the 1698-, 1140-, and 1090-cm^{-1} bands and weakening of the 977-cm^{-1} band. Two new bands were present at 910 and 950 cm^{-1}.

A second reaction was carried out as above except that the Ph_3P was present from the beginning of the reaction. This yielded 1.55 g of light green solid whose ir spectrum contained the same absorptions as the product from the $MoCl_5$–NO–Ph_3P reaction but with differences in the relative intensities of several bands. A recrystallized sample showed weakening of the 1698-cm^{-1} band and an increase in intensity of the 977- and 1160-cm^{-1} bands; new bands appeared at 910 and 950 cm^{-1}.

Results and Discussion

The room-temperature reaction of either $MoCl_5$ or $MoOCl_3$ with NO in C_6H_5Cl, $CHCl_3$, or CCl_4 yields the same dark green solid. The material is insoluble in these solvents and precipitates during the reaction. Recrystallization was not possible since the material was sufficiently soluble only in solvents, *i.e.*, CH_3CN, $(C_2H_5)_2O$, and $(CH_3)_2CO$, with which it formed strong complexes. The ir spectrum of the green solid contains two very strong bands at 1815 and 1708 cm^{-1} with the lower frequency band being appreciably broader. The green solid reacts with Ph_3P or C_5H_5N to give the known[5] complexes $MoCl_2(NO)_2L_2$ (L = Ph_3P, C_5H_5N). On the basis of its low solubility, ir spectrum, and reactions with Ph_3P and C_5H_5N it was formulated to be $[MoCl_2(NO)_2]_n$. This polymeric dinitrosyl complex of molybdenum has been previously prepared by the reaction of $Mo(CO)_6$ with NOCl.[5]

Examination of the reaction mixture from the interaction of $MoCl_5$ and NO in C_6H_5Cl by ir and glpc established the presence of NOCl. This suggests that a possible pathway for the formation of $MoCl_2(NO)_2$ would be

$$MoCl_5 + 5NO \rightarrow MoCl_2(NO)_2 + 3NOCl$$

No evidence for the presence of dichlorobenzenes was found by glpc analysis.

The formation of $[MoCl_2(NO)_2]_n$ in the reaction of $MoCl_5$ or $MoOCl_3$ with NO explains the activating effect toward olefin disproportionation which NO has upon these compounds since we have previously shown[1] dichlorodinitrosylmolybdenum to be a catalyst precursor.

As mentioned above, the $[MoCl_2(NO)_2]_n$ obtained from the reaction of NO with either $MoCl_5$ or $MoOCl_3$ reacts with Ph_3P or C_5H_5N to yield the octahedral, monomeric complexes $MoCl_2(NO)_2L_2$. Thus, $MoCl_5$ or $MoOCl_3$ can serve as starting material for this class of olefin disproportionation catalysts.

The sequential reaction of $MoCl_5$ with NO and Ph_3P without isolation of the intermediate $[MoCl_2(NO)_2]_n$ was also investigated. In this case, a complex mixture of products was obtained. Infrared analysis of the mixture revealed the presence of three bands in the N–O stretching region at 1775, 1698, and 1655 cm^{-1} and four bands in the P–O stretching region at 1180, 1160, 1150, and 1140 cm^{-1}. A medium-intensity band appeared at 978 cm^{-1}. Comparison of the ir of the mixture with the spectra of known compounds suggested a major component to be $MoCl_2(NO)_2(Ph_3PO)_2$. Indeed, this complex was isolated in low yield by repeated recrystallization of the mixture. The bands at 1160, 1140, and 978 cm^{-1} are all present in the ir spectrum of $MoOCl_3(Ph_3PO)_2$ which suggests that this complex is present in the mixture. Recrystallization of the mixture in the atmosphere resulted in the virtual disappearance of the 1698-cm^{-1} band and the appearance of two new bands at 910 and 950 cm^{-1}. The latter two absorptions are typical of a MoO_2^{2+} species.[6]

The sequential reaction of $MoCl_5$ with Ph_3P followed by NO was also investigated. Infrared analysis indicated a mixture containing the same components as were formed in the $MoCl_5$–NO–Ph_3P reaction. In this case, however, the 1698-cm^{-1} band was stronger than the ν_{N-O} bands due to $MoCl_2(NO)_2(Ph_3PO)_2$ while the 1160- and 978-cm^{-1} bands were reduced in intensity. Diminution of the 1698-cm^{-1} band and appearance of absorptions at 910 and 950 cm^{-1} also accompanied recrystallization of this mixture.

The reaction of the molybdenum(IV) derivative, $MoCl_4(Ph_3P)_2$, with NO gave a mixture of products very

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(3) S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, 1, 122 (1962).

(4) E. A. Allen, K. Feenan, and G. W. A. Fowles, *J. Chem. Soc.*, 1636 (1965).

(5) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, 3, 1609 (1964).

(6) M. L. Larson and F. W. Moore, *Inorg. Chem.*, 5, 801 (1966).

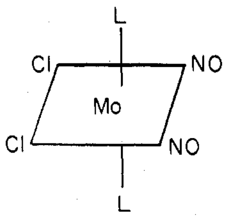
similar to that obtained by the sequential *in situ* reaction of $MoCl_5$ with NO and Ph_3P.

Oxidation of the triphenylphosphine in the above reactions could be effected either by the NO or the NOCl generated in the $MoCl_5$-NO reaction.[7,8]

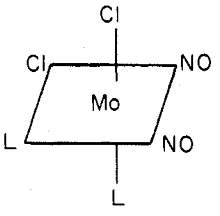
The apparent presence of $MoOCl_3(Ph_3PO)_2$ in the reaction products was surprising since we had found that $MoOCl_3$ is readily reduced by NO. To illuminate this point, we examined the reaction of $MoOCl_3(Ph_3PO)_2$ with NO in C_6H_5Cl. After a reaction period of 5 hr at room temperature, 67% of the complex was recovered. Under the same conditions, $MoOCl_3$ is essentially completely consumed. Apparently, some slow reaction does occur since not all the $MoOCl_3(Ph_3PO)_2$ was recovered. Indeed, a yellow solid was isolated in a small amount from the reaction. This material was not identified; however, the ir spectrum clearly indicated the absence of nitrosyl groups. This result indicates that the Ph_3PO ligands stabilize the $MoOCl_3$ toward reduction by NO and that the limited extent of reaction that does occur follows a different course. This would also explain why a higher proportion of $MoCl_2(NO)_2(Ph_3PO)_2$ (derived from $MoCl_2(NO)_2$) was present in the mixture obtained when the Ph_3P was added after the NO.

At present, we do not know the identity of the species exhibiting the N-O stretching vibration at 1698 cm^{-1}; it is possibly due to a molybdenum-mononitrosyl derivative. The complex $[MoCl_3(NO)]_n$, prepared by the reaction of $[MoCl_2(CO)_4]_2$ with NOCl, has been reported[9] but no details concerning its properties were given.

The Ph_3P complexes obtained from either $MoCl_5$- or $MoOCl_3$-derived $[MoCl_2(NO)_2]_n$ show two strong N-O stretching vibrations at 1789 and 1672 cm^{-1} in $CHCl_3$ solution. This suggests that the NO groups are mutually cis. Cotton and Johnson reported values for ν_{NO} of 1790 and 1670 cm^{-1} (in CH_2Cl_2) for the Ph_3P complex derived from $[MoCl_2(NO)_2]_n$ prepared by the reaction of $Mo(CO)_6$ with NOCl.[5] Our Ph_3P complexes exhibit splitting of the ν_{NO} bands in Nujol with absorptions appearing at 1790, 1775, and 1670, 1660 cm^{-1}. In the far-ir spectra of the Ph_3P complexes we find only two absorptions in the 200-400-cm^{-1} region at 288 and 306 cm^{-1}. These we attribute to the Mo-Cl stretching vibrations of cis chloro ligands. Two isomers, **1** and **2**, are possible which possess cis NO and cis Cl groups.



1



2

To assist in differentiating between **1** and **2** we prepared the diphenylmethylphosphine complex $MoCl_2(NO)_2(Ph_2PCH_3)_2$. This complex shows two strong ν_{NO} bands at 1788 and 1677 cm^{-1} (in $CHCl_3$) and two ν_{Mo-Cl} vibrations at 281 and 303 cm^{-1}. The similarity of the ν_{NO} and ν_{Mo-Cl} frequencies between the Ph_3P and Ph_2PCH_3 complexes suggests that the NO and Cl ligands are in similar environments in the two complexes. The 60-MHz ^1H nmr spectrum of the Ph_2PCH_3 complex contains a well-defined 1:2:1 triplet in the methyl proton region (δ 2.26, 4-Hz spacings). As shown by Jenkins and Shaw, this pattern is characteristic of mutually trans methylphosphine ligands.[10] The combined ir and nmr data strongly suggest a cis Cl, cis NO, trans phosphine geometry (**1**) for the Ph_2PCH_3 and, because of the similarity in its ir spectrum, the Ph_3P complex.[11]

Registry No. $MoCl_2(NO)_2(Ph_3PO)_2$, 14095-87-5; $MoCl_5$, 10241-05-1; NO, 10102-43-9; $MoCl_2(NO)_2$, 30731-17-0; $MoCl_2(NO)_2(Ph_3P)_2$, 37402-68-9; $MoCl_2(NO)_2(C_5H_5N)_2$, 14024-95-4; $MoOCl_3$, 13814-74-9; Ph_3P, 603-35-0.

(7) M. Halmann and L. Kugel, *J. Chem. Soc.*, 3272 (1962).

(8) D. Klamann and P. Weyerstahl, *Angew. Chem.*, **75**, 574 (1963).

(9) B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McCleverty, *J. Chem. Soc. A*, 1668 (1969).

(10) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 279 (1963).

(11) Note Added in Proof. A single-crystal X-ray diffraction study has established the cis-dichloro, cis-dinitrosyl, trans-bisphosphine configuration for $MoCl_2(NO)_2(Ph_3P)_2$ [M. O. Visscher and K. G. Caulton, *J. Amer. Chem. Soc.*, **94**, 5923 (1972)].

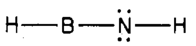
Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada

Ab Initio Calculations for the Boron-Nitrogen Analog of Cyclobutadiene[1]

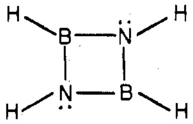
N. Colin Baird

Received May 26, 1972

In a previous publication, *ab initio* calculations were reported for iminoborane (**1**), the boron-nitrogen analog of acetylene.[2] Dimerization of **1** can yield several interesting molecules, one of which—1,3,2,4-diazadiboretidine (**2**)—would correspond to the boron-nitrogen analog of the antiaromatic hydrocarbon cyclobutadiene **3**.[3] To determine the similarities and differences in properties between the "inorganic" and "organic" cyclobutadiene systems, *ab initio* STO-*N*G calculations have been performed for **2**.[4,5]



1



2

3

In contrast to cyclobutadiene itself, the D_{2h} planar form of **2** in which all four ring bond lengths are equal is *not* subject to Jahn-Teller distortion in the lowest singlet state and may well correspond to the optimum geometry. In fact, the D_{2h} structure may well be more stable than the "alternating" C_{2h} geometry for all type **4** ring systems in which the elec-

(1) Research supported by the National Research Council of Canada.

(2) N. C. Baird and R. K. Datta, *Inorg. Chem.*, **11**, 17 (1972).

(3) Other possible dimers would be the B-N analog of tetrahedrane and a planar four-membered ring with one B-B, one N-N, and two B-N bonds. The latter could also be considered an analog of **3**.

(4) (a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). (b) *Ab initio* calculations for a variety of B-N systems, including **2** have recently been reported: D. R. Armstrong and D. T. Clark, *Theor. Chim. Acta*, **24**, 307 (1972).

(5) The B-H and N-H bond lengths, as well as the STO exponents for the σ and π atomic orbitals, used in the calculations were taken from ref 1. Only planar structures in which all NBH angles are equal (and similarly for the BNH angles) were considered.