Chemistry of the Methoxyfluorotungsten(VI) Series

By LARRY B. HANDY† and FREDERICK E. BRINCKMAN*

(*Institute for Materials Research, National Bureau of Standards, Washington, D.C.* 20234)

Summary The series of compounds $(MeO)_nWF_{6-n}$, $n =$ 1—5, has been prepared by the reaction of WF_6 and Me_3SiOMe and the stereochemical configuration of each member has been assigned on the basis of ^{19}F and ^{1}H n.m.r. data.

ALTHOUGH an extensive metathetical chemistry of the main group fluorides is known, very little is known about the chemistry of the transition metal fluorides stabilized in their highest oxidation states. Several of the mixed chloride-fluorides of tungsten(VI) have been reported by Fraser,

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† NRC–NBS Postdoctoral Research Associate, 1968—1970.

Mercer, and Peacock,[1] and by O'Donnell and Stewart,[2] and $MeOWF_5$ has recently been reported by Noble and Winfield.[3] Stable tungsten(VI) compounds have also been prepared in the reactions of WCl_6 with PhOH and *p*-$Me{\cdot}C_6H_4OH$ to yield $(ArO)_6W$,[4] and WCl_6 with $LiNMe_2$ to yield $(Me_2N)_6W$.[5]

TABLE 1. ^{19}F *n.m.r. data*

Compound	N.m.r. system	Chemical shift[a]	Reference	$J(F_A - F_X)$[b]	$J(W - F_X)$[b]
$(MeO)WF_5$[c]	AX_4	−89·5 (F_A)	I	66	
		−118·5 (F_X)	I		43
cis-$(MeO)_2WF_4$	A_2X_2	−44·8 (F_A)	I	65	
		−63·9 (F_X)	I		44
cis–cis-$(MeO)_3WF_3$	A_3	−17·7	E	—	—
cis–trans-$(MeO)_3WF_3$	AX_2	−10·7 (F_A)	E	60	
		−35·0 (F_X)	E		45
cis-$(MeO)_4WF_2$	A_2	+15·1	I		
$(MeO)_5WF$	A	+42·5	E		

[a] Chemical shifts are in p.p.m. relative to CCl_3F, either internal (I) or External (E). The estimated uncertainty is ±0·2 p.p.m. or less, but concentration and solvent effects could easily account for larger deviations. All spectra run in C_6F_6 solvent.

[b] Coupling constants are estimated to be accurate to within ±2 Hz.

[c] Data from ref. 3.

TABLE 2. ^1H *n.m.r. data*

Compound	Chemical shift[a]	Description	Splitting[b]
$MeOWF_5$[c]	5·60	Multiplet	1 Hz
cis-$(MeO)_2WF_4$	5·10	Unresolved multiplet	
cis–cis-$(MeO)_3WF_3$	4·79	Unresolved multiplet	
cis–trans-$(MeO)_3WF_3$	4·93	Doublet of triplets	1·8 Hz (doublet) 1·2 Hz (triplet)
	4·65	Triplet	1·0 Hz
cis-$(MeO)_4WF_2$	4·45	Triplet	1·2 Hz
	4·25	Singlet	
$(MeO)_5WF$	4·35	Doublet	2·0 Hz
	4·15	Doublet	0·5 Hz

[a] Chemical shifts in p.p.m. are relative to external Me_4Si, with estimated uncertainty of ± 0·05 p.p.m. All spectra run in C_6F_6 solvent.

[b] Estimated uncertainty of ±0·3 Hz.

[c] Data taken from ref. 3.

We have found that the reaction of WF_6 with Me_3SiOMe in C_6F_6 is a convenient method of preparation for $MeOWF_5$ as well as the hitherto unreported members of the series $(MeO)_nWF_{6-n}$ with $n = 2$—4. Each member of the series can be initially prepared in about 90% purity, free of the neighbouring members of the series, by careful control of stoicheiometry. In addition, $(MeO)_4WF_2$ reacts slowly (*ca.* 50% in 5 days) with Me_3SiOMe to form $(MeO)_5WF$. The final member of the series, $(MeO)_6W$, has been prepared by Bradley and his co-workers[6] from $(Me_2N)_6W$, but has not been prepared by reaction of the tungsten fluorides with an excess of Me_3SiOMe. ^1H and ^{19}F n.m.r. data have been obtained for each member of the series, and $(MeO)_4WF_2$ has been further characterized by elemental analysis and by *M* determination in C_6F_6. The analytical results are within 0·5% of theory for all elements, with oxygen by difference, and the *M* of 342 ± 15 confirms that $(MeO)_4WF_2$ is monomeric in C_6F_6. The tetramethoxy-compound is readily sublimable at 50—60° (10^{-4} torr) and melts without decomposition at 81—83° (uncorrected).

The n.m.r. data for these compounds are shown in Tables 1 and 2. The lines in the fluorine spectra typically have half-widths of 5—10 Hz, possibly due to unresolved H–F coupling. H–F coupling is evident in the ^1H n.m.r. spectra, and the resulting complexity makes the detailed assignment of coupling constants difficult in several cases. Double irradiation experiments should be useful in both the fluorine and proton spectra. On the basis of the n.m.r. data from the reported reaction, $(MeO)_2WF_4$ and $(MeO)_4WF_2$ are formed exclusively as the *cis*-isomers, while $(MeO)_3WF_3$ is a mixture of the two possible isomers, 60% *cis–cis* (^{19}F n.m.r. system A_3) and 40% *cis–trans* (^{19}F n.m.r. system AX_2). Both the ^1H and the ^{19}F chemical shifts vary in a regular manner as a function of the degree of substitution, in contrast to the case of the fluorine shifts in the mixed chloride–fluorides.

Reactivity of the remaining fluorine atoms decreases with increasing methoxy-substitution, as shown by the slow formation of the pentamethoxy-species. This attenuated reactivity is expected to be of value in introducing σ-bonded groups such as NMe_2 *via* the silazane.

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