Solutions were prepared by melting the salt mixture under a stream of dry N_2 and adding the appropriate metal salt. After dissolution, the solution was filtered through a glass frit, cooled, and handled in a drybox; the sulfate and zinc chloride systems were not filtered, however. Formation of the various glasses has been described by Duffy and Ingram.[12,19] Concentrations used were varied for each system and were limited by solubility. Generally, they were of the order 1% metal ion by weight.

In the mixed SCN^-–CN^- system, separate melts of Ni(II) in KSCN and KCN in KSCN were made up, mixed in various proportions and then filtered. This procedure minimized decomposition reactions which have previously been noted.[9]

Metal concentrations were determined by EDTA titration or by atomic absorption spectroscopy. CN^- content of the SCN^-–CN^- mixture was obtained by adding a known excess of NaCN to prevent formation of insoluble $[Ni(H_2O)_6][Ni(CN)_4]$ and titrating with $NiSO_4$ using a diphenylcarbazone indicator.

Acknowledgment. Support from National Science Foundation Grant GP-17528 is gratefully acknowledged.

Registry No. Co(II), 22541-53-3; Ni(II), 14701-22-5; KSCN, 333-20-0; KNO_3, 7757-79-1; $Ca(NO_3)_2$, 10124-37-5; $NaCH_3CO_2$, 127-09-3; $LiCH_3CO_2$, 546-89-4; K_2SO_4, 7778-80-5; $ZnSO_4$, 7733-02-0; $ZnCl_2$, 7646-85-7.

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Reductive Fluoride Elimination Syntheses of Transition Metal Fluorides. Synthesis of Molybdenum Pentafluoride and Molybdenum Tetrafluoride[1]

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Received November 7, 1973 AIC30815F

Previous methods for preparing second- and third-row transition metal pentafluorides MF_5 and tetrafluorides MF_4 include the direct fluorination of the metal, halogen exchange with a corresponding chloride, and decomposition or chemical reduction of a higher oxidation state metal fluoride.[2] In particular, molybdenum pentafluoride has been reported to be a product of reactions between $Mo(CO)_6$ and F_2,[3] $Mo(CO)_6$ and MoF_6,[4] $W(CO)_6$ and MoF_6,[4] Mo and F_2,[4] Mo and MoF_6,[4] and MoF_6 and PF_3.[5] More simply, MoF_4 has only been reported as a product from the reaction of MoS_2 and SF_4[6] and from the thermal decomposition of MoF_5.[3,4]

In our hands, most of these syntheses have been found to give poor yields and impure products and to be generally unreliable. In addition, no one reaction has been reported to be generally applicable to the synthesis of both metal pentafluorides and tetrafluorides. Since a comprehensive application of these interesting compounds to new synthetic systems has been impeded by preparative problems we have attempted to develop a simple, convenient, and general synthetic method for the preparation of second- and third-row transition metal pentafluorides and tetrafluorides. We report here two simple, novel reductive-fluoride elimination routes to MoF_5 and MoF_4.

Experimental Section

The manipulation of the volatile compounds was accomplished in a Monel vacuum line[7] fitted with auxiliary Kel-F reaction tubes.[8] The molybdenum hexafluoride was purchased from Ozark-Mahoning Co., Tulsa, Okla., and was purified by trap to trap vacuum distillation. Hydrogen fluoride was purchased from Matheson Co. The crude HF was purified by trap to trap distillation. The resulting liquid was stored over K_2NiF_6. The mass spectra were recorded with a modified Bendix Model 12 time-of-flight spectrometer using a solids-probe attachment. Thin-film infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer (4000–400 cm^{-1}). The Raman spectra were recorded with a Cary 82 spectrometer using 6471-Å Kr^+ laser excitation. The Raman samples were contained in sealed thin-wall 5-mm glass nmr tubes.

Syntheses of MoF_5. In a typical one-electron reduction reaction 1.0 g (4.76 mmol) of MoF_6 and 10 ml of anhydrous HF were condensed into a Kel-F reaction tube containing 30.8 mg (1.1 mmol) of pure silicon powder frozen in 5 ml of HF. *Caution! Metal hexafluorides should not be condensed directly into silicon powder without solvent present. Explosions may result.* After 1 hr at 23° the reaction is complete as evidenced by the disappearance of the silicon powder and the cessation of gas (SiF_4) evolution. Vacuum evaporation of the volatile products (HF, SiF_4, excess MoF_6) afforded 0.84 g (100%, based on Si) of bright yellow MoF_5. By a second method, 1.0 g (4.76 mmol) of MoF_6 and 10 ml of anhydrous HF were condensed into a Kel-F reaction tube. The tube was warmed to room temperature and hydrogen gas (2.3 mmol, P_0 = 2000 Torr) was added to the stirred solution. After 3 days the volatile products (HF, unreacted MoF_6) were vacuum evaporated leaving about 0.60 g (68%, based on H_2) of MoF_5.

Synthesis of MoF_4. In a typical two-electron reduction reaction, 1.0 g (4.76 mmol) of MoF_6 and 10 ml of anhydrous HF were combined with 64.4 mg (2.3 mmol) of silicon powder and 5 ml of HF in a Kel-F reactor. Three days of stirring at 23° resulted in a green oil from which MoF_5 could be sublimed at 90–100°. A pale yellow-green, nonvolatile powder, MoF_4 (0.19 g, 22% based on Si), remained. In a second, more satisfactory reaction, 1.0 g (5.23 mmol) of MoF_5 isolated above, 34.0 mg (1.2 mmol) of silicon powder and 10 ml of HF were combined in a Kel-F reactor. The silicon powder disappeared from the stirred solution in 6–12 hr. Vacuum evaporation of the volatile products afforded 0.9 g (97%, based on Si) of yellow-green MoF_4.

Characterization of Products. MoF_5. The yellow, moisture-sensitive, crystalline MoF_5 was found to sublime at *ca.* 50° and melt at 63°. The mass spectrum of the vapors above the solid (25°) was recorded at 70 eV, and the principal ions are as follows [*m/e* (assignment) relative intensity]: 193 ($^{98}MoF_5^+$) 20, 174 ($^{98}MoF_4^+$) 100, 155 ($^{98}MoF_3^+$) 47, 136 ($^{98}MoF_2^+$) 24, 117 ($^{98}MoF^+$) 10. Ion envelopes corresponding to $Mo_3F_x^+$ and $Mo_2F_x^+$ were easily detected, but individual ion resolution at *m/e* >300 was not possible. The ions listed above are for ^{98}Mo only; ions due to ^{92}Mo, ^{95}Mo, and ^{96}Mo also could be easily discerned. The infrared absorptions (cm^{-1}) from a cold (77°K) sublimed thin-film sample (Figure 1) are 765 (w), 739 (m), 691 (s), 654 (vs, sh), and 521 (m). The Raman data (cm^{-1}), recorded at 30° from a premelted, rapidly cooled sample are 747 (s, pol), 701 (w, pol), 228 (w), and 200 (w). The yellow solid is soluble without decomposition in anhydrous HF.

MoF_4. The pale yellow-green, moisture-sensitive MoF_4 obtained from the one-electron reduction of MoF_5 and from the thermal decomposition of the green oil was found to be insoluble in anhydrous HF. *Anal.* Calcd for MoF_4: F, 44.2. Found: F, 44.0. Powder X-ray diffraction data are d_{obsd} = 8.1 (vw), 6.9 (vw), 5.5 (w), 4.7 (m, br), 4.4 (m), 4.0 (m), 3.8 (s), 3.55 (br, s), 3.17 (w), 3.13 (w),

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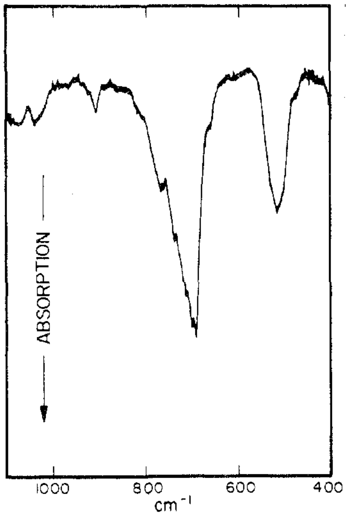

Figure 1. Infrared spectrum of a thin film of MoF_5 at 77°K.

2.63 (w), 2.0 (m), 1.92 (vw), 1.86 (vw), 1.78 (vw), 1.73 (vw), and 1.48 (vw). The infrared data (cm^{-1}) from a powder sample are 738 (m, sh), 731 (s, sh), 723 (s), and 554 (m, br).

Results and Discussion

Molybdenum hexafluoride in anhydrous HF solution reacts with either molecular hydrogen or silicon metal according to the equations

$$MoF_6 + {}^1/_2H_2 \xrightarrow[3d]{HF} MoF_5 + HF \qquad (1)$$

$$MoF_6 + {}^1/_4Si \xrightarrow[1\ hr]{HF} MoF_5 + {}^1/_4SiF_4 \qquad (2)$$

$$MoF_5 + {}^1/_4Si \xrightarrow[6-12\ hr]{HF} MoF_4 + {}^1/_4SiF_4 \qquad (3)$$

$$MoF_6 + {}^1/_2Si \xrightarrow[2d]{HF} \text{green oil } (Mo_2F_9?) \qquad (4)$$

The mechanism for the silicon reduction of MoF_6 and MoF_5 is not clearly understood. It has been suggested that a reaction $Si + 4HF \rightarrow SiF_4 + 4H$ may be involved and nascent hydrogen could be the effective reducing agent.[9] A detailed study of this reaction is under way. Preliminary results, however, indicate that in the absence of a metal fluoride the rate of hydrogen production is slow.

The slightly volatile, yellow product from the one-electron reductions of MoF_6 was characterized by its melting point, powder X-ray photograph, and mass, infrared, and Raman spectra. The color and melting point agree with published data for MoF_5.[3,4] Powder X-ray photographs confirm that the yellow solid, WF_5, and TaF_5 are isomorphous in agreement with single-crystal X-ray diffraction studies of MoF_5.[4,10] Mass spectra of the vapors over the yellow solid show a low-intensity parent ion, MoF_5^+; the most intense ion is MoF_4^+. The aggregate ions $Mo_2F_x^+$ and $Mo_3F_x^+$ first observed by Falconer[11] in a molecular beam study also were detected. This result is consistent with the presence of polymeric $(MoF_5)_x$ species in the effusion vapors. An infrared spectrum of cold (20°K), solid, and matrix-isolated MoF_5 has been recently reported by Acquista and Abramowitz.[12] Unexpectedly, the infrared spectrum (Figure 1) of a thin-film sample of MoF_5 at 77°K recorded in our study shows much more well-defined and diagnostic bands. The band at 521 cm^{-1} may be assigned to a solid-state Mo-F-Mo bridge mode. The Raman spectrum of a cooled melt sample is similar to melt spectra at 25 and 80° reported by Sharp and coworkers.[13] All data are consistent with the presence of oligomers in the melt. The overall agreement of the characterization data assures us an unambiguous identification of the yellow solid as MoF_5.

Molybdenum tetrafluoride, though reported to exist,[3,4,6] has not been characterized beyond a chemical analysis[3] and a Raman spectrum.[14] Fluoride chemical analysis of the pale yellow-green solid obtained in this study is consistent with the molecular formula assignment MoF_4. The powder X-ray pattern and infrared spectra represent new characterization data which will be compared with similar data of other metal tetrafluorides as they become available.[15]

Previous to our investigations, a high-yield, general method for the synthesis of pure transition metal pentafluorides or tetrafluorides had not been described. During the course of our studies, Falconer, Peacock, and coworkers,[16] using a hot-filament reactor described by Schroder and Grewe,[17] reported the reduction of gaseous MoF_6, WF_6, ReF_6, and OsF_6 with the formation of the corresponding pentafluorides. Though convenient, the technique is not entirely general as evidenced by the formation of IrF_4 but not IrF_5 from IrF_6.[18] In addition, except for iridium, the hot-filament technique does not provide a route to metal tetrafluorides.

The present study shows that MoF_6 is conveniently reduced in a stepwise manner with elemental silicon and molecular hydrogen in anhydrous HF solution. The one-electron reduction of MoF_6 to MoF_5 is most efficiently accomplished using silicon (eq 2); 1 g of MoF_6 is converted to MoF_5 in less than 1 hr. The hydrogen reduction (eq 1) is relatively slow and less efficient (68% conversion after 3 days).[19] Molybdenum tetrafluoride is best prepared in two one-electron reduction steps (eq 1 or 2, and 3); 1 g of MoF_5 is converted by silicon to MoF_4 in 6-12 hr. The direct reaction of MoF_6 with 2 equiv of silicon (eq 4) stops with the formation of a green oil which occludes the unreacted silicon. The oil thermally decomposes at *ca.* 100° releasing MoF_5 and a small amount of MoF_4. This behavior is similar to observations of Peacock[3] and suggests that the oil is a polymerized mixture of MoF_5 and MoF_4 (Mo_2F_9?). All attempts to complete a two-electron reduction with molecular hydrogen were unsuccessful.

The simple reactions described here offer a considerably improved method for the preparation of MoF_5 and MoF_4. The potential general utility of the reaction is obvious.

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

Registry No. MoF_5, 13819-84-6; MoF_6, 7783-77-9; MoF_4, 23412-45-5.

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

X-Ray Photoelectron Spectroscopy Study of $MoCl_2(NO)_2(P(C_6H_5)_3)_2$

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Received November 9, 1973 AIC30821B

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]

$$q_{\mathrm{Mo}} = \sum_{\mathrm{L}} I_{\mathrm{L}} \qquad (1)$$

I_{L} is related to the electronegativity difference between the bonded atoms by the Pauling equation[16]

$$I_{\mathrm{L}} = 1 - e^{-0.25(\chi_{\mathrm{Mo}} - \chi_{\mathrm{L}})^2} \qquad (2)$$

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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