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The Metathetical Chemistry of Halotungsten(VI) Compounds. Synthesis and Geometry of Organooxy Fluorides and Chlorides[1]

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Tungsten(VI) halides can be selectively metathesized with organooxysilanes and, where appropriate, with methoxide ion. Reactions proceed without reduction of the metal and degree of substitution can be regulated by control of stoichiometry. In this manner, the compounds $(CH_3O)_nWX_{6-n}$, where $n = 1$-4 and X = F or Cl, can be synthesized from the reaction of $CH_3OSi(CH_3)_3$ and WX_6. Further substitution does not efficiently take place with $CH_3OSi(CH_3)_3$ but can be effected with CH_3O^-, again with maintenance of the W(VI) state, to give the $(CH_3O)_5WCl$ and $(CH_3O)_6W$ species. The two series may be interconverted *via* fluorination of W–Cl bonds with SbF_3 or chlorination of W–F bonds with $(CH_3)_3SiCl$. The stereochemical disposition of all products has been determined by ^1H and, where possible, ^{19}F nmr.

Introduction

General Comments.—The principles embodied in the extensive metathetical chemistry relating to reactions between covalent main group halides and suitable "organometallics"[4] are now well exemplified by a broad range of elements and functional groups.[5] Thus, in recent times such exchange reactions have permitted novel syntheses of compounds possessing significantly different chemical properties, through routes where anticipated or undesirable side reactions do not occur. Rather, useful avenues are made possible that avoid reduction (*e.g.*, HPF_4[6]) or disproportionation [$Si_2F_5NHSi(CH_3)_3$[7]], as well as offering stereoselectivity [*cis*-$[(CH_3)_2N]_2TeF_4$[8]]. Moreover, it is a common feature in these systems that protic reactants and ionizing solvents are avoided, thereby permitting isolation of uncomplexed products. Only recently, however, has corresponding attention been devoted to systematically exploring comparable synthetic potentialities for analogous covalent transition metal halides, where the metal can be available in its highest oxidation states. Heretofore, efforts with such sytems have been directed toward, or at least resulted in, incorporation of the transition element under reduced conditions. Then too, past efforts have generally involved metal chlorides or oxychlorides treated with protic ligands (*e.g.*, ROH[9] or RNH_2,[10] where R = alkyl or aryl) and in some instances salts ($RONa$,[11] R_2NLi,[12] or C_5H_5Na[13]). No simple general trends are obvious for even an individual element, since while effective substitution reactions may result in some cases $\{[(CH_3)_2N]_6W$,[12] $[(CH_3)_3SiCH_2]_6W$[14]$\}$, other procedures can produce reduced, oligomeric products $\{(C_2H_5O)_6W_2Cl_4$,[15] $(C_6F_5)_3W[O(C_2H_5)_2]_3$[16]$\}$. Nonetheless, in all these regards, a key feature of the main group element synthetic experience has not been generally exploited, that is, use of many metal– or metalloid–ligand exchange carriers familiar to that field. This situation is presently undergoing change. One new reaction route utilizes ternary borate esters as ligand carriers; however, simple metathesis or redistribution on the transition element does not occur.[17] This behavior is in marked contrast to the straightforward scission of Si–O bonds in analogous organooxysilanes on treatment with halides of tungsten(VI) or other metals

$$WX_6 + n(CH_3)_3Si\text{–}OR \longrightarrow (RO)_nWX_{6-n} + n(CH_3)Si\text{–}X \quad (1)$$

In the present paper we relate in greater detail our extension of reaction 1 which was earlier communicated[1,18] and which was independently described[19] for the WF_6 case. Comparison with new work in the WCl_6 series now permits a more comprehensive inter-

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[1] Portions of this work have been presented at the Summer Fluorine Symposium of the American Chemical Society, Marquette University, Milwaukee, Wis., June 1970, and at the Sixth Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, Md., Feb 1971.

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[4] Strictly speaking the use of the term "organometallic" is overgeneral in the present connection since while typical reactions involve organometal or -metalloid moieties bound to the leaving functional group of interest, this group very commonly is not bonded to the carrier atom through carbon σ or π bonds. In the present work we use the term organometallic to signify such reagents as chlorotrimethylsilane or methoxytrimethylsilane; however, in another paper we refer to such intermediates with formal intent, *viz.*, $(CH_3)_3SiCN$. See F. E. Brinckman, K. L. Jewett, and L. B. Handy, Abstracts, XXIIIth International Congress on Pure and Applied Chemistry, Boston, Mass., July 1971, p 78.

[5] Useful general sources are found in a collection of papers presented at a recent conference on redistribution in chemistry [see D. R. Weyenberg, *et al.*, or P. M. Maitlis, *Ann. N. Y. Acad. Sci.*, **159**, 1–334 (1969)] and in a recent review [K. Moedritzer in "Organometallic Reactions," Vol. 2, E. I. Becker and M. Tsutsui, Ed., Wiley, New York, N. Y., 1971, pp 1–115].

[6] P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Amer. Chem. Soc.*, **89**, 2017 (1967).

[7] F. E. Brinckman, T. D. Coyle, and L. Fishman, "Progress in Organometallic Chemistry," Proceedings of the Fourth International Conference on Organometallic Chemistry, M. I. Bruce and F. G. A. Stone, Ed., Bristol, U. K., 1969, p D 14.

[8] G. W. Fraser, R. D. Peacock, and P. M. Watkins, *Chem. Commun.*, 1248 (1967); *J. Chem. Soc. A*, 1125 (1971).

[9] A. Fischer and L. Michiels, *Z. Anorg. Chem.*, **81**, 102 (1913), H. Funk, W. Weiss, and G. Mohaupt, *Z. Anorg. Allg. Chem.*, **304**, 238 (1960), and H. Funk and G. Mohaupt, *ibid.*, **315**, 204 (1962), provide an overview for tungsten alkoxide chemistry. For aryloxytungsten reactions see H. Funk and W. Baumann, *Z. Anorg. Allg. Chem.*, **231**, 264 (1937), and S. Prasad and K. S. R. Krishnaiah. *J. Indian Chem. Soc.*, **37**, 681 (1960).

[10] B. J. Bridson, G. W. A. Fowles, and B. P. Osborne, *J. Chem. Soc.*, 1330 (1962).

[11] O. J. Klejnot, "Proceedings of the International Symposium on Decomposition Organometallic Compounds to Refractory Ceramics, Metals, and Metal Alloys," University of Dayton Press, Dayton, Ohio, 1968, p 331.

[12] D. C. Bradley, M. H. Chisholm, C. E. Heath, and M. B. Hursthouse, *Chem. Commun.*, 1261 (1969).

[13] S. P. Anand, R. K. Multani, and B. D. Jain, *Bull. Chem. Soc. Jap.*, **42**, 3459 (1969).

[14] G. Yagupsky, W. Mowat, A. Shortland, and G. Wilkinson, *Chem. Commun.*, 1369 (1970).

[15] O. J. Klejnot, *Inorg. Chem.*, **4**, 1668 (1965).

[16] F. E. Brinckman and K. L. Jewett, unpublished results. Treatment of WCl_6 with C_6F_5Li in hydrocarbon solvents at low temperatures yields σ-aryltungsten products with the metal in reduced form. Use of ether as solvent permits isolation of a chlorine-free derivative analogous to the well-known $(C_6H_5)_3Cr(THF)_3$; *cf.* H. Zeiss, "Organometallic Chemistry," H. Zeiss, Ed., American Chemical Society Monograph No. 147, Reinhold, New York, N. Y., 1960, p 392.

[17] R. C. Wade, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 69.

[18] L. B. Handy and F. E. Brinckman, *Chem. Commun.*, 214 (1970).

[19] A. M. Noble and J. M. Winfield, *J. Chem. Soc. A*, 2574 (1970).

TABLE I

PROTON MAGNETIC RESONANCE PARAMETERS FOR $(CH_3O)_nWX_{6-n}$

	X = Cl			X = F			
Compound	Nmr system	Chem shift[a]	J_{W-H}[b]	Nmr system[26]	Chem shift[c]	J_{H-F}[b]	J_{W-H}[d]
CH_3OWX_5	A_3	−6.22	5.1	A_3V_4X	−5.90	0.9 (F_V) 2.0 (F_X)	5.3
cis-$(CH_3O)_2WX_4$	$(A_3)_2$	−5.74	4.2	$(A_3)_2V_2X_2$	−5.47	1.0 (F_V) 1.0 (F_X)	3.5
trans-$(CH_3O)_2WX_4$	$(A_3)_2$	−5.93	3.3				
cis,cis-$(CH_3O)_3WX_3$				$(A_3)_3X_3$	−5.09	0.9	2.1
cis,trans-$(CH_3O)_3WX_3$	$(A_3)_2M_3$	−5.41 (H_A) −5.38 (H_M)	2.5 2.6	$(A_3)_2M_3V_2X$	−4.96 (H_A) −5.24 (H_M) (H_M)	1.0 (F_V) 1.2 (F_V) 1.8 (F_X)	
cis-$(CH_3O)_4WX_2$	$(A_3)_2(M_3)_2$	−5.00 (H_A) −4.94 (H_M)	<2	$(A_3)_2(M_3)_2X_2$	−4.84 (H_A) −4.65 (H_M)	1.2	
trans-$(CH_3O)_4WX_2$	$(A_3)_4$	−5.03[e]	~1				
cis-$(CH_3O)_4WClF$				$(A_3)_2G_3M_3X$	−4.84 (H_A) −4.92 (H_G) −4.98 (H_M)	 0.9 1.7	
$(CH_3O)_5WX$	$(A_3)_4M_3$	−4.64 (H_A) −4.74 (H_M)		$(A_3)_4M_3X$	−4.52 (H_A) −4.73 (H_M)	0.5 2.0	
$(CH_3O)_6W$	$(A_3)_6$	−4.48			−4.47		

[a] Chemical shifts in ppm from $(CH_3)_4Si$. Run in CH_2Cl_2 solution, where $\delta_{CH_2Cl_2} - \delta_{(CH_3)_4Si} = -5.30 \pm 0.03$ ppm. [b] Estimated uncertainty of ±0.2 Hz. [c] In ppm from internal $(CH_3)_4Si$ and C_6F_6 solutions. Estimated uncertainty is ±0.01 ppm. [d] Estimated uncertainty is ±0.4 Hz. [e] Run in C_6F_6; δ measured from internal $(CH_3)_3SiF$, where $\delta_{(CH_3)_3SiF} - \delta_{(CH_3)_4Si} = -0.20 \pm 0.03$ ppm.

pretation of relative substituent effects of the two halogens on the stereochemistry of the $(RO)_nWX_{6-n}$ system along with other properties.

Stereochemistry.—Although a large number of aryloxy derivatives of tungsten(VI) have been prepared, little is known about the stereochemical consequences of substitution on W(VI) chlorides. The hexaphenoxides, known to be monomeric in solution, are assumed to have an octahedral arrangement of oxygen atoms about the metal.[20] No stereochemical inferences appear to have been made concerning the tetraphenoxide, $(C_6H_5O)_4WCl_2$.[20] Reactions of WCl_6 with primary aliphatic amines produce a series of compounds, $(RNH)_nWCl_{6-n}$, with n = 1–4, and while the compounds $(RNH)_4WCl_2$ are found to be monomeric in benzene, no additional understanding of their structures is available.[10] A preliminary account of the octahedral disposition of N atoms in $[(CH_3)_2N]_6W$ should be noted.[12] In contrast, a somewhat more detailed picture emerges for mononuclear W(V) complexes, where trans structures have been proposed for the anions $(RO)_2WX_4^-$ (R = CH_3, C_2H_5, or C_3H_7; X = Cl or Br) on the basis of their electronic[21] or infrared[22] spectra.

For tungsten(VI) stereochemical information is now available for the series $(CH_3O)_nWF_{6-n}$, where a pronounced tendency to form cis isomers is observed.[18,19] These results may also be compared with the observations on the WF_nCl_{6-n} system which suggest trans isomers occupy a more important role.[23] Thus it was also of interest to us to compare the stability of the *cis*-$(CH_3O)_4W$ skeleton to competing directional influences of several halogen ligands under exchange conditions, in addition to characterizing the final disposition of ligands for the $(CH_3O)_nWCl_{6-n}$ series.

Experimental Section

Materials and Manipulations.—Metal halides were obtained from commercial sources and purified prior to use by sublimation or trap-to-trap fractionation. Purities in each instance were deemed suitable on the basis of infrared or nmr spectrometry and/or elemental analyses.[24] Organooxysilanes acquired from commercial sources were used as received following verification and purity check by nmr. Solvents were dried as required by distillation from $LiAlH_4$ or molecular sieves prior to use. All manipulations were conducted in the absence of air and moisture, utilizing an efficient recirculating drybox (N_2 atmosphere) and grease-free all-metal or all-glass high-vacuum systems of conventional design. Pressure measurements for highly reactive metal halides handled in the metal line were obtained with a diaphragm-type pressure transducer of Monel construction; thus WF_6 amounts were taken volumetrically. Reactions up to approximately 1–2 mmol scale can usually be conducted conveniently in suitably prepared nmr tubes. Reactions conducted on a larger scale were customarily carried out in a simple glass reactor constructed of 20-mm borosilicate tubing fitted with 15-mm "O" ring connectors and a grease-free high-vacuum stopcock. A locking type clamp must be employed on the "O" ring joint, both to ensure vacuum-tight closure and to provide a pressure seal in reactions where $(CH_3)_3SiF$ is a product.

Nmr Samples.—As with all-glass reactors employed in the work, nmr tubes (5-mm o.d, wall thickness 0.76 or 1.4 mm) were flamed out and degassed *in vacuo* ($<10^{-4}$ Torr) prior to loading. Typically, reactions or measurements involving WF_6 were conducted in the sealed heavier walled tubes. Satisfactory control of stoichiometry for reactants was obtained for heterophase systems [*e.g.*, WCl_6 with $ROSi(CH_3)_3$] by transferring the solid halide into tared nmr tubes in the drybox, followed by degassing on the vacuum system, whereupon the more volatile reactants or solvents could be introduced by vacuum transfer with appropriate weight or volumetric determinations.

Spectral Measurements.—High-resolution proton and fluorine nmr spectra were obtained on modified commercial instrumentation operating at 60 and 56.4 MHz, respectively. Details of instrumental stability, resolution, and calibration have been described elsewhere.[25] Both internal and external standards were employed (see tables) as compatibility dictated. Since for the tungsten compounds newly reported in the present work and previously described,[18,19] many instances of complex nmr spectra arose, all non-first-order spectral parameters were analyzed by digital computer procedures and appropriate simulated spectra compared by methods adopted in this laboratory in previous

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(20) H. Funk, H. Matschiner, and H. Naumann, *Z. Anorg. Allg. Chem.*, **340**, 75 (1965); P. I. Mortimer and M. I. Strong, *Aust. J. Chem.*, **18**, 1579 (1965).

(21) D. P. Rillema, W. J. Reagan, and C. H. Brubaker, Jr., *Inorg. Chem.* **8**, 587 (1969).

(22) D. P. Rillema and C. H. Brubaker, Jr., *ibid.*, 1645 (1969).

(23) (a) G. W. Fraser, M. Mercer, and R. D. Peacock, *J. Chem. Soc. A*, 1091 (1967); G. W. Fraser and R. D. Peacock, Abstracts, Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967, p 48; (b) G. W. Fraser, C. J. W. Gibbs, and R. D. Peacock, *J. Chem. Soc. A*, 1708 (1970).

(24) All microanalyses reported herein were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. 11377.

(25) R. B. Johannesen, T. C. Farrar, F. E. Brinckman, and T. D. Coyle, *J. Chem. Phys.*, **44**, 962 (1966).

TABLE II
FLUORINE MAGNETIC RESONANCE PARAMETERS FOR $(CH_3O)_nWF_{6-n}$

Compound	Nmr system[a]	Chem shift[b]	$J_{F_X-F_V}$[c]	J_{W-F}[c]
WF_6	X_6	−164.5	...	44
CH_3OWF_5	V_4X	−83.7 (F_X) −115.8 (F_V)	66	32 (F_X) 43 (F_V)
cis-$(CH_3O)_2WF_4$	V_2X_2	−51.4 (F_X) −66.3 (F_V)	65	44 (F_V)
cis,cis-$(CH_3O)_3WF_3$	X_3	−17.7	...	...
cis,trans-$(CH_3O)_3WF_3$	V_2X	−10.7 (F_X) −35.0 (F_V)	60	45 (F_V)
cis-$(CH_3O)_4WF_2$	X_2	+16.9	...	...
cis-$(CH_3O)_4WClF$	X	+2.8[d]	...	...
$(CH_3O)_5WF$	X	+42.1	...	...

[a] Excluding proton interactions; see Table I for complete classifications. [b] In ppm relative to external CCl_3F and C_6F_6 solutions. Estimated uncertainty is ±0.1 ppm or less, but concentration and solvent effects doubtless can account for larger deviations; *cf.* T. D. Coyle, R. B. Johannesen, F. E. Brinckman, and T. C. Farrar, *J. Phys. Chem.*, **70**, 1682 (1966). [c] Estimated to be accurate to within ±2 Hz; better accuracy is achieved for cases permitting computer solution of non-first-order splittings. [d] Run in C_6F_6 solution, where $\delta_{(CCl_3F)ext} = \delta_{(C_6F_6)int} - 165.3 \pm 0.3$ ppm.

work.[26] An illustration of this technique is provided in Figure 1 where non-first-order F–F splittings for the ^{19}F spectrum of CH_3OWF_5 along with H–F coupling are solved, exclusive of ^{183}W–F coupling.

Infrared spectra for solids (mulls or melts) and volatile substances (gas cells) were conducted on a commercial double-grating spectrophotometer affording the range 4000–400 cm^{-1}. All cells used were constructed of inert metal or plastic materials and fitted with KBr windows.

Preparation of $(CH_3O)_nWCl_{6-n}$. (a) $n = 1$.—Methoxytrimethylsilane (0.83 g, 8 mmol) in 5 ml of carbon disulfide was added slowly to a chilled (0°), stirred solution of tungsten hexachloride (3.2 g, 8 mmol) in 20 ml of carbon disulfide. Reaction was rapid, with the formation of chlorotrimethylsilane and methoxypentachlorotungsten(VI). The reaction solution undergoes a slight change in color during the course of the reaction, from deep purple to dark red. The free compound was not isolated; attempts to remove the volatile chlorosilane and solvent resulted in partial or complete decomposition of the CH_3OWCl_5 into $WOCl_4$, mp 208–210°,[27] and CH_3Cl. Yield of CH_3OWCl_5 in freshly prepared solutions, however, is estimated to be greater than 90%, based on the expected 1:3 integration of the ^1H nmr spectrum of the W–OCH_3 resonance at −6.2 ppm relative to the $(CH_3)_3SiCl$ resonance at −0.5 ppm.

(b) $n = 2$.—A procedure analogous to that employed in the preparation of CH_3OWCl_5 was followed, but with a 2:1 mole ratio of $CH_3OSi(CH_3)_3$:WCl_6. A very distinct color change was observed in the reactant solution, from the deep purple characteristic of WCl_6 solutions to bright red-orange. ^1H nmr of the product solution indicated the presence of CH_3OWCl_5, two isomers of $(CH_3O)_2WCl_4$, and $(CH_3O)_3WCl_3$ in the approximate ratios 6:7:7:4, respectively. Integration of the total W–OCH_3 region *vs.* $(CH_3)_3SiCl$ indicated that little decomposition occurred during the course of the reaction (*ca.* 15 min) and no appreciable decomposition resulted from prolonged storage of the product solution at −80°.

(c) $n = 3$.—Finely ground WCl_6 (4.0 g, 10 mmol) was added slowly to neat $CH_3OSi(CH_3)_3$ (3.1 g, 30 mmol). The reaction proceeded rapidly to form a yellow solution of $(CH_3O)_3WCl_3$ in $(CH_3)_3SiCl$. The solution was allowed to stand for 15 min after addition of WCl_6 was completed. If excess $CH_3OSi(CH_3)_3$ is present and WCl_6 is added rapidly, significant amounts of $(CH_3O)_4WCl_2$ are formed. The chlorosilane was removed under vacuum and the remaining yellow solid sublimed at 60° and 10^{-4} Torr to give yellow crystals, mp 78–78.5°; yield of sublimed product 3.5 g, 88%. *Anal.* Calcd for $C_3H_9O_3Cl_3W$: C, 9.40; H, 2.37; Cl, 27.75; W, 47.96. Found: C, 9.36; H, 2.46; Cl, 27.94; W, 48.10.

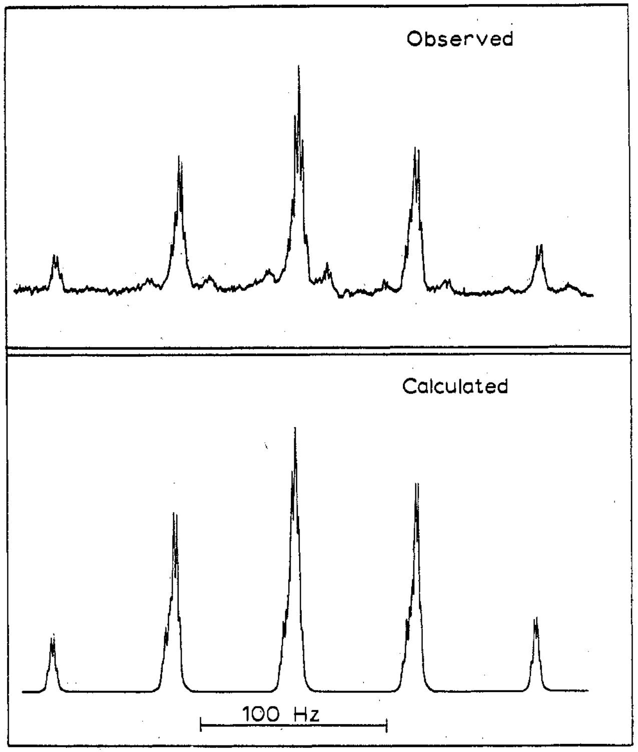

Figure 1.—^{19}F nmr spectrum of CH_3OWF_5 in C_6F_6, showing above the "quintet" for the axial fluorine trans to the CH_3O group and below the facsimile spectrum generated by computer solution of the ^{19}F V_4X case, incorporating ^1H coupling from CH_3O. The ^{183}W–F splittings seen in the observed spectrum are not reproduced in the calculation. Magnetic field increases to the left.

(d) $n = 4$.—$(CH_3O)_4WCl_2$ was prepared by slow addition of finely ground WCl_6 to excess (greater than 4:1 silane:tungsten) neat $CH_3OSi(CH_3)_3$ under N_2. Reaction was rapid for the formation of $(CH_3O)_3WCl_3$. Further substitution was slow at room temperature. The reaction mixture was degassed and then heated to 100° *in vacuo* for 1 hr, followed by cooling to 0°, whereupon the $(CH_3)_3SiCl$ and excess $CH_3OSi(CH_3)_3$ were pumped off. The remaining light brown solid sublimes readily at 60° and 10^{-4} Torr to give 70–80% yields of pale yellow crystals of $(CH_3O)_4WCl_2$, mp 79–81°. *Anal.* Calcd for $C_4H_{12}O_4Cl_2W$: C, 12.68; H, 3.19; Cl, 18.72; W, 48.52. Found: C, 12.80; H, 3.26; Cl, 18.70; W, 48.23.

(e) $n = 5, 6$.—Solutions of 1.0 g (2.6 mmol) of $(CH_3O)_4WCl_2$ dissolved in 5 ml of anhydrous methanol plus 0.2 ml of CH_2Cl_2 were treated with 2.6 or 5.2 mmol of $NaOCH_3$ (taken by volume from a freshly prepared 1.0 *M* methanol solution) for either the preparation of $(CH_3O)_5WCl$ or $(CH_3O)_6W$, respectively. Reactions were instantaneous with the formation of a white precipitate. Relative intensities of the ^1H nmr signals for the CH_2Cl_2 and $(CH_3O)_4WCl_2$ contained in the starting solutions as compared with those for $(CH_3O)_5WCl$ or $(CH_3O)_6W$ in the respective final product solutions showed that reactions were quantitative. The CH_3OH–CH_2Cl_2 mixtures were removed under vacuum. Pentakis(methoxy)tungsten(VI) chloride was sublimed at 80° and 10^{-4} Torr from the resulting viscous liquid–solid residue to yield 0.4 g (40%) of colorless crystals, mp 25–30°. *Anal.* Calcd for $C_5H_{15}O_5ClW$: C, 16.04; H, 4.04; Cl, 9.47; W, 49.10. Found: C, 15.86; H, 4.23; Cl, 9.35; W, 49.23.

Similarly, hexakis(methoxy)tungsten(VI) was sublimed at 90° and 10^{-4} Torr from the solid residue to yield 0.57 g (58%) of white crystalline product, mp 42–43°. *Anal.* Calcd for $C_6H_{18}O_6W$: C, 19.48; H, 4.90; W, 49.68. Found: C, 19.52; H, 4.92; W, 49.39.

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(26) R. B. Johannesen, J. A. Ferretti, and R. K. Harris, *J. Magn. Resonance*, **3**, 84 (1970). Nonetheless, even more precise spectral classifications than those cited are prerequisite to such detailed solutions. Thus, for example, *cis*-$(CH_3O)_4WF_2$ and *cis,cis*-$(CH_3O)_3WF_3$ are corrrctly written as $A_3A'_3M_6XX'$ and $A_3A'_3A''_3XX'X''$, respectively, in order to fully incorporate all H–H, H–F, and F–F interactions.

(27) S. E. Feil, S. Y. Tyree, Jr., and F. N. Collier, *Inorg. Syn.*, **9**, 123 (1967).

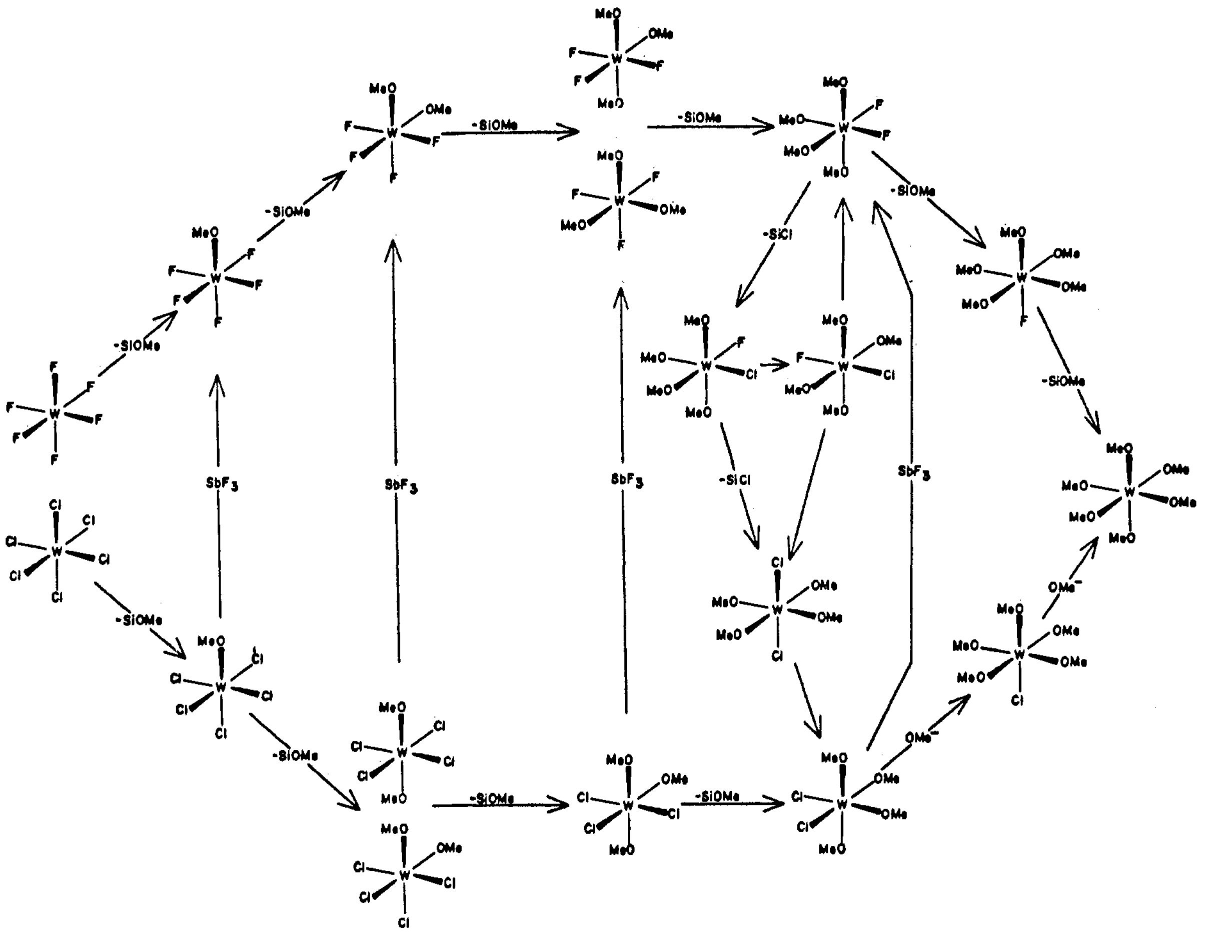

Figure 2.—Summary of preparative routes for the series $(CH_3O)_nWCl_{6-n}$ and $(CH_3O)_nWF_{6-n}$, showing steps where interconversion of Cl and F have been effected. Also depicted are the stereochemical assignments for products and intermediates as determined from nmr spectra, although with the latter, isolation has not been possible and involvement of a *trans*-$(CH_3O)_4WClF$ species, for example, is inconclusive at this point.

Preparation of $(CH_3O)_nWF_{6-n}$. (a) $n = 1$.—CH_3OWF_5 was prepared by allowing stoichiometric amounts of WF_6 and $CH_3OSi(CH_3)_3$ to react without solvent. A 10–50-mmol scale is convenient in a 20-mm borosilicate glass reactor. The two reactants were condensed into the reaction tube which was closed and then allowed to warm and stand at room temperature for 2–3 days. After this time, a white solid had separated and the immiscible reactant phases had been replaced by $(CH_3)_3SiF$. The reaction tube was cooled to 0° and the $(CH_3)_3SiF$ was removed under vacuum, leaving a slightly yellow solid. This sublimed at 40–50° and 10^{-4} Torr to yield a white crystalline solid, mp 80° dec. A variable amount of viscous yellow liquid remained when the sublimation was nearly complete, and the sublimation was terminated when the first yellow material began to sublime. The residue was a mixture of CH_3OWF_5, $(CH_3O)_2WF_4$, WOF_4, and small amounts of unidentified products. Yield of sublimed material varies from 70 to 90%. The solid decomposes slowly at room temperature but is stable indefinitely at −80°.

(b) $n = 2$.—This compound was prepared by reaction of stoichiometric amounts of WF_6 and $CH_3OSi(CH_3)_3$ as for n = 1, 3, or 4 but was more conveniently prepared *via* the redistribution reaction between CH_3OWF_5 and $(CH_3O)_4WF_2$. In a typical reaction, $(CH_3O)_4WF_2$ (0.35 g, 1 mmol) and CH_3OWF_5 (0.65 g, 2 mmol) were dissolved in 5 of ml C_6F_6, and the reaction vessel was sealed. Redistribution is complete in 24 hr at room temperature, and the yield is quantitative. $(CH_3O)_2WF_4$ is a liquid at room temperature, mp 17–19°, but can be readily sublimed *in vacuo* onto a 0° cold finger.

(c) $n = 3$.—$CH_3OSi(CH_3)_3$ (3.12 g, 30 mmol) and 2–3 ml of C_6F_6 were added to a reaction tube and then degassed and WF_6 (10 mmol) was condensed into the tube. Reaction proceeded rapidly and smoothly upon warmup to room temperature, and a pale yellow solid formed in the tube. The reaction mixture was allowed to stand, with occasional agitation, for 1 hr, and then was cooled to 10° whereupon the solvent and $(CH_3)_3SiF$ could be removed under vacuum. The remaining solid sublimed at 60° and 10^{-4} Torr to yield 3.1 g (92%) of colorless crystals of $(CH_3O)_3WF_3$, mp 57–59°.

(d) $n = 4$.—A procedure analogous to that for $n = 3$ was followed with the exceptions that a slight excess of $CH_3OSi(CH_3)_3$ was used (*i.e.*, >4:1) and that the reaction mixture was allowed to stand overnight at room temperature to ensure complete reaction. The colorless crystals (mp 82–83°) obtained from vacuum sublimation at 60° (>80% yield) are stable at room temperature, and C_6F_6 solutions are not significantly decomposed by prolonged heating at 110°. *Anal.* Calcd for $C_4H_{12}O_4WF_2$: C, 13.89; H, 3.50; F, 10.98; W, 53.10. Found: C, 13.83; H, 3.57; F, 11.34; W, 52.65. Molecular weight: calcd for monomer, 346; by osmometry in $CHCl_3$, 323; cryoscopic in C_6F_6, 331, 352.

(e) $n = 5, 6$.—Additional substitution of CH_3O for F beyond tetrasubstitution was very slow if solutions of $(CH_3O)_4WF_2$ and $CH_3OSi(CH_3)_3$ in C_6F_6 were maintained at room temperature but proceeded to a limited extent upon prolonged (1–2 days) heating at 120° in a sealed borosilicate tube. The resulting solutions contained $(CH_3O)_4WF_2$, $(CH_3O)_5WF$, and $(CH_3O)_6W$, in addition to $(CH_3)_3SiF$ and excess $CH_3OSi(CH_3)_3$. Thus, nmr parameters reported herein for the penta- and hexasubstituted species were obtained from solutions which contained the three tungsten species, generally with only a small amount of $(CH_3O)_4WF_2$.

Fluorination of $(CH_3O)_nWCl_{6-n}$.—Solutions of the appropriate $(CH_3O)_nWCl_{6-n}$ species in C_6F_6 were conveniently fluorinated in nmr tube reactors to their corresponding fluoro analogs by reaction with excess powdered SbF_3. However, while the products corresponded in stoichiometry, these did not necessarily correspond in geometry. No pure samples of either CH_3OWCl_5 or $(CH_3O)_2WCl_4$ have been prepared; hence the course of the fluorination is complicated by the presence of additional components. Rapid fluorination took place at room temperature, and CH_3OWF_5 was readily identified as the principal proton-containing material resulting from the fluorination of CH_3OWCl_5. Similarly, formation of *cis*-$(CH_3O)_2WF_4$, *and not the trans* isomer, was observed from treatment of solutions containing the mixture of isomers of $(CH_3O)_2WCl_4$ with SbF_3. Identification was based on the characteristic chemical shift and H-F coupling parameters in the ^1H spectra. Quantitative fluorinations of $(CH_3O)_3WCl_3$ and $(CH_3O)_4WCl_2$ were effected at 60 and 100°, respectively, by the same procedure. Stereochemical assignments of the products based on ^1H nmr parameters were in complete accord with the relative isomer distributions obtained directly from the reactions of WF_6 and $CH_3OSi(CH_3)_3$, as illustrated in Figure 2.

Halogen-Exchange Reactions between *cis*-$(CH_3O)_4WF_2$ and $(CH_3)_3SiCl$.—Into an nmr tube fitted with "O" ring connectors and a separable stopcock, along with provision for sealing off, 0.173 g (0.50 mmol) of *cis*-$(CH_3O)_4WF_2$ was placed. Following this *ca.* 0.25 ml of C_6F_6 was introduced by syringe, and the closed assembly was placed on the vacuum system for degassing. Coreactant chlorotrimethylsilane (21.2 cm³ at STP, 0.95 mmol) was condensed into the tube maintained at $-196°$, and the reactor was sealed off. Since these chlorinations proceed at a fairly rapid rate, the nmr tube was not warmed (30°) until just before placement into the spectrometer.

Evidence for immediate reaction was observed, notably by the fast appearance of the doublet characteristic for $(CH_3)_3SiF$ in its proton spectrum[28] and by the disappearance of the singlet–triplet pair of peaks associated with the starting compound, *cis*-$(CH_3O)_4WF_2$. These general features are summarized in Figure 3, where it may be also seen that new peaks correspondingly grew in the CH_3O–W region ($\sim$5 ppm) indicating formation of an initial W(VI) product in several hours, followed by its diminution during formation of a final tungsten species after several days. During the course of overall reaction, no evidence for displacement of methoxy groups from W to Si appeared, *i.e*, development of peaks associated with the CH_3O–Si moiety at 3–4 ppm. The spectrum of the transient tungsten chlorofluoride intermediate (*cf.* 3-hr spectrum insert) is obviously more complex than that found for the final reaction product. It consists of three peaks (relative areas 2:1:1): a singlet at δ -4.84 ppm[29] and two downfield doublets at δ -4.92 and -4.98 ppm with H–F spin couplings of 0.9 and 1.7 Hz,[29] respectively. The existence of J_{HF} was verified by heteronuclear decoupling, $^1H-\{^{19}F\}$, which was consistent with direct observation of the fluorine attached to tungsten by ^{19}F nmr in the chemical shift region anticipated from $(CH_3O)_5WF$ and $(CH_3O)_4WF_2$ spectra (Table II). The singularity of the final product's spectrum [*e.g.*, $(A_3)_4$] suggested that workup of the tube's contents at this point might offer the isolable trans isomer of the previously characterized *cis*-$(CH_3O)_4WCl_2$.[30]

The tube was opened to the vacuum line and the volatile contents were carefully removed. Product $(CH_3)_3SiF$ and solvent were separated by trap-to-trap fractionation; the fluorosilane collected following repeated passage through a trap maintained at $-80°$ was identified by comparison of its infrared spectrum with that for an authentic sample,[28] and its volume was measured. The nonvolatile residue remaining in the tube consisted of well-formed pale lemon crystals. *Anal.* Calcd for $C_4H_{12}O_4Cl_2W$: C, 12.68; H, 3.19; Cl, 18.72; W, 48.52. Found: C, 12.66; H, 3.20; Cl, 18.45;[31] W, 48.29. The overall reaction may be represented as

$$\begin{array}{lll}
\textit{cis}\text{-}(\mathrm{CH_3O})_4\mathrm{WF_2} & +\ 2(\mathrm{CH_3})_3\mathrm{SiCl} \longrightarrow & \\
\quad 0.173\ \mathrm{g} & \quad 21.2\ \mathrm{cm^3} & \\
0.50\ \mathrm{mmol} & \quad 0.95\ \mathrm{mmol} & \\
 & & \textit{trans}\text{-}(\mathrm{CH_3O})_4\mathrm{WCl_2} + 2(\mathrm{CH_3})_3\mathrm{SiF} \quad (2)\\
 & & \qquad >98\% \qquad\qquad 20.9\ \mathrm{cm^3}\\
 & & \qquad\qquad\qquad\qquad\quad 0.93\ \mathrm{mmol}
\end{array}$$

These results are consistent with those derived from nmr spectra, with the significant exception that redissolving the dichloride crystals in fresh C_6F_6 yielded a clear solution which consisted exclusively of the cis isomer (nmr spectrum). The presence of acidic $(CH_3)_3SiF$ as a coproduct under moderate pressure in the original nmr tube could be involved in inducing slow or rapid exchange processes leading to back-reactions or isomerization. This was tested for by loading another nmr tube with authentic *cis*-$(CH_3O)_4WCl_2$ and amounts of fluorotrimethylsilane and hexafluorobenzene necessary to reproduce the previous reaction conditions. As a result of comparable thermal cycling, or even heating to 50°, no alteration in the doublet cis isomer spectrum [*e.g.*, $(A_3)_2(M_3)_2$] occurred, although the chemical shift difference between H_A and H_M was seen to diminish.

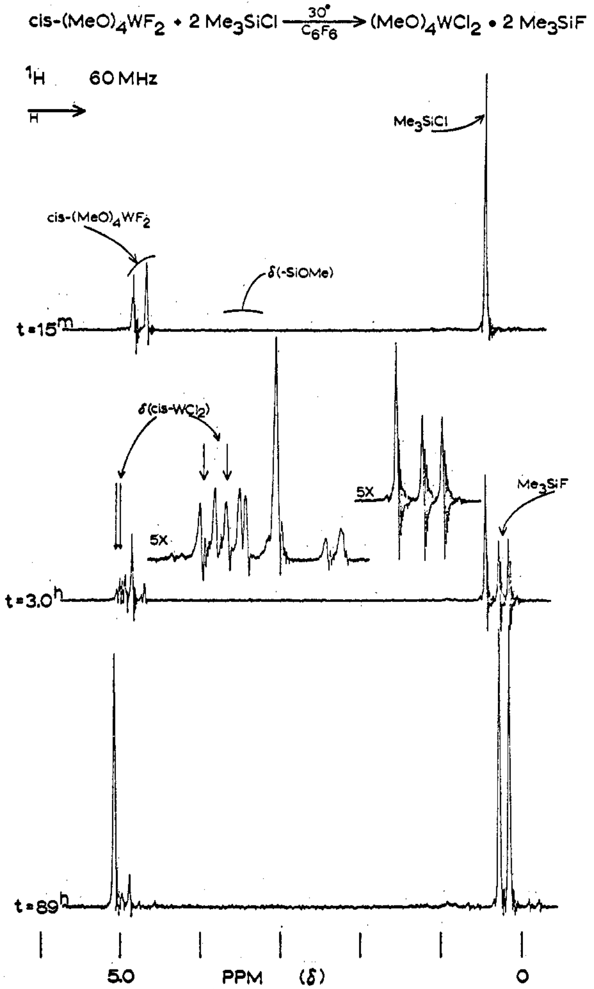

Figure 3.—The reaction between *cis*-$(CH_3O)_4WF_2$ and $(CH_3)_3SiCl$ observed by ^1H nmr as a function of time. The inset shown in the 3-hr scan illustrates a fivefold sweep expansion permitting display of the new peaks associated with the *cis*-WClF, *trans*-WCl_2, and $(CH_3)_3SiF$ products. Arrows indicate expected positions for growth of *cis*-WCl_2 peaks.

An analogous reaction between *cis*-$(CH_3O)_4WF_2$ and dichlorodimethylsilane was conducted (1:1 molar ratio) under conditions indicated above. Similar results were obtained with formation of a mixed chlorofluoride intermediate and, ultimately, production of the trans WCl_2 isomer in solution along with expected quantitative formation of $(CH_3)_2SiF_2$. Other experiments involving an equimolar ratio of cis difluoride and $(CH_3)_3SiCl$ as reactants under the same conditions produced no qualitative differences from the above results, but the relative amount of intermediate chlorofluoride produced in a given time could be increased. In this manner it was found that the intermediate underwent slow synproportionation exclusively to cis difluoride plus trans dichloride, following the initial rapid consumption of Si–Cl bonds.

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(28) H. Schmidbaur, *J. Amer. Chem. Soc.*, **85**, 2336 (1963); R. B. Johannesen, F. E. Brinckman, and T. D. Coyle, *J. Phys. Chem.*, **72**, 660 (1968).

(29) Estimated uncertainties are given in Table I, footnotes *b* and *d*.

(30) That this sharp singlet did not arise from some rapid exchange process (on the nmr time scale) was held reasonable on the basis of satellites ($J \approx 1$ Hz) observed under optimum spectrometer conditions; these were assigned to coupling between ^{183}W ($I = {}^1/_2$) and methoxy protons which implies a stable W–O linkage. Although self-exchange or intramolecular rearrangements were not excluded, our initial view was complemented by the fact that only rigid, nonexchanging structures are consonant with the spectral features observed for coreactants cis difluoride and mixed-halide intermediate. See E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

(31) This value was estimated from the extent of Si–Cl exchange as based on recovered $(CH_3)_3SiF$.

Results and Discussion

Metathetical Reactions.—Reaction between methoxytrimethylsilane and tungsten hexachloride proceeds according to the equation

$$WCl_6 + nROSi(CH_3)_3 \longrightarrow (RO)_nWCl_{6-n} + n(CH_3)_3SiCl \quad (3)$$

where $n = 1$–4. CH_3OWCl_5 is of limited stability, eliminating methyl chloride with the formation of $WOCl_4$ at room temperature. The disubstituted product is somewhat more stable in this respect but cannot be melted without decomposition. Similar behavior has been observed for CH_3OWF_5[32] and for $ROWCl_5^-$ [21,22] where elimination is viewed as a concerted bimolecular reaction involving the trans chlorine atom. In contrast, the tri- and tetrasubstituted methoxytungsten chlorides are found to be thermally stable at room temperature and above (*ca.* 110°) both as solids and in solution. Reaction beyond tetrasubstitution (eq 3) could not be effected by treatment with excess methoxytrimethylsilane, even on prolonged heating at 110°. This result is not surprising in view of the slow reaction noted for the more reactive *cis*-$(CH_3O)_4WF_2$ with excess $CH_3OSi(CH_3)_3$[18] and of the fact that the hexaphenoxides are produced by treating WCl_6 with neat phenols, generally over 100°; less vigorous conditions lead to formation of the tetraphenoxydichlorotungsten(VI) compounds.[20] Attempts to prepare $(CH_3O)_4WCl_2$ by direct reaction between CH_3OH and WCl_6, as suggested by Funk and his coworkers,[33] have not been successful. Rather, the course of this reaction appears to follow a reductive route outlined by Klejnot.[11] *cis*-Tetrakis(methoxy)dichlorotungsten(VI) itself, however, is stable in methanol solution, suffering neither reduction, isomerization, nor additional methoxylation. Further methoxylation is obtained, however, by treatment of methanolic $(CH_3O)_4WCl_2$ with strongly basic methoxide ($NaOCH_3$), thereby producing either $(CH_3O)_5WCl$ or $(CH_3O)_6W$ depending on the relative amounts of reactants.

It is important to note that these results significantly differ from previously reported courses of events which preliminarily involve interaction (and reduction) of the metal halide with an alcohol, followed by alkoxide ion treatment to yield a diamagnetic alkoxytungsten(V) chloride dimer.[11,15] In the present case, not only does the *cis*-$(CH_3O)_4W$ moiety survive strongly nucleophilic displacement reactions usually promoted by CH_3O^-, but we find, moreover, that this structure withstands electrophilic conditions associated with fluorination and other substitution reactions. Thus *cis*-$(CH_3O)_4WCl_2$ may be readily converted to the difluoride, with complete retention of geometry, by treatment with antimony trifluoride in solution at elevated temperatures. This resistance of the $(CH_3O)_4W$ structure to subsequent vigorous exchange reactions presages a useful synthetic tool whereby a number of mixed-halogen derivates can be evaluated for their effects on its geometry.[34] In the present paper we confine our discussion to an examination of the compounds depicted in the reaction schemes shown in Figure 2.

The route by which *cis*-$(CH_3O)_4WF_2$ may be chlorinated appears to be a selective reaction in that choice of chlorination reagents seems quite limited. On treatment of the difluoride, for example, with trimethyltin chloride in solution at 100° for several days no detectable metathesis occurs,[35] whereas both extensive chlorination and exchange of methoxy groups from W immediately result if titanium tetrachloride solution is used at room temperature. The choice of chlorotrimethylsilane appears optimum at this point for selective chlorination, and such relative reactivity parallels similar experience noted earlier for chlorination of WF_6.[23]

Nmr Studies and Stereochemical Features.—Stereochemical configurations for each compound can be established from the nmr data. All isomers can be accounted for on the basis of octahedral coordination of the metal and concomitant monomer behavior in solution. For example, only one isomer of CH_3OWCl_5 is possible and gives rise to a single peak in its ^1H nmr spectrum.[36] Similarly, two isomers of $(CH_3O)_2WCl_4$ are comprised of a cis form [point group C_{2v}, nmr system $(A_3)_2$] and trans form [D_{4h}, $(A_3)_2$], each producing a single methyl resonance. In point of fact two such signals are observed, with similar intensity, indicating that both isomers are present in approximately equal amounts. It cannot be unequivocally determined from these nmr data alone which line may be assigned to which isomer, but sufficient general nmr data are available from previous and present work to permit probable assignments based on empirical chemical shift relationships. These parameters are collected along with appropriate nmr data from the earlier and current work in Tables I and II, wherein each nmr system is classified.

The chemical shift information for each observed resonance line (or multiplet center in the cases where multiplets result from H–F coupling) can be plotted as if a linearization scheme of the sort $\delta(Z) = pC + qT$[37] were appropriate. Here, C and T are adjustable parameters characteristic of a ligand and p and q are the number of halides (X) cis and trans, respectively, to the group whose resonance (for Z) is to be fit by the equation. Such an approach to additive substituent effects is appealing, particularly since it has been applied to another regular series of octahedral species, $SnL_nF_{6-n}{}^{2-}$, with the conclusion that empirical constants characteristic for the ligand L may be derived.[37] A similar view was stated in connection with like treatment of ^{19}F chemical shifts obtained for the WCl_nF_{6-n} series,[23b] and most recently approximately additive effects were ascribed to fluorine nmr data derived from the $(CH_3O)_nWF_{6-n}$ series.[19] In both of these latter instances involving W–F bonds, a sensible "trans effect" was also noted. For the tungsten chlorofluorides the line broadening seen only for F trans to Cl was thought to arise possibly from a preferential chlorine quadrupolar

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(32) A. M. Noble and J. M. Winfield, *J. Chem. Soc. A*, 501 (1970).

(33) H. Funk, E. Ebert, and F. Modry, *Z. Chem.*, **1**, 190 (1961).

(34) Among them bromides, as well as the pseudohalides cyanide and isocyanate. See ref 4.

(35) Nor indeed does an ionic process occur through formation of a seven-coordinate tungsten anion, *i.e.*, $(CH_3)_3SnCl + (CH_3O)_4WF_2 \rightarrow [(CH_3)_3Sn]^{-}$-$[(CH_3O)_4WF_2Cl]^{-}$. This possibility is suggested by formation of analogous salts from presumably stronger Lewis acids CH_3OWF_5 or $C_6H_5OWF_5$ interacting with phosphine donors,[32] as well as preparation of other stannonium salts, such as $(CH_3)_3SnCF_3 + BF_3 \rightarrow [(CH_3)_3Sn]^+[CF_3BF_3]^-$, reported by R. D. Chambers, H. C. Clark, and C. J. Willis, *J. Amer. Chem. Soc.*, **82**, 5298 (1960).

(36) It should be pointed out that far greater complexity is introduced in actual fact where ^{183}W nuclei ($I = {}^1/_2$) couple with H in H_3C–O–W bonds, and this situation is amplified for the fluoride members where non-first-order F–F couplings as well as H–F couplings require analysis.[26] Apparently, however, $J_{HH} \approx 0$ Hz for dissimilar CH_3O groups.

(37) P. A. W. Dean and D. F. Evans, *J. Chem. Soc. A*, 1154 (1968).

interaction, while for the methoxy compounds a larger upfield shift effect found for trans CH_3O was believed to be consistent with the assumption that the ability of ligands to act as π donors to tungsten t_{2g} orbitals follows the order $CH_3O > C_6H_5O > F$.[38]

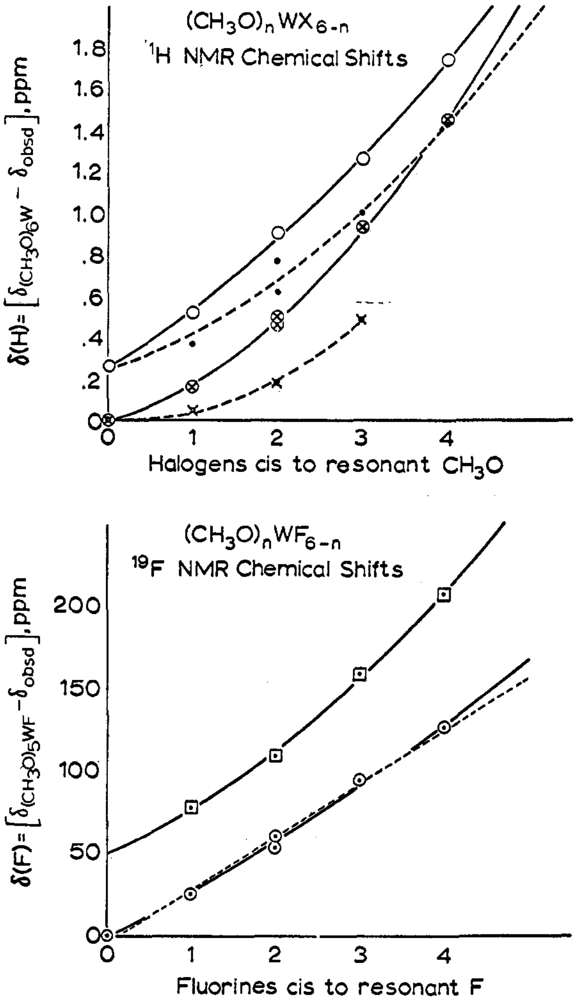

Figure 4.—Plots of δ(Z) *vs.* number of halogens cis to resonant Z in the series $(CH_3O)_nWX_{6-n}$. Experimental nmr shifts are superimposed (as circles) on calculated best-fit curves. Size of smallest circles indicates relative uncertainty in measured δ. Upper diagram: Z = H; solid lines for X = Cl; dashed lines for X = F; for $q = 0$ read ⊗ or ✖; for $q = 1$ read ○ or ●. Lower diagram: Z = X = F; for $q = 0$ read ○; for $q = 1$ read □; the dashed line with the lower curve represents a best linear fit of data.[39]

For the two series of compounds reported here, p ranges from 0 to 4, while q is either 0 or 1; thus the results are presented separately for $q = 0$ and $q = 1$ in Figure 4. It is immediately evident that observed parameters do not conform to a linear relationship but do fall closely on smooth curves which have similar shapes for both the fluorides and chlorides.[39] Further, these correlations afford bases for consistent spectral interpretation. For example, only assignment of the lower field nmr peak of the *cis*- and *trans*-$(CH_3O)_2WCl_4$ mixture to the trans isomer retains the smooth chloride curves illustrated. In another ambiguous case, namely, the assignment of the two proton peaks arising from the $(A_3)_2(M_3)_2$ spectrum derived from *cis*-$(CH_3O)_4WCl_2$, a best fit of *all* pertinent chemical shift data requires the adoption of the H_A protons as those in the methoxy groups trans to chlorine atoms. Fortunately, with other cases of geometry unambiguous identifications are possible as a result of unequal numbers of methoxy groups. For the methoxyfluorotungsten series [including the special case of *cis*-$(CH_3O)_4WClF$] additional questions emerge for both specific assignments of chemical shifts to each coordination site as well as the magnitude of applicable spin-coupling constants.

Just as with unsymmetrical methoxychlorides, analogous members of the fluoride series (*i.e.*, X, V_2X, and V_4X) permit unequivocal assignments of their ^1H or ^{19}F chemical shifts, but again application of some chemical shift correlation scheme is necessary to infer appropriate shifts for protons or fluorines at all coordination sites in molecules with highest symmetry. In the fluorine case, however, some additional support is derived from comparison of unequivocal H–F spin couplings determined for unsymmetric species where trends are observed. For all the definitive cases involving fluorine $J_{H-F} = 0.9$–1.2 Hz for CH_3O groups cis to the coupled fluorine, except where the cis CH_3O and the F are each trans to another methoxy group, whereupon $J \leq 0.5$ Hz.[40] For F coupling to trans CH_3O, $J_{H-F} = 1.8$–2.0 Hz in these cases.

cis,trans-$(CH_3O)_3WF_3$, *cis*-$(CH_3O)_4WF_2$, and *cis*-$(CH_3O)_4WClF$ represent useful examples of unequivocal, ambiguous, and partially resolved cases, respectively. On the bases of all site and symmetry considerations inferred from the chemical shift correlations in Figure 4 and in conjunction with J_{H-F} relationships just enumerated, a cohesive assignment may be derived for these three examples, as illustrated in Figure 5. For the unsymmetric WF_3 isomer all pertinent information is readily taken directly from ^1H and ^{19}F nmr spectra, but for the cis difluoride site assignments are derived from compatibility with the chemical shift curves previously discussed along with the J_{H-F} trends just described. The case for the cis chlorofluoride is partic-

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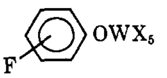
[38] Some prospect of a more quantitative comparison of transmission of substituent effects through metal–ligand $d\pi$–$p\pi$ interactions is possible from a consideration of Taft–Hammett parameters derived from ^{19}F nmr data for the series of isomers



where X = F or Cl: F. E. Brinckman, R. B. Johannesen, and L. B. Handy, *J. Fluorine Chem.*, in press.

[39] The curves shown all derive from a least-squares fit of equations of the form $\delta(Z) = ap^2 + bp + c$, where the following data are found.

Z	δ(Z)	X	q	a	b	c
H	$\delta_{(CH_3O)_6W} - \delta_{obsd}$	F	0	0.065	−0.035	0.005
			1	0.412	0.032	0.244
		Cl	0	0.061	0.123	−0.008
			1	0.030	0.250	0.256
F	$\delta_{(CH_3O)_5WF} - \delta_{obsd}$	F	0	1.54	25.8	−0.86
			1	4.35	22.05	49.75

The quality of fit can be demonstrated by comparing mean deviations of δ obtained by application of the parabolic function as opposed to a linear one. Curves compared for δ(*F*) where $q = 0$ (Figure 4, lower plot) give an extreme test: linear fit, 3.01 ppm, *vs.* parabolic fit, 2.25 ppm.

[40] In point of fact it is not presently possible to differentiate between J_{H-F} for methoxy groups either cis or trans to F in the special cases of symmetric molecules *cis,cis*-$(CH_3O)_3WF_3$ and *cis*-$(CH_3O)_4WF_2$. The respective trio and duo of fluorines appear to couple equivalently to the corresponding sets of OCH_3 but this actually depends on the magnitude of J_{H-H} for each case.[36] Thus for cis difluoride if $J_{H-H} \neq 0$, the spectrum becomes AA′XX′, and highly detailed nmr analysis might clarify this.[26] For the present work, the simple trends assumed appear adequate generally to assign coordination sites.

ularly interesting in that it offers a test of the foregoing general ideas yet provides a partially unambiguous system independent of the chemical shift or spin-coupling relationships rationalized from the $(CH_3O)_nWX_{6-n}$ series. As shown in Figure 5, assignment of sites for H_A protons is unambiguous from proton nmr intensities (see Figure 7); hence only the assignments for H_G and H_M sites must be inferred. Employing principally the J_{H-F} trends noted, preferred selections are indicated in Figure 5 and in Table I.

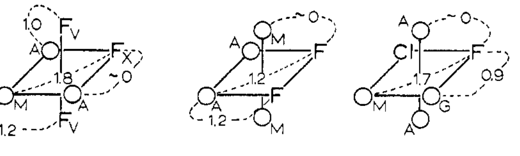


Figure 5.—Illustration of site and symmetry considerations employing chemical shift and H–F spin-coupling correlations. Shown left to right are *cis,trans*-$(CH_3O)_3WF_3$, *cis*-$(CH_3O)_4WF_2$, and *cis*-$(CH_3O)_4WClF$. All methoxy groups are symbolized by O. Pertinent nmr symmetry classes are denoted by sub- or superscripts A, G, M, V, or X; magnitudes for J_{H-F} assignments are indicated in hertz within dashed curves between appropriate ligands.[40]

These interpretations are consistent with proton chemical shift trends noted for the methoxychloride homologs, in that CH_3O groups on the chlorides display a general downfield shift relative to their fluoro analogs and that unlike the fluorides, Cl atoms trans to the observed methoxy groups do not confer a significantly larger downfield shift as compared with Cl atoms cis to CH_3O.

Based on the foregoing, it is important to recognize that use of chemical shift data for nuclei *both* directly bonded and indirectly bonded to tungsten(VI) appears to offer a reasonable approach to stereochemical assignments based on nonlinear correlations. The skeletal stability of $(CH_3O)_nW$ moieties is apparent from the reaction chart shown in Figure 2; hence the further application of methoxy protons as structural "probes" in related metathetical chemistry seems promising. It should also be stressed in this discussion that adherance to strictly linear chemical shift relationships of the sort used by others is ill suited for the interpretation of all the ^{19}F chemical shift parameters in the series $(CH_3O)_nWF_{6-n}$ and has led to the incorrect assignment of $(CH_3O)_5WF$ as the presently unknown trans isomer of $(CH_3O)_4WF_2$.[19] The correct assignment is clearly indicated by the ^1H spectrum which consists of two principal resonances in the ratio 4:1, each of which is split into a doublet due to H–F coupling. Moreover, this interpretation is also fully consistent with the appropriate nonlinear plot of ^1H chemical shift *vs.* p, illustrated for the methoxyfluoride resonances in Figure 4.

Retention and Conversion of Geometry during Exchange Reactions.—The formation of both cis and trans isomers is observed for the mixed chloride–fluorides of tungsten,[23] but both the $(CH_3O)_2$– and $(C_6H_5O)_2$–WF_4 compounds exist exclusively in the cis configurations.[18,19,41] The tendency toward formation of trans chloride geometries is further emphasized in the trisubstituted species, where $(CH_3O)_3WCl_3$ is formed exclusively as the cis,trans (C_{2v}) isomer, while the corresponding fluoride, whether prepared *via* fluorination of the preformed chloride or from the reaction of the methoxysilane and WF_6, exists as a 60:40 mixture of cis,cis (C_{3v}) and cis,trans isomers, respectively.

Both the tetramethoxydichloride and -difluoride, as formed *via* reaction of $CH_3OSi(CH_3)_3$ and WX_6, are found in the cis dihalo configuration as depicted in Figure 2. Moreover, complete fluorination of the chloride with SbF_3 proceeds exclusively with overall retention of this cis geometry, but no evidence is yet available regarding the nature of intermediate steps in the process (*e.g.*, formation of chlorofluorides), either for this step or the other fluorinations shown in the reaction chart.

In contrast to this, selective chlorination of the difluoride with $(CH_3)_3SiCl$ takes place in a homogeneous solution on a time scale suitable for detailed examination of the course of the reaction by nmr. Since it is clear that the final dichloride product forms in solution as a trans isomer [point group D_{4h}, nmr system $(A_3)_4$], barring unlikely rapid exchange processes, the appearance of a complex spectrum assignable to the intermediate chlorofluoride provides a further understanding for the overall inversion of geometry in proceeding from cis difluoride to trans dichloride. Two fundamental pathways can be envisioned whereby a trans isomer can uniquely form: these are illustrated in Figure 6, along with appropriate nmr classifications for participants. A closer examination of the time-dependent features in the proton nmr spectrum of methoxy groups bound to tungsten is informative; such an example is provided in Figure 7 where over 3 days the triplet–singlet $[(A_3)_2(M_3)_2X_2]$ pattern for cis difluoride (I) is seen to decay to a sharp downfield singlet assigned to trans dichloride (III). During the course of this reaction an initial growth and attenuation is seen for a five-line pattern for which formulation as a $(A_3)_2G_3M_3X$ spectrum is required on the basis of ^1H, ^{19}F, and ^1H-$\{^{19}F\}$ observations (*vide supra*). This is confirmation of the involvement of *cis*-tetrakis(methoxy)tungsten(VI) chlorofluoride (IIb) rather than the alternate trans isomer (IIa) as principal intermediate in the chlorination. In consequence, it must be concluded that isomerization does not occur in the first chlorination

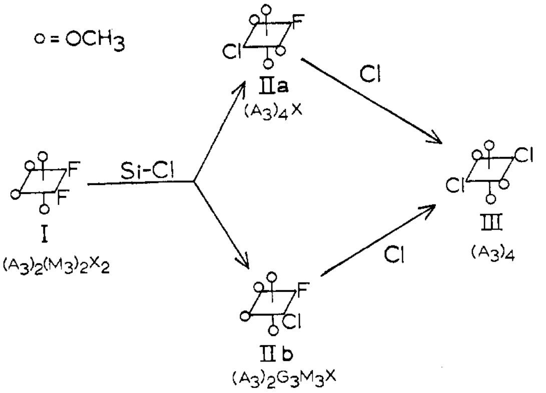


Figure 6.—Possible stereochemical courses for formation of *trans*-$(CH_3O)_4WCl_2$, showing the anticipated nmr spectral pattern associated with each intermediate possibility. Methoxy groups are signified by O.

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[41] F. E. Brinckman, R. B. Johannesen, K. L. Jewett, K. G. Sharp, and L. B. Handy, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. INOR 84.

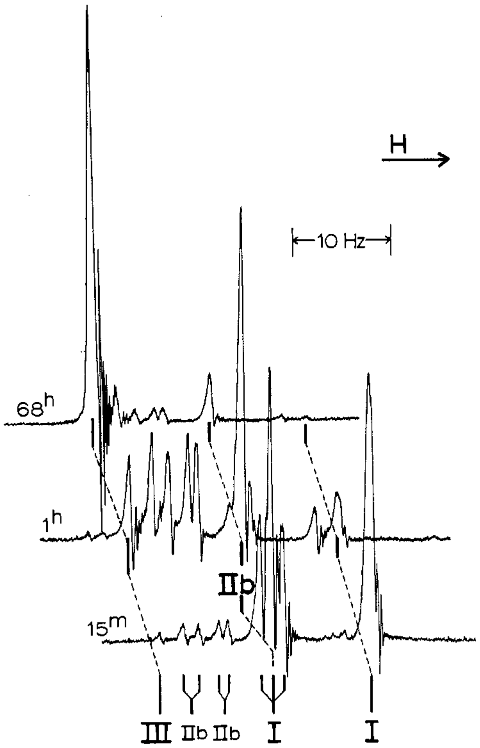

Figure 7.—The reaction between *cis*-$(CH_3O)_4WF_2$ and $(CH_3)_3SiCl$ observed by ^1H nmr as a function of time. Assignments for reactant cis difluoride (I), intermediate cis chlorofluoride (IIb), and final product trans dichloride (III) are indicated.

step, which involves Si–Cl and W–F bonds,[42] but rather reorganization results from a second W–Cl bond forming. It should be noted that either another Si–Cl or another W–Cl can now interact. The latter prospect is favored since it was seen that upon consumption of $(CH_3)_3SiCl$ in 1:1 reactions the cis WClF spontaneously synproportionates stereospecifically to cis difluoride and trans dichloride, in addition to the fact that either dichloride isomer is unaffected by the presence of $(CH_3)_3SiF$. On the whole, the specificity seen for the Cl–F exchange reaction is entirely consistent with the essentially quantitative production of geometrically pure *cis*-$(CH_3O)_2WF_4$ by redistribution between $(CH_3O)WF_5$ and *cis*-$(CH_3O)_4WF_2$.

Production of the trans dichloride isomer is in marked contrast to the stereochemistry found as a result of the reaction of $CH_3OSi(CH_3)_3$ and WCl_6, where the cis isomer only is formed. The ability to prepare separately the two isomers is particularly noteworthy in that rather different methods of preparation of various other members of the series have produced identical isomer distributions; for example, in the preparation of $(CH_3O)_3WF_3$ the same isomer mixture is obtained whether the compound is prepared by fluorination of the chloride, by reaction of $CH_3OSi(CH_3)_3$ with WF_6, or by the exchange reaction between $(CH_3O)_2WF_4$ and $(CH_3O)_4WF_2$. Additionally, no partial or complete separation or selective reaction of the isomeric pairs was obtained in the series of mixed chloride–fluorides.[23] Thus the separate preparation of the two dichloro isomers is of considerable importance, as it may allow subtle differences in reactivity to be investigated as a function of stereochemical configuration alone. The trans form is, however, converted into the cis isomer in the process of crystallization, isolation, and redissolution, and further investigation of the stability relationship between the two isomers is required.

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(42) A four-center transition state has been discussed for this and the W–Cl + W–F cases as well, where presumably tungsten adopts a coordination number of 7. See ref 23b.

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The Rates of Hydrolysis of the Monomeric Ruthenium(II) Chloride Complexes

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The electrochemical generation and identification of some monomeric ruthenium(II) chloride complexes and their rates of hydrolysis are reported. Cyclic voltammetry showed that these complexes undergo fairly rapid hydrolysis to ultimately form uncomplexed ruthenium(II). The rates of hydrolysis of the reduction products formed from $RuCl^{2+}$ and *cis*- and *trans*-$RuCl_2^+$ have been measured in 0.10 *M* *p*-toluenesulfonic acid.

Until recently the deep blue color of solutions formed by the action of strong reducing agents on ruthenium(III) and -(IV) compounds in chloride solution had been attributed to ruthenium(II) chloride complexes. We have shown[2] that the blue complexes are dimeric ruthenium(II,III) species which probably involve chloride bridges. The reversible polarograms[3] of the monomeric ruthenium(III) chloride complexes[4] suggested that the ruthenium(II) chloride complexes existed as

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(1) Work carried out by P. E. Dumas in partial fulfillment of the Ph.D. degree, University of South Carolina, 1971.

(2) E. E. Mercer and P. E. Dumas, *Inorg. Chem.*, **10**, 2755 (1971).

(3) R. R. Buckley and E. E. Mercer, *J. Phys. Chem.*, **70**, 3103 (1966).

(4) (a) H. H. Cady and R. E. Connick, *J. Amer. Chem. Soc.*, **80**, 2646 (1958); (b) D. A. Fine and R. E. Connick, *ibid.*, **82**, 4187 (1960); (c) D. A. Fine and R. T. Connick, *ibid.*, **83**, 3414 (1961).