Pantex Plant, Amarillo, Tex., for the assistance in obtaining the mass spectra.

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Contribution from the Research and Development Department,
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X-Ray Photoelectron Spectroscopy Study of $MoCl_2(NO)_2(P(C_6H_5)_3)_2$

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Nitric oxide is unique among simple ligands because of its ability to coordinate to a transition metal either in a linear way (∠M-N-O = 180°) as a Lewis base or in a bent fashion (∠M-N-O = 120°) as a Lewis acid. In reality, the above angles represent limiting cases of the bonding arrangement and various intermediate situations are known. M-N-O angles of 160-180° are designated "linear" while angles of 120-140° are classified as "bent." Thus, nitric oxide can give rise to a range of complexes distinguished by differences in M-N-O bond angles. Recently, evidence that the two forms of metal-nitrosyl bonding may coexist[1] or rapidly interconvert[2] within the same molecule has been obtained.

Traditionally, infrared N-O stretching frequencies have been used as criteria for assigning the bonding mode of metal-complexed nitrosyl groups.[3] However, recent X-ray diffraction studies have shown infrared stretching frequency data to be unreliable as a means for judging the M-NO bond type.[4] We report here our results concerning the use of X-ray photoelectron spectroscopy (ESCA)[5] as a tool for the study of transition metal-nitrosyl complexes. We have chosen $MoCl_2(NO)_2(P(C_6H_5)_3)_2$ as a model compound to study for two reasons: its intrinsic interest as an example of a bis-nitrosyl complex and its ability, when combined in solution with organoaluminum reagents, to catalyze the olefin disproportionation reaction.[6] Knowledge of the electron distribution in the complex could aid in understanding its efficacy as a catalyst precursor.

Experimental Section

The complexes were prepared by literature methods as cited: $Mo(CO)_5(P(C_6H_5)_3)$,[7] *trans*-$Mo(CO)_4(P(C_6H_5)_3)_2$,[8] $MoCl_2(CO)_3(P(C_6H_5)_3)_2$,[9] $MoCl_2(NO)_2(P(C_6H_5)_3)_2$,[10] $MoCl_4(P(C_6H_5)_3)_2$,[11] and $MoOCl_3(P(C_6H_5)_3)_2$.[12] The photoelectron spectra were obtained with a Varian 15 Induced Electron Emission spectrometer using a Mg anode (1253.6 eV). The samples were crushed, dusted onto Scotch 810 transparent tape under dry nitrogen, and transferred to the spectrometer with minimal exposure to the atmosphere. No sample decomposition was observed during the ESCA measurements. At least three separate sample preparations were measured for each complex. All binding energies are referenced to 285.0 eV for the C 1s peak of the triphenylphosphine ligands which were well resolved (*ca.* 3.5 eV) from the carbonyl carbons of the CO-containing complexes and 4-5 fold more intense than "background" carbon. Standardization to the 4f level of vacuum-deposited gold showed the C 1s peak of the phenyl groups to be *ca.* 0.2 eV lower than that of a tape blank. The experimental binding energies for Mo, Cl, P, and N are listed in Table I.

Results and Discussion

Our approach to the study of $MoCl_2(NO)_2(P(C_6H_5)_3)_2$ by ESCA has been to compare the molybdenum binding energies of this complex with those of similar complexes in which the metal-ligand bonding is less ambiguous. By comparing complexes which are similar in structure and in the types of ligands present we may reasonably assume that shifts in binding energies result from changes in the valence electron distribution. Accordingly, the binding energies of the series of molybdenum complexes listed in Table I were determined.

The binding energies of the $2p_{3/2}$ electrons for both chlorine and phosphorus increase slightly on going from the Mo(0) complex $Mo(CO)_5(P(C_6H_5)_3)$ to the Mo(V) complex $MoOCl_3(P(C_6H_5)_3)_2$. This behavior is consistent with the expected increase in electronegativity of the molybdenum in higher oxidation states. Only one N 1s peak was observed in the ESCA spectrum of $MoCl_2(NO)_2(P(C_6H_5)_3)_2$ indicating that the two NO groups are equivalent.[13,14]

The data of Table I clearly illustrate the dependence of the molybdenum 3d and 3p electron binding energies on the formal oxidation state of the metal. To assess this dependence in a more quantitative manner, we have utilized a calculated charge parameter, q_{Mo}, equal to the sum of the partial ionic character of all molybdenum-ligand (L) bonds[15]

$$q_{Mo} = \sum_{L} I_L \tag{1}$$

I_L is related to the electronegativity difference between the bonded atoms by the Pauling equation[16]

$$I_L = 1 - e^{-0.25(\chi_{Mo} - \chi_L)^2} \tag{2}$$

Previous ESCA studies of transition metal-triphenylphosphine complexes have shown this ligand does not generate appreciable charge on the metal.[17] Our results for $Mo(CO)_5(P(C_6H_5)_3)$ *vs.* $Mo(CO)_4(P(C_6H_5)_3)_2$ as well as those of Hercules and Swartz for Mo metal *vs.* $Mo(CO)_6$[18]

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Table I. Experimental Binding Energies of Molybdenum Complexes

	Binding energy,[a] eV						
	Mo				P	Cl	N
Molybdenum complex	$3d_{5/2}$	$3d_{3/2}$	$3p_{3/2}$	$3p_{1/2}$	$2p_{3/2}$	$2p_{3/2}$	1s
$Mo(CO)_5(P(C_6H_5)_3)$	227.6	230.8	393.5	410.9	130.6		
trans-$Mo(CO)_4(P(C_6H_5)_3)_2$	228.0	230.9	393.7	411.1	131.2		
$MoCl_2(CO)_3(P(C_6H_5)_3)_2$	229.0	232.8	395.7	413.0	131.6	198.3	
$MoCl_4(P(C_6H_5)_3)_2$	232.1	235.2	397.7	415.3	131.6	198.9	
$MoOCl_3(P(C_6H_5)_3)_2$	232.5	235.5	398.4	415.3	132.9	198.9	
$MoCl_2(NO)_2(P(C_6H_5)_3)_2$	230.5	233.4	396.5	413.7	131.6	198.5	401.6

[a] Experimental uncertainties are nominally ±0.2 eV.

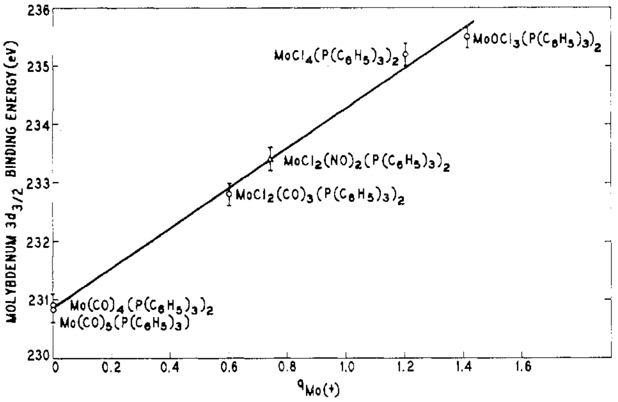

Figure 1. Correlation of $3d_{3/2}$ binding energies of molybdenum in various complexes with a charge parameter calculated as the sum of the partial ionic characters over the metal–ligand bonds.

indicate a similar electroneutrality for the CO ligand. Consequently, in our calculation of q_{Mo} we have taken $I_{P(C_6H_5)_3} = I_{CO} = 0$. Pauling electronegativities[16] have been utilized in the application of eq 2. Figure 1 shows a plot of q_{Mo}, calculated by eq 1, *vs.* the experimental Mo $3d_{3/2}$ binding energies for the first five complexes of Table I. Similar plots were obtained for the Mo $3d_{5/2}$, $3p_{3/2}$, and $3p_{1/2}$ electron binding energies.

The correlation of q_{Mo} with binding energy is quite good and can be used to assess the electron distribution in $MoCl_2(NO)_2(P(C_6H_5)_3)_2$. The observed $3d_{3/2}$ binding energy for the complex corresponds to a q_{Mo} value of 0.74+ (see Figure 1). Since the contribution of the two chlorines to q_{Mo} is 0.60+ and that of the triphenylphosphines is zero, the remaining charge (*ca.* 0.14+) on the molybdenum must be the result of a net transfer of electron density to the nitrosyl groups.[19] The nitrosyl ligands can best be described as $NO^{\delta-}$. In terms of a formal oxidation state, the molybdenum would be closest to Mo(II).

Current interpretations of the bonding of nitric oxide to transition metals associate near-linear coordination with NO^+ and a bent M-N-O linkage with NO^-. A recent single-crystal X-ray diffraction study of $MoCl_2(NO)_2(P(C_6H_5)_3)_2$ found the Mo-N-O angles to average 161.8°.[20] These bond angles fall within the range (*vide supra*) assigned to "linear" or NO^+ nitrosyl groups. Our finding of a partial negative charge on the NO groups in the above complex indicates that nitrosyls which are nominally "linear" (NO^+) can, in fact, be net electron acceptors resulting from a strong $d\pi \rightarrow NO\ \pi^*$ interaction. The large deviation from linearity of the Mo-N-O bonds is most likely a consequence of an anisotropic distribution of electron density between the two orthogonal NO π^* orbitals.[21]

The X-ray study also found the two nitrosyl groups to be structurally equivalent in agreement with our observation of only one N 1s binding energy.

A comparison of the isoelectronic dichloro complexes $MoCl_2(CO)_3(P(C_6H_5)_3)_2$ and $MoCl_2(NO)_2(P(C_6H_5)_3)_2$ is interesting (see Table I). Despite the larger number of potential back-bonding ligands in the CO complex, the molybdenum binding energies of the NO derivative are on the average 0.9 eV higher. This is further evidence of the greater π acidity of NO compared to CO.

The present study indicates that X-ray photoelectron spectroscopy, with suitable reference spectra for comparison, can provide information about the mode of metal-NO bonding in nitrosyl complexes. The good correlation between experimental molybdenum binding energies and an electronegativity-based calculated charge for a variety of complexes suggests that ESCA will be valuable in the study of molybdenum compounds in general.

Registry No. $Mo(CO)_5(P(C_6H_5)_3)$, 14971-42-7; *trans*-$Mo(CO)_4(P(C_6H_5)_3)_2$, 16244-53-4; $MoCl_2(CO)_3(P(C_6H_5)_3)_2$, 17250-39-4; $MoCl_4(P(C_6H_5)_3)_2$, 12103-10-5; $MoOCl_3(P(C_6H_5)_3)_2$, 12103-08-1; $MoCl_2(NO)_2(P(C_6H_5)_3)_2$, 14730-11-1.

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(19) A plot like that of Figure 1 in which $q_{Mo(+)}$ was calculated using a variable electronegativity for molybdenum (A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961)), which largely compensates for changes in Mo-Cl and Mo-$P(C_6H_5)_3$ interactions with the Mo oxidation state, did not materially affect this result.

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Preparation of Dinitrogen-Rhenium Complexes with Tertiary Arsines as Coligands. Interaction of Indium Trichloride with Rhenium(I)-Dinitrogen Species

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A number of dinitrogen complexes of rhenium-containing phosphine ligands have been reported.[1] However, no arsine-

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