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Preparation and Properties of Nitrosyl Complexes of Molybdenum[1)]

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Reactions of some dpe(dpe$=Ph_2PCH_2CH_2PPh_2$) complexes of molybdenum with nitrosyl hexafluorophosphate ($NOPF_6$) have been investigated. The reaction of $MoH_4(dpe)_2$ with $NOPF_6$ in benzene–methanol affords two types of complexes, a protonated species, *trans*-[MoF(HNO)(dpe)$_2$]PF_6 (**1a**) and a non-protonated species, *trans*-MoF(NO)(dpe)$_2\cdot 1/2C_6H_6$. From the nitroxyl complex **1a**, a series of nitrosyl complexes has been obtained. Some nitrosyl complexes exhibit *cis-trans* isomerism. Reactions of the nitrosyl complexes with protonic acids afford the corresponding nitroxyl complexes or the anion substitution products. Cationic nitrosyl complexes are obtained by the reactions of Mo(CO)L(dpe)$_2$ (L$=N_2$ or C_2H_4) and Mo(C_2H_4)$_2$(dpe)$_2$ with $NOPF_6$. Attempts were also made to prepare nitrosyl complexes of molybdenum by use of other nitrosylating agents.

Recently dinitrogen,[2)] isonitriles,[3)] thiocarbonyl,[4)] and ethylene,[5)] which are attached to the electron-rich site of M(dpe)$_2$ (M=Mo or W, dpe$=Ph_2PCH_2CH_2PPh_2$), have been shown to be susceptible to electrophilic attack. Such attack at coordinated dinitrogen has been extensively investigated, leading to the formation of nitrogen–hydrogen and nitrogen–carbon bonds.[2)] This finding prompted us to prepare metal complexes containing nitrogen monoxide activated by coordination to this site. We describe below the nitrosylation of some dpe complexes of molybdenum by use of versatile nitrosylating agents[6,7)] and the protonation of the nitrosyl complexes thus obtained. Chatt *et al.* briefly commented on the formation of MoX(NO)(dpe)$_2$ (X= F and Br) from MoX(N_2H)(dpe)$_2$ and nitrogen monoxide.[8)] Very recently King and Leigh reported the preparation of a series of nitrosyl complexes of molybdenum and tungsten with only halide and tertiary phosphine as coligands.[9)] The reactions of nitrosyl compleses with electrophiles such as HCl, HBr, $PhCH_2Br$, O_2, and NO have recently been reviewed.[10)]

Results and Discussion

Reaction of Phosphine Complexes of Molybdenum with $NOPF_6$. The reaction of a hydride complex, $MoH_4(dpe)_2$, with $NOPF_6$ ($NOPF_6$/Mo=1.05) in benzene–methanol solution gives *trans*-[MoF(HNO)(dpe)$_2$]PF_6 (**1a**) and *trans*-MoF(NO)(dpe)$_2\cdot 1/2C_6H_6$ (**2a**). Complex (**1a**) is a purple crystalline diamagnetic solid. The ^{31}P NMR spectrum of **1a** exhibits a doublet (J_{P-F}=39 Hz) at −45 ppm (relative to PPh_3) assigned to the four equivalent phosphorus nuclei, suggesting a *trans* configuration. Complex **2a** is a yellow crystalline diamagnetic solid which also has a *trans* configuration since its ^{31}P NMR spectrum shows a doublet (J_{P-F}= 27 Hz) at −58 ppm. This complex appears to be identical with that prepared by an alternative route.[8)] Without methanol as a cosolvent, the starting material was recovered almost quantitatively. Complex (**1a**) is apparently a protonation product of **2a** by HPF_6. Treatment of **2a** with a benzene–methanol solution of $NOPF_6$ gives **1a** in good yield. HPF_6 must have been formed *in situ* by Eq. 1.[7)] Expectedly, reaction of **2a** with aqueous HPF_6 in benzene affords **1a**.

$$NOPF_6 + MeOH \rightleftharpoons HPF_6 + MeONO \qquad (1)$$

In the reactions of nitrosonium salts with transition metal complexes, three types of reaction products have been found;[7)] *i.e.*, formation of cationic nitrosyl species, one-electron oxidation, and protonation affording metal hydrides (in methanol). The basic character of the NO ligand of **2a** (see below) results in its rapid protonation but prevents the selective preparation of its complex by addition of 1 mol eq. of $NOPF_6$ to the hydride. One might expect that as the $NOPF_6$/Mo ratio is increased, **1a** would be exclusively obtained. In fact, however, the yield of **1a** decreased, whereupon benzene-soluble unknown complexes were obtained.

Treatment of the dinitrogen complex, *trans*-Mo(N_2)$_2$(dpe)$_2$, with $NOPF_6$ afforded no nitrosyl complex; dark red crystals of [MoF(N_2H_2)(dpe)$_2$]PF_6 (**3a**) were obtained which show the antisymmetric and symmetric N–H stretching frequencies at 3350 and 3260 cm^{-1}, respectively. Presumably the ligating dinitrogen was protonated by the *in situ*-formed HPF_6. This complex seems to be analogous to the hydrazido(2−) complex [MoF(NNH_2)(dpe)$_2$]BF_4.[11)] Complex **3a** is isoelectronic to **1a**. Chatt *et al.* isolated MoF(N_2H)(dpe)$_2$, which is isoelectronic to **2a** and can be protonated in a similar way with **2a** to afford N_2H_2 complexes.

In contrast, *trans*-Mo(CO)(N_2)(dpe)$_2\cdot 1/2C_6H_6$ reacted with $NOPF_6$ to yield the known [Mo(CO)(NO)(dpe)$_2$]PF_6 (**3b**).[12)] In this reaction, we have also detected *cis*-[Mo(CO)$_2$(dpe)$_2$]PF_6 and *cis*-Mo(CO)$_2$(dpe)$_2$ by IR. Mo(CO)(C_2H_4)(dpe)$_2$ showed a similar behavior toward $NOPF_6$. It should be noted that **3b** cannot obtained from *cis*-Mo(CO)$_2$(dpe)$_2$ and $NOPF_6$.[13)] In the reactions of *trans*-Mo(CO)(N_2)(dpe)$_2\cdot$ $1/2C_6H_6$ and Mo(CO)(C_2H_4)(dpe)$_2$, *cis*-[Mo(CO)$_2$(dpe)$_2$]PF_6 would be formed by way of *cis*-Mo(CO)$_2$(dpe)$_2$ since these monocarbonyl complexes slowly changed to the *cis*-dicarbonyl in the absence of $NOPF_6$. In the reaction of Mo(C_2H_4)$_2$(dpe)$_2$ with $NOPF_6$, [Mo(C_2H_4)(NO)(dpe)$_2$]PF_6 (**3c**) was obtained in very poor yield.

Reaction of trans-*Mo(N_2)$_2$(dpe)$_2$ and MoH_4(dpe)$_2$ with NO Gas and Some NO Sources* Treatment of *trans*-Mo(N_2)$_2$(dpe)$_2$ in benzene with NO at atmospheric pressure afforded an orange yellow solution, from which yellow crystals were obtained. Elemental analysis suggests the empirical formula [Mo(NO)(dpe)]$_2\cdot 2C_6H_6$ (**4**) for the complex. The complex [Mo(NO)(dpe)$_2$]$_2\cdot$ CH_2Cl_2 has been prepared previously from [Mo(CO)$_3$(NO)(dpe)]PF_6 and dpe.[13)] Since **4** reacts successively

TABLE 1. NITROSYL COMPLEXES OF MOLYBDENUM

	Complex	Found (Calcd), %				IR, cm^{-1} a) ν(NO)	Color
		C	H	N	Halogen		
2a	*trans*-MoF(NO)(dpe)$_2$·1/2C$_6$H$_6$	68.0 (67.4)	5.4 (5.2)	1.2 (1.4)	1.5 (1.9)	1528	yellow
2b	*cis*-MoCl(NO)(dpe)$_2$	64.6 (65.2)	5.0 (5.0)	1.5 (1.5)	3.5 (3.7)	1567	yellow
2c	*cis*-MoBr(NO)(dpe)$_2$	61.7 (62.3)	5.0 (4.8)	1.1 (1.4)	8.3 (8.0)	1567	yellow
2d	MoI(NO)(dpe)$_2$	59.2 (59.5)	4.6 (4.6)	1.2 (1.3)		1570	yellow brown
2e	Mo(NCS)(NO)(dpe)$_2$	64.6 (64.9)	4.9 (4.9)	2.5 (2.9)		1570	yellow
2f	*trans*-MoCl(NO)(dpe)$_2$·1/2C$_6$H$_6$	67.1 (67.5)	5.1 (5.2)	1.4 (1.4)	3.5 (3.6)	1542	yellow
2g	Mo(OCOCF$_3$)(NO)(dpe)$_2$	63.3 (63.6)	4.8 (4.7)	1.2 (1.4)		1570	yellow
3b	[Mo(CO)(NO)(dpe)$_2$]PF$_6$	58.5 (58.1)	4.4 (4.4)	1.1 (1.3)		1648	pink
3c	[Mo(C$_2$H$_4$)(NO)(dpe)$_2$]PF$_6$	58.6 (59.2)	4.7 (4.7)	1.1 (1.3)		1606	brown
4	[Mo(NO)(dpe)$_2$]$_2$·2C$_6$H$_6$	70.1 (69.6)	5.6 (5.4)	1.2 (1.4)		1516	yellow

a) Recorded in KBr.

with NO to afford a brown powder, contaminated with the phosphine oxide(IR), the yield of **4** is low, but it can be isolated under appropriate conditions. The reaction of MoH$_4$(dpe)$_2$ with NO under similar conditions gave no nitrosyl complexes; MoH$_4$(dpe)$_2$ being recovered unchanged. With *N*-methyl-*N*-nitroso-*p*-toluenesulfoamide, the reagent known to be capable of nitrosylating metal hydrides,[7] MoH$_4$(dpe)$_2$ was recovered quantitatively.

The reaction of *trans*-Mo(N$_2$)$_2$(dpe)$_2$ with NOCl (NOCl/Mo=10) was carried out in toluene giving a greenish yellow solid, the IR spectrum of which suggested that it was a mixture of two known complexes, MoCl$_3$(NO){Ph$_2$P(=O)CH$_2$CH$_2$PPh$_2$(=O)},[14] MoCl$_2$(NO)$_2${Ph$_2$P(=O)CH$_2$CH$_2$PPh$_2$(=O)},[15] and free phosphine oxide. In the case of NOCl/Mo=1, a yellow solid was obtained, whose IR spectrum shows the presence of **2f′** (see below), MoCl$_2$(NO)$_2${Ph$_2$P(=O)-CH$_2$CH$_2$PPh$_2$(=O)}, and the starting dinitrogen complex. In either case the components of these mixtures were inseparable by crystallization and thus as a nitrosylating agent NOCl is not suitable for the clean synthesis of nitrosyl complexes.

*Product Derived from the Nitroxyl Complex (**1a**).* The reaction of **1a** with appropriate alkali metal salts (MX) in acetone afforded MoX(NO)(dpe)$_2$ [X=Cl(**2b**), Br(**2c**), I(**2d**), and NCS(**2e**)] (Table 1). With NaN$_3$ and NaNCO, **1a** gives **2a**. From the position of the C–S frequencies at 840 cm^{-1}, it was concluded that in the complex (**2e**) the nitrogen of the thiocyanate group is coordinated to molybdenum. With NaBH$_4$, **1a** gives **4** in good yield.

In CH$_2$Cl$_2$ the ^{31}P NMR spectrum of **2b** shows a broad multiplet centered at −60 ppm, suggesting a *cis* configuration. Refluxed in benzene, **2b** is converted into yellow crystals analyzing as *trans*-MoCl(NO)(dpe)$_2$·1/2C$_6$H$_6$ (**2f**). The ^{31}P NMR spectrum of **2f** shows a sharp singlet at −58 ppm, suggesting a *trans* configuration. Preliminary X-ray data of **2f** also shows the presence of benzene as a crystal solvent, and essentially linear M–N–O system.[16] Dissolved in CH$_2$Cl$_2$, **2f** is slowly converted into **2b** (Eq. 2).

$$\underset{\textbf{(2b)}}{cis\text{-MoCl(NO)(dpe)}_2} \underset{CH_2Cl_2}{\overset{C_6H_6\ \text{reflux}}{\rightleftarrows}} \underset{\textbf{(2f)}}{trans\text{-MoCl(NO)(dpe)}_2\cdot 1/2C_6H_6} \qquad (2)$$

In the *trans* compound ν(NO) is shifted to lower frequency by 20 cm^{-1}. These data are compatible with Feltham and Nyholm's interpretation.[17] They prepared a series of six-coordinate nitrosyl complexes [CoX(NO)(diars)$_2$]X (X=Cl, Br, I, and NCS; diars=*p*-Me$_2$AsC$_6$H$_4$AsMe$_2$) in which there were two NO frequencies present. On the basis of examination of bands in the 900 cm^{-1} region in their IR spectra, they suggested that these complexes were a mixture of *cis* and *trans* isomers. The isomer with lower NO frequency was assigned to the *trans* configuration, while the isomer with the higher frequency was assigned to the *cis* one. Since both the molybdenum nitrosyls and the cobalt nitrosyls are six-coordinate complexes having the ligands such as NO, halogen, and four group VB donors, it is natural that the ν(NO) frequencies are assumed to shift similarly on change of configuration. On refluxing in benzene the bromo analog (**2c**) was not converted into its *trans*-isomer. But we could find the presence of *trans*-MoBr(NO)(dpe)$_2$ (ν(NO)=1547 cm^{-1}) in a separate experiment (see below). The iodo (**2d**) and NCS (**2e**) analogs exhibit no such isomerism. Unfortunately the low solubility of the complexes in usual organic solvents precluded the direct determination of their molecular structure by NMR spectroscopy.

In the $[CoX(NO)(diars)_2]X$ complexes, Feltham and Nyholm observed an effect of the halogen ligand (X) on the preference of one configuration over the other. Their data are indicative of increasing stability of the *trans* configuration up the halogen group. The tendency observed holds in our $MoX(NO)(dpe)_2$ (X=F, Cl, and Br) series as well. Graham estimated the order of σ-inductive strength F>Cl>Br>I and π-donor strength F>Cl>Br>I.[18] Since the NO ligand has a strong π-acidity, we expect that the ligand which has a considerable π-donor ability may be preferred for the *trans* ligand to NO. We may conclud that is the reason why we can obtain only the *trans* isomer of the fluoro complex. The ν(NO) of the *trans* complexes are lowered with increasing π-donor strength of halogens.

Table 2. XPS data for some molybdenum nitrosyl complexes

Complex	N 1s(eV)	Mo 3p3/2(eV)
cis-$MoCl(NO)(dpe)_2$ (**2b**)	400.4	394.5
trans-$MoCl(NO)(dpe)_2 \cdot 1/2C_6H_6$(**2f**)	400.0	394.4
$Mo(NO)_2Cl_2(PPh_3)_2$	401.6	396.5
$Mo(CO)_5(PPh_3)$		393.5
$MoCl_2(CO)_3(PPh_3)_2$		395.7

The XPS data of **2b**, **2f**, and related complexes are given in Table 2. Hughes and Baldwin have observed a linear relationship between 3d and 3p binding energies of molybdenum and a charge parameter q calculated as the sum of the partial ionic characters over the metal-ligand bonds.[19] The observed 3p3/2 binding energy for the complexes (**2b**) and (**2f**) corresponds to a q_{Mo} value nearly intermediate between $Mo(CO)_5(PPh_3)$ and $MoCl_2(CO)_3(PPh_3)_2$, indicating a substantial electroneutrality for the NO ligand. In terms of a formal oxidation state, the molybdenum would be closest to Mo(I). The nitrogen 1s binding energies for **2b** and **2f** are fairly low as expected from the low ν(NO) in their IR spectra. As stated above, however, the M–N–O system is found to be essentially linear. The low N 1s energy of these complexes is responsible for their reactivity to protonic acids, which will be described in the following section.

Reaction of Nitrosyl Complexes with Protonic Acids. As stated above, **1a** is prepared from the reaction of **2a** with aqueous HPF_6 in benzene. Similarly with HBF_4, **2a** gives $[MoF(HNO)(dpe)_2]BF_4$ (**1b**). $[MoF(HNO)(dpe)_2]I_3$ (**1c**) was obtained by the reaction of **1a** with I_2. It has been tried to prepare some cationic HNO (nitroxyl) complexes by using common protonic acids (Table 3). King and Leigh reported that in CH_2Cl_2, $MoCl(NO)(dpe)_2$ did not react with hydrogen chloride.[9] Treatment of **2b** with an excess of dry hydrogen chloride in benzene, however, gives the complex formulated as $MoCl_2(HNO)(dpe)_2$ (**1d**) as a violet precipitate. From **2f**, **1d** was also obtained similarly. We can not determine whether **1d** is a seven-coordinate 18-electron species or a cationic complex. So far suitable crystals for X-ray crystal structure determination have not been obtained. The one chlorine atom is labile and easily replaced by a non-coordinating anion, *i.e.*, PF_6 or BPh_4 to afford stable crystalline products, $[MoCl(HNO)(dpe)_2]X$ [X=PF_6(**1e**) and BPh_4(**1f**)]. In contrast with **1e** and **1f**, the protonic H of the HNO ligand of **1d** is very labile; dissolved in acetone, **1d** releases hydrogen chloride spontaneously to afford *trans*-$MoCl(NO)(dpe)_2$ (**2f′**).

With dry hydrogen bromide, **2c** gives $MoBr_2(HNO)(dpe)_2$ (**1g**) as a violet precipitate. Complex **1g** decomposed easily in acetone to afford a mixture of yellow and orange yellow crystals. The IR spectrum of the former indicated that it was the starting material (**2c**). That of the latter show ν(NO) at 1547 cm^{-1} and its elemental analysis suggests that it has the same composition as **2c**. We may conclude that it is the *trans* isomer of $MoBr(NO)(dpe)_2$ and that the isomer with higher NO

Table 3. HNO complexes of molybdenum

	Complex	Found(Calcd),%				IR, cm^{-1} a) ν(NO)	Color
		C	H	N	Halogen		
1a	$[MoF(HNO)(dpe)_2]PF_6$	58.2 (57.4)	4.5 (4.5)	1.3 (1.3)	12.2 (12.2)	1624	dark red
1b	$[MoF(HNO)(dpe)_2]BF_4$	59.8 (60.6)	4.8 (4.8)	1.2 (1.4)		1631	violet
1c	$[MoF(HNO)(dpe)_2]I_3$	47.4 (47.2)	3.7 (3.7)	1.0 (1.1)	F, 1.4 (1.4)	1625	orange
1d	$MoCl_2(HNO)(dpe)_2$	61.8 (62.8)	4.9 (4.9)	1.2 (1.4)	7.5 (7.1)	1640	violet
1e	$[MoCl(HNO)(dpe)_2]PF_6$	57.0 (56.5)	4.3 (4.4)	1.0 (1.3)		1646	violet
1f	$[MoCl(HNO)(dpe)_2]BPh_4$	70.9 (71.4)	5.7 (5.4)	1.0 (1.1)		1645	light blue
1g	$MoBr_2(HNO)(dpe)_2$	56.5 (57.6)	4.5 (4.5)	1.1 (1.3)	15.8 (14.8)	1641	light blue
1h	$MoClBr(HNO)(dpe)_2$	59.5 (60.1)	4.7 (4.7)	1.1 (1.3)	Cl,2.8; Br,9.4 (3.4) (7.4)	1639	light blue
1i	$MoFBr(HNO)(dpe)_2$	59.6 (61.1)	4.7 (4.7)	1.0 (1.4)	Br,9.1 (7.8)	1610	blue

a) Recorded in KBr.

frequency (**2c**) is the *cis* one. The mixture was recrystallized from CH_2Cl_2 to give pure crstals of **2c**. The *trans* isomer could not be obtained free from the *cis* isomer.

Complex **2a** reacts similarly with dry hydrogen chloride or hydrogen bromide giving the complex consisting almost entirely of **1d** or **1g**, fluorine content being negligible. The reaction of **2f′** with dry hydrogen bromide affords a complex approximately formulated as $MoClBr(NO)(dpe)_2$ (**1h**). But chlorine seems to be partially replaced by bromine. In contrast, treatment of **2a** with an excess of aqueous hydrochloric or hydrobromic acid gives the neutral complex **2b** or **2c**. Complex **2a** was also treated with benzoyl chloride, with the aim of isolating compounds incorporating the organic moiety, but the formation of such derivatives was not observed, **2f** being the only product isolated. Protonation of N_2H, N_2R, or N_2COR ligands in the complexes formally isoelectronic to **2a** took place even with aqueous hydrochloric acid.[8,21,22] This means that the ligating NO is a weaker base than those ligands. Trifluoroacetic acid reacted with **2a** giving yellow crystals of $Mo(OCOCF_3)(NO)(dpe)_2$ (**2g**). IR bands for $\nu_{asym}(CO_2) = 1700\ cm^{-1}$ and $\nu_{sym}(CO_2) = 1410\ cm^{-1}$ are characteristic of those of the unidentate trifluoroacetate-complexes.[23]

Complex **4** also reacts with aqueous HPF_6 in toluene–methanol to yield **1a** and H_2. With aqueous hydrogen chloride, **4** gives the mixture of **2b** and **2f** with the evolution of H_2. In contrast with $MoX(NO)(dpe)_2$ (X=F, Cl, and Br) and **4**, the complexes such as **3b**, **3c**, and $MoCl_2(NO)_2(PPh_3)_2$ did not react with HPF_6. These results are consistent with the expectation that the protonation of the nitrosyl group leading to HNO derivatives is possible only in the case of nitrosyl complexes of particularly low $\nu(NO)$, *i.e.*, with a substantial negative charge localized on the NO ligand.[20] The nitrosyl complexes (**2a**—**g**) were unreactive to other electrophiles such as NO or O_2.

On treatment of **2a** with benzoyl bromide, a blue solid was obtained, which although slightly impure, proved to be $MoFBr(HNO)(dpe)_2$ (**1i**). The simple addition of hydrogen bromide, which was presumably provided by adventitious moisture, seems to have occurred.[22]

Characterization of Nitroxyl Complexes. Protonation of the NO ligand may occur at either the nitrogen or oxygen atom. The ^1H NMR spectrum of **1a** shows a doublet, integrating for one proton, centered at 10.1 ppm, which is assigned to the N–H proton. This assignment is consistent with the observation that the H atom attached to a nitrogen atom adjacent to a transition metal ion exhibits a ^1H NMR resonance at much lower field than δ 6 ppm.[24] This resonance disappared on addition of ^2H_2O. The HNO resonance of a previously reported cobalt complex is δ 7.9.[25] The anomalously large coupling constant ($J = 130$ Hz) is tentatively assigned to the long-range coupling with the Mo–F fluorine atom. Unfortunately, the ^{19}F NMR spectrum of **1a** showed only a P–F signal and no Mo–F was observed possibly because of its multiplicity. The doublet pattern of ^{31}P NMR spectrum of the DPE ligands is ascribed to the coupling not with the N–H proton but with the Mo–F fluorine atom. The N–H proton NMR resonance was observed only for **1a**. In the other complexes the N–H proton resonance may coincide with other resonance or be very broad,[26] or the measurement was impossible due to their instability.

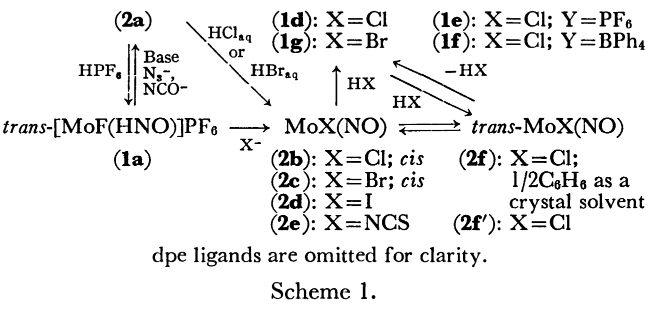
All the HNO complexes show a strong band at 1600—1650 cm^{-1} assigned to $\nu(NO)$ in their IR spectrum, in the $\nu(NO)$ region observed for $RhCl(HNO)(PPh_3)_3$.[27] The complex $RhCl(NOH)(PPh_3)_3$, which is the only one example of a proton attack at oxygen, was reported to have no band ascribable to $\nu(NO)$. It is noticiable that $\nu(NO)$ of the complexes containing fluorine ligands is lower than those containing chlorine or bromine. We were able to detect very weak N–H IR absorptions only in **1c** (2400 cm^{-1}) and **1i** (2386 cm^{-1}). In the other complexes, perhaps because of an electronic effect, the IR absorptions may be very weak and broad. Similar behavior was observed in the diazenido complexes of Mo and W,[8] and HNO complexes of Re.[26]

Based upon the ^1H NMR and IR data, we propose that the protonation of the NO ligand occurred at the nitrogen atom. Several examples of protonation of metals to give hydrides have been reported in reactions with NO^+ in the presence of methanol.[7] No signals, however, were observed in the hydride region. The presence of protonic H in **1a** was also supported by the reaction with triethylamine, which afforded $[NEt_3H]PF_6$ with the formation of Complex (**2a**) (Eq. 3).

$$\underset{(\mathbf{1a})}{trans\text{-}[MoF(HNO)(dpe)_2]PF_6} \xrightleftharpoons[HPF_6]{NEt_3} \underset{(\mathbf{2a})}{trans\text{-}MoF(NO)(dpe)_2\cdot 1/2C_6H_6} \quad (3)$$

Other complexes having a non-coordinating anion also react with the amine to afford the corresponding nitrosyl complex with concomitant formation of ammonium salts. As stated above, the others decompose spontaneously to the neutral nitrosyls in solution, whereas evolved hydrogen halides can be trapped as ammonium halides in the presence of triethylamine.

Reaction Pathways of the Interconversion of Nitrosyl and Nitroxyl Complexes. The reactions of the nitrosyl and nitroxyl complexes are summarized in Scheme 1. We observed the selective formation of *trans*-nitrosyl complex (**2f′**) by decomposition of **1d** in acetone,



dpe ligands are omitted for clarity.

Scheme 1.

whereas *cis* isomer (**2b**) was exclusively obtained by the reaction of **1a** with LiCl. The stereochemistry of **1d** is unknown because of its instability. For the seven-coordinate polyhedra, geometrical isomers are not yet established by X-ray diffraction, as shown in a recent review.[28] If **1d** is seven-coordinate with both the chlorine atoms *trans* to the HNO ligand, loss of one chlorine with concomitant proton dissociation would result in the formation of *trans*-nitrosyl complex.

Preferential formation of *cis* isomer from **1a** and LiCl makes a marked contrast with the finding above. Two possible pathways are conceivable in the fluoride displacement reaction; a dissociative path and an associative path.[29] The simple case is that of a dissociative mechanism. If the intermediate is a square-pyramid having an open face where the leaving group was located, one would expect that the addition of a new group yields 100% *trans* product. The trigonal-bipyramidal intermediate is expected to yield a mixture of *cis* and *trans* product.

One possible elucidation of selective formation of *cis* isomer is that the entering group X attacks the complex by an associative mechanism and furthermore that Y attacks through any one of the edges of the octahedron *trans* to the leaving group, that is, from the back of the complex. If attack of X had been *cis* to the leaving group, 100% *trans* product would be obtained. We consider that the back side attack of X does occur since it is possible that X makes some hydrogen bond to H of the HNO ligand. That is, the entering group X is anchored to the back side of the complex, attack from the front side having been made impossible. In fact such hydrogen bonding of N_2H_2 ligand with BF_4^-,[11] and I^- [30] was observed from X-ray analysis.

Fluorine displacement was widely observed in the reactions in Scheme 1: simple anion exchange, **2a**→**2b**, **2c**; nitroxyl formation with anion exchange, **2a**→**1d**, **1g**; nitrosyl formation with anion exchange, **1a**→**2b**, **2c**, **2d**, **2e**. In these reactions a seven-coordinate complex must be included as the intermediate or at least in the transition state. In contrast, fluorine was retained in the reactions of **1a** with N_3^- or NCO^-. The product selectivity in these reactions may be apprehensible in terms of pK_a of the conjugated acid (HX) of the anion X. The pK_a of HX is as follows: HF, 3.14; HCl, −7, HBr, −9; HI, −10; HNCS, 0.85; HOCN, 3.46; HN_3, 4.72; CF_3COOH, <0.6. The anion X with pK_a(HX) lower than pK_a(HF) undergoes substitution of the fluorine ligand by X, whereas those with greater pK_a results in the retention of the fluorine, elimination of the weaker acid having occurred preferentially. That is, direct correlation was found between pK_a of various acids in water and the propensity to add to metal complexes.

Experimental

All operations were conducted under nitrogen at room temperature or as otherwise stated. $MoH_4(dpe)_2$, *trans*-$Mo(N_2)_2$ (dpe)$_2$, *trans*- Mo (CO) (N_2)(dpe)$_2$, Mo(CO) (C_2H_4) (dpe)$_2$, Mo(C_2H_4)$_2$ (dpe)$_2$, and *cis*-Mo(CO)$_2$ (dpe)$_2$ were prepared accoding to the published methods. ^{1}H (100 MHz), ^{19}F (94.2 MHz), and ^{31}P (40.5 MHz) NMR spectra were recorded on a computer-assisted EOL PS-100 spectrometer. IR spectra were recorded on a JASCO IRA-2 spectrophotometer. X-ray photoelectron binding energies were recorded on a JASCO ESCA-1 electron spectrometer and were referenced to the carbon ls line (taken to be 285.0 eV) of each sample. The Mg K_α X-ray line (1253.6 eV) was used as a photoelectron excitation source.

Reaction of $MoH_4(dpe)_2$ with $NOPF_6$. To a suspension of MoH_4 (dpe)$_2$ (4.4 g) in benzene (350 ml) was added a freshly prepared solution of $NOPF_6$ (0.9 g) in methanol (10 ml). The evolution of hydrogen was observed. The mixture was stirred at room temperature for 4 h. After the mixture turned dark brown, a dark red solid precipitated. Addition of hexane to the mixture deposited an additional quantity of the complex. The precipitate was filtered, washed with ether, recrystallized from acetone–ether and dried *in vacuo* to yield dark red crystals of **1a** (2.3 g, 43%). Further addition of hexane to the mother liquor precipitated yellow crystals. The crystals were filtered, washed with methanol, recrystallized from benzene–hexane and dried *in vacuo* to yield **2a** (0.70 g, 15%). The presence of benzene as the crystal solvent was confirmed by gas chromatography of a toluene solution of the complex.

Reaction of Diphosphine Complexes of Mo (0) with $NOPF_6$. To a solution of *trans*-$Mo(N_2)_2(dpe)_2$ (0.95 g) in benzene (50 ml) was added a freshly prepared solution of $NOPF_6$ (0.35 g) in methanol (5 ml). After the mixture was stirred at ambient temperature for 4 h, the mixture deposited dark red crystals, which were filtered, washed with hexane and dried *in vacuo* to yield 0.59 g (54%) of $[MoF(N_2H_2)(dpe)_2]PF_6$ (Found: C, 58.0; H, 4.7; N, 2.3%. Calcd for $C_{52}H_{50}N_2F_7P_5Mo$: C, 57.5; H, 4.6; N, 2.6%). Similarly, the reaction of *trans*-$Mo(CO)(N_2)(dpe)_2 \cdot 1/2C_6H_6$ with $NOPF_6$ afforded **3b** [ν(CO) = 1934 cm^{-1}] (17%) and a mixture of *cis*-$Mo(CO)_2(dpe)_2$ and *trans*-$[Mo(CO)_2(dpe)_2]PF_6$. The reaction of $Mo(CO)(C_2H_4)(dpe)_2$ afforded **3b** (16%) and a mixture of the dicarbonyl complexes. The reaction of $Mo(C_2H_4)(dpe)_2$ afforded **3c** (5%).

$[Mo(NO)(dpe)_2]_2 \cdot 2C_6H_6$. To a solution of *trans*-$Mo(N_2)_2(dpe)_2$ (200 mg) in benzene (30 ml) was bubbled NO_2-free NO. When the reaction was complete, as indicated by the color, the undissolved brown solid [IR ν(NO) = 1775 and 1665 cm^{-1}] were removed from the solution by filtration. Addition of hexane to the filtrate deposited yellow crystals, which were filtered, washed with hexane and dried *in vacuo* to yield 42 mg (20%) of **4**. The presence of benzene as the crystal solvent was checked by gas chromatographic analysis of a toluene solution of the complex. The undissolved brown solid increased with time; apparently it is a product of successive reaction of **4** with NO. Its purification, however, was unsuccessful.

Reaction of trans-*$Mo(N_2)_2(dpe)_2$ with NOCl.* To a solution of *trans*-$Mo(N_2)_2(dpe)_2$ (155 mg) in toluene (10 ml) was added 6% NOCl in toluene (2 ml) (NOCl/Mo = 10). The mixture was stirred for 40 min during which time dinitrogen was evolved. A greenish brown solid precipitated, which was filtered, washed with hexane and recrystallized from CH_2Cl_2–hexane, yield 80 mg. The IR spectrum of the product showed that it was a mixture of two complexes, $MoCl_3(NO)\{Ph_2P(=O)CH_2CH_2PPh_2(=O)\}$ [ν(NO) = 1690 cm^{-1}], and $MoCl_2(NO)_2\{Ph_2P(=O)CH_2CH_2PPh_2(=O)\}$ [ν(NO) = 1770 and 1660 cm^{-1}]. In the case of NOCl/Mo = 1, a mixture of three complexes, 2f′ [ν(NO) = 1543 cm^{-1}], $MoCl_2(NO)_2\{Ph_2P(=O)CH_2CH_2PPh_2(=O)\}$], and the starting material was obtained.

Reaction of 1a with Alkali Metal Salts. Acetone (20 ml) was added to the mixture of **1a** (500 mg) and LiCl (240 mg).

The resulting orange brown suspension was quickly filtered. From the filtrate yellow crystals deposited on standing, which were filtered, washed with acetone and dried *in vacuo* to yield 221 mg (50%) of **2b**. Similar procedures using LiBr, LiI, NaSCN, NaNCO, and NaN_3 afforded **2c** (55%), **2d** (17%), **2e** (50%), **2a** (48%), and **2a** (41%), respectively.

Reaction of 1a with $NaBH_4$. Tetrahydrofuran (50 ml) was added to **1a** (385 mg) and $NaBH_4$ (43 mg), and the mixture was stirred for 8 h. Solvent was then evaporated off *in vacuo* to leave a brown solid, which was recrystallized from benzene–hexane to yield yellow crystals of **4** (156 mg, 44%) (Found: C, 70.1, H, 5.6; N, 1.1%. Calcd for $C_{116}H_{108}O_2N_2P_8Mo$: C, 69.6; H, 5.4; N, 1.4%).

Interconversion of 2b and 2f. The solution of **2b** (52 mg) in benzene (5 ml) was refluxed for 1 h. On addition of hexane, yellow crystals precipitated, which were filtered, washed with hexane and dried *in vacuo* to yield 34 mg (63%) of **2f**. Similarly, dissolved in CH_2Cl_2, **2f** was converted to **2b** (61%) after 1 d.

Reaction of 2a with Protonic Acids. To a solution of **2a** (30 mg) in benzene (3 ml) was added a 65% aqueous solution of HPF_6 (0.1 mg). The mixture, which turned orange brown immediately, was stirred for 1 h at room temperature. Solvent was then evaporated off *in vacuo* to leave a reddish brown powder, which was recrystallized from acetone–ether to yield dark red crystals of **1a** (23 mg, 70%). Similar procedures using $NOPF_6$–MeOH, HBF_4, and I_2 afforded **1a** (76%), **1b** (72%), and **1c** (24%), respectively.

$MoCl_2(HNO)(dpe)_2$. On bubbling HCl gas into a solution of **2a** (91 mg) in benzene (10 ml) for 30 min, a violet powder precipitated. The complex, which was too unstable for recrystallization, was filtered, washed with benzene and hexane, and dried *in vacuo*, to yield 74 mg (80%) of **1d**. The complex contained no fluorine and complete displacement by chlorine seems to have occurred (Found: Cl, 7.0; F, 0%. Calcd for $C_{52}H_{49}ONP_4Cl_2Mo$: Cl, 7.1; F, 0%). Similarly the reactions of **2b** and **2f** with HCl gas afforded **1d** in 87 and 85% yield, respectively. The reactions of **2a**, **2c**, and **2f′** with HBr gas afforded **1g** (70%), **1g** (82%), and **1h** (73%), respectively.

Conversion of 1d and 1g into Nitrosyl Complexes. Complex **1d** (122 mg) was dissolved in acetone (5 ml). The initial violet suspension became a yellow solution, from which a yellow precipitate was obtained and analyzed as **2f′** (91 mg-77%) (Found: C, 64.6; H, 4.9; N, 1.2%. Calcd for $C_{52}H_{48}ONP_4ClMo$: C, 65.2; H, 5.0; N, 1.5%). The IR spectrum shows ν(NO) at 1543 cm^{-1}. Recrystallization of **2f′** from benzene–hexane yielded yellow crystals containing 1/2 mol solvated benzene. Similarly, **1g** was converted into a mixture of yellow crystals[ν(NO) = 1567 cm^{-1}] and orange yellow crystals[ν(NO) = 1547 cm^{-1}]. The former was formulated as **2c**. The latter was also analyzed as $MoBr(NO)(dpe)_2$ and supposed to have the *trans* configuration (Found: C, 62.0; H, 5.0; N, 1.2; Br, 7.8%. Calcd for $C_{52}H_{48}ONP_4BrMo$: C, 62.3; H, 4.8; N, 1.4; Br, 8.0%). Recrystallization of the mixture from CH_2Cl_2–ether gave yellow crystals of **2c** (60%).

Reaction of 1d with Non-coordinating Anions. Acetone (10 ml) was added to the mixture of **1d** (124 mg) and KPF_6 (50 mg). After stirring for 10 min the mixture was filtered. The filtrate, a light-green solution was evaporated to dryness and the solid residue was recrystallized from acetone–ether to give 100 mg (73%) of **1e** as violet crystals. A similar procedure using $NaBPh_4$ afforded **1f** (79%).

Anion Substitution of 2a. Aqueous hydrogen chloride (0.5 ml, 35% solution) was added to **2a** (80 mg) in acetone (5 ml). After stirring for 1 h, the precipitate was filtered, recrystallized from CH_2Cl_2–ether to yield 47 mg (60%) of **2b**. Similar procedures using aqueous hydrogen bromide, benzoyl chloride, and trifluoroacetic acid afforded **2c** (54%), **2b** (83%), and **2g** (41%), respectively. The reaction of **2a** with benzoyl bromide afforded **1i** (39%), but no satisfactory analyses were obtained for the product (see Table 3), which was found to be contaminated with a small amount of **1g** (IR).

Reaction of 4 with Protonic Acids. On addition of 65% aqueous solution of HPF_6 (0.07 ml) to a solution of **4** (80 mg) in toluene (5 ml)–methanol (1 ml), an immediate reaction took place yielding a reddish brown solution. Evolution of hydrogen was confirmed by GLC. Addition of hexane deposited dark red crystals, which were filtered to yield 61 mg (70%) of **1a** (Found: C, 57.7; H, 4.8; N, 1.2%. Calcd for $C_{52}H_{49}ONF_7P_5Mo$: C, 57.4; H, 4.5; N, 1.3%). A similar procedure using aqueous hydrogen chloride afforded a mixture of **2b** and **2f**, which was recrystallized from CH_2Cl_2–ether to give **2b** (45%) (Found: C, 64.9; H, 5.2; N, 1.2%. Calcd for $C_{52}H_{48}ONP_4ClMo$: C, 65.2; H, 5.0; N, 1.5%).

Reaction of 1a with Triethylamine. To a solution of **1a** (99 mg) in acetone (5 ml) was added triethylamine (0.5 ml) in benzene (3 ml). On standing the resulting yellow solution, a yellow powder precipitated, which was filtered, washed with ether and dried *in vacuo* to yield 41 mg (46%) of **2a**. Addition of hexane to the filtrate deposited an additional quantity of **2a** contaminated with $[NEt_3H]Cl$ (IR) which was washed with methanol and dried. The combined yield amounted to 68%.

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