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SHORT COMMUNICATION

Trifluoroethoxy Molybdenum(VI) Fluorides

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The substitution chemistry of tungsten hexahalides has undergone extensive development in recent years, with a large number of organo-oxy tungsten(VI) chlorides or fluorides now available [1-4]. In contrast, very little similar chemistry has been reported for molybdenum, a consequence of the greater oxidizing ability of Mo(VI) than W(VI) [5]. Notably, however, Walker and Winfield [6] have reported the preparation of penta-methoxy molybdenum fluoride and tetramethoxy molybdenum difluoride *via* the reaction of MoF_6 with methoxy methyl silanes. These authors report the lower members of the series $(\text{CH}_3\text{O})_n\text{MoF}_{6-n}$ to be unstable, and explosions were noted if the reaction mixtures warmed too rapidly, a dramatic demonstration of the greater reactivity of Mo(VI) than W(VI).

We have recently reported ^{19}F nmr data for the tungsten series ROWF_5 [4], and noted that the oxygen appears to interact more and more like a fluorine as the effective electron withdrawing ability of R increases. We therefore felt that the molybdenum (VI) alkoxides could be stabilized toward reduction by employing electron withdrawing alkyl groups, rather than the methyl group, and report here the series $(\text{CF}_3\text{CH}_2\text{O})_n\text{MoF}_{6-n}$, $n=1-6$.

Trifluoroethoxytrimethylsilane reacts with MoF_6 in CHFCl_2 solutions to give the corresponding trifluoroethoxy molybdenum fluorides and trimethylfluorosilane. For the less substituted members of the series the degree of substitution is readily controlled by reactant stoichiometry. *Hexakis* trifluoroethoxy molybdenum(VI) is formed slowly over a period of several days in the presence of excess silyl ether, and is sparingly soluble in the $\text{CHFCl}_2-(\text{CH}_3)_3\text{SiF}$ solvent mixture. Solutions of these compounds are stable at 25°C for several days, although for $n = 1-3$ there is a slow decomposition to a blue solid on the walls of the nmr tubes, but

only in the vapor phase region. No evidence for the formation of the alkyl fluoride, $\text{CF}_3\text{CH}_2\text{F}$, has been observed [1,2].

^1H and ^{19}F nmr data for these compounds are collected in the Table. The trends in chemical shifts, both ^{19}F , Figures 1 and 2, and ^1H , are the same as found for tungsten(VI) alkoxides, with a general upfield shift observed as the number of alkoxy groups increases. These data, therefore, are consistent with the same oxygen $p\pi$ to metal $d\pi$ donation proposed for the tungsten compounds [1-4,7]. The chemical shift range for the Mo-F fluorine nuclei, however, is substantially larger than for the W-F fluorine nuclei, as would be expected for the more oxidizing Mo(VI). From MoF_6 to

TABLE 1

^{19}F and ^1H NMR data for $(\text{CF}_3\text{CH}_2\text{O})_n\text{MoF}_{6-n}$ molecules^a

Compound	δMoF_{-A}^b	δMoF_{-B}^b	δCF_{3A}^c	δCF_{3B}^c	δCH_{2A}^d	δCH_{2B}^d
MoF_6	0					
$\text{CF}_3\text{CH}_2\text{OMoF}_5^e$	46.7	64	-3.64		-1.00	
<i>cis</i> $(\text{CF}_3\text{CH}_2\text{O})_2\text{MoF}_4^f$	102.6	117.1	-2.50		-0.90	
<i>gac</i> $(\text{CF}_3\text{CH}_2\text{O})_3\text{MoF}_3$	┌ 165 ┐		-1.72		┌	┐ ^h
<i>met</i> $(\text{CF}_3\text{CH}_2\text{O})_3\text{MoF}_3$	└		-2.13	-1.55	└	-0.62 ┘
<i>cis</i> $(\text{CF}_3\text{CH}_2\text{O})_4\text{MoF}_2$	214		-1.37	-0.95	-0.45	-0.47
$(\text{CF}_3\text{CH}_2\text{O})_5\text{MoF}$	253		i	-0.31	i	-0.27
$(\text{CF}_3\text{CH}_2\text{O})_6\text{Mo}$				0		0

- (a) All chemical shifts are in ppm, with positive shifts upfield. The subscript "A" indicates a fluorine *trans* to the resonant nucleus, "B" indicates an oxygen *trans* to the resonant nucleus. Estimated uncertainties are ± 1 in the least significant recorded digit. $J_{\text{CF}_3-\text{CH}_2} = 7.8 \pm 0.2$ Hz for all compounds.
- (b) For CCl_3F (external) reference, subtract 278 ppm from the tabulated values.
- (c) For CCl_3F (external) reference, add 74.5 ppm to the tabulated values.
- (d) For $(\text{CH}_3)_4\text{Si}$ (external) reference, subtract 4.82 ppm from the tabulated values.
- (e) $J_{\text{FA}-\text{FB}} = 96 \pm 2$ Hz, $J_{\text{MoF}-\text{CH}_2} = 1.1 \pm 0.1$ Hz
- (f) $J_{\text{FA}-\text{FB}} = 97 \pm 1$ Hz
- (g) Peak width at half height is 50 Hz
- (h) Overlapping quartets not resolved
- (i) Assignment uncertain.

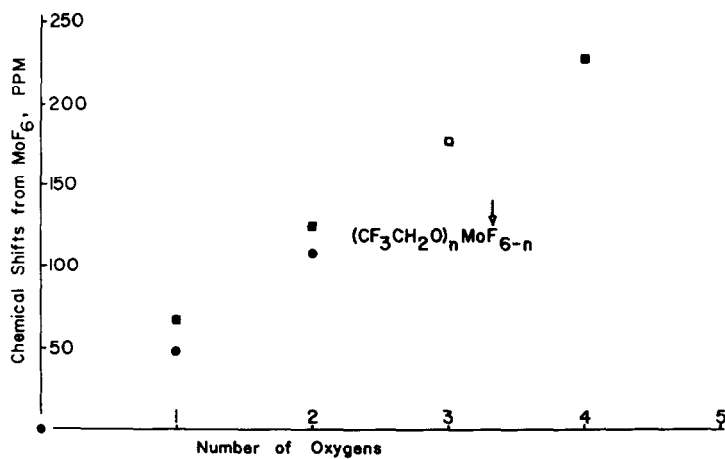


Figure 1. Chemical shifts of Mo-F fluorine nuclei in $(\text{CF}_3\text{CH}_2\text{O})_n\text{MoF}_{6-n}$ molecules. Circles have fluorine *trans* to the resonant nucleus, squares have oxygen *trans* to the resonant nucleus. The open symbol for $n = 3$ is an exchange averaged value.

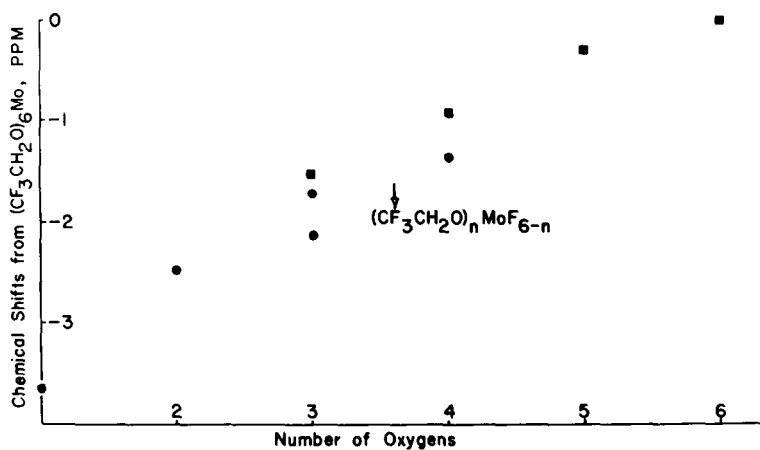


Figure 2. Chemical shifts of CF_3 fluorine nuclei in $(\text{CF}_3\text{CH}_2\text{O})_n\text{MoF}_{6-n}$ molecules. Circles have fluorine *trans* to the resonant nucleus, squares have oxygen *trans* to the resonant nucleus.

$(CF_3CH_2O)_5MoF$ spans 252 ppm, compared to 206 ppm from WF_6 to $(CH_3O)_5WF$ [2,7]. Furthermore, from the $ROWF_5$ data [4], we would expect the chemical shift range for CH_3O derivatives to be larger than for CF_3CH_2O derivatives. The ^{19}F chemical shift for $(CH_3O)_5MoF$ reported by Walker and Winfield [6] is in accord with this expectation, being about 37 ppm upfield from the value we observe for $(CF_3CH_2O)_5MoF$. It also appears that the MoF linkages may be considerably more labile than their W-F counterparts, perhaps a consequence of the lower Mo-F bond energy of 448 KJ mole^{-1} versus 506 KJ mole^{-1} for WF_6 [8]. This lability is particularly noticeable for the trisubstituted species, which give a single broad ^{19}F resonance in the Mo-F region, but a well resolved set of resonances in the CF_3 region which clearly show the presence of both isomeric forms with an approximate *gauche* ratio of 25:75. Unfortunately, it was not possible, due to equipment difficulties, to obtain nmr spectra at reduced temperatures.

It is clear, however, that just as electronegative substituents on nitrogen stabilize the L_2N-Xe bond [9], the LO-M linkage can be stabilized for rather strongly oxidizing metals by judicious choice of the group attached to oxygen.

Experimental

Trifluoroethanol, dichlorofluoromethane, and molybdenum hexafluoride were purchased from commercial sources. Trifluoroethoxytrimethylsilane was prepared from the alcohol and hexamethyldisilazane [10], and carefully distilled (b.p. 80.5-81.0) to minimize excess hexamethyldisilazane in the product. 1H nmr indicated less than 1% impurity in the product silyl ether. 5 mm O.D. medium wall nmr tube reactors [2] were flamed in vacuo, then between 0.3 and 4 mmoles of $CF_3CH_2OSi(CH_3)_3$ was added in a nitrogen atmosphere. The reaction tube and silyl ether were then degassed on an all-metal vacuum line, 1 mmole of $CHFCl_2$ was condensed into the tube, followed by 0.5 mmole of MoF_6 , and then 3 mmoles of $CHFCl_2$. The tubes were sealed under vacuum and placed nearly horizontally in a safety hood to warm from liquid air temperature. No chemical explosions were ever observed, but the volume change on melting of $CHFCl_2$ caused one tube to break when it was allowed to warm in a vertical position, thus melting more rapidly at the bottom of the tube.

1H nmr spectra were recorded on a commercial instrument at 60 MHz. ^{19}F spectra were recorded on a modified Bruker HFX-90 with a Nicolet

Fourier Transform system. The high field proton resonance of CHFCl_2 was the lock signal, with the observe channel frequency standard generated by a Schomandl ND 100 M frequency synthesizer. The frequency synthesizer was referenced to the proton lock frequency to avoid oscillator drift errors. Approximate corrections to the familiar CCl_3F ^{19}F chemical shift reference are given in the Table. The ν values (resonant frequencies at a field strength which gives a resonance frequency of exactly 100 MHz for the protons in $(\text{CH}_3)_4\text{Si}$ [11] of the fluorine nuclei in MoF_6 and $(\text{CF}_3\text{CH}_2\text{O})_6\text{Mo}$ are 94,120,793 Hz and 94,086,885 Hz, respectively.

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