Diethylamido- and Pentafluorophenoxo-tungsten(VI) Fluorides †

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Tungsten hexafluoride reacts with trimethylsilyldiethylamine or trimethyl(pentafluorophenoxo)silane at or below ambient temperature with the replacement of F by $-NEt_2$ or $-OC_6F_5$ groups. Compounds isolated were monomeric $WF_2(NEt_2)_4$, polymeric $WF_4(NEt_2)_2$, and monomeric $WF_5OC_6F_5$. $WF_4(OC_6F_5)_2$ appears to exist in *cis*- and *trans*-forms and undergoes reorganisation to give other members of the series.

CLEAVAGE of element–silicon bonds in Me_3Si-X compounds has been used to prepare substituted derivatives of tungsten hexafluoride of the type $WF_{6-n}X_n$, where X = Cl,[1] OMe [2] or OPh,[2a] and WF_5NEt_2.[3] With the exception of WF_5NEt_2, these compounds are monomeric in solution, *cis*-isomers being favoured for $WF_4(OR)_2$ and $WF_2(OMe)_4$. WF_5NEt_2 is a viscous liquid which appears to be polymeric. It was of interest therefore to prepare other members of the series $WF_{6-n}(NEt_2)_n$ from reactions of WF_6 with trimethylsilyldiethylamine. Similar work involving niobium or tantalum pentafluorides has shown that substitution does not proceed beyond $MF_3(NEt_2)_2$ (M = Nb or Ta) at room temperature.[4] Dialkylamide-groups are potentially π-donor ligands to d^0 transition metals,[5] and thus we have also investigated pentafluorophenoxo-derivatives of WF_6 to compare the possible π-donor properties of this ligand with those of the MeO– and PhO– groups. Since the completion of this work the n.m.r. spectrum of $WF_5OC_6F_5$ has been reported although the compound was not isolated.[6]

EXPERIMENTAL

All operations were performed *in vacuo* or in a Lintott inert-atmosphere box in which the concentrations of H_2O and O_2 were $\leqslant 14$ p.p.m. Techniques used for the purification of materials, for the reactions, for obtaining n.m.r., i.r., Raman, and electronic spectra, and for density measurements were as described previously.[2a,3,4,7] N.m.r. chemical shifts are expressed as δ values from internal Me_4Si (^1H) or CCl_3F (^{19}F), a positive value indicating a low-field shift.

Molecular weights in C_6F_6 were determined by lowering of vapour pressure by use of WF_5OMe, which is monomeric in C_6F_6,[7] as calibrant [Found: *M* (mole fraction in C_6F_6), 358 (0·118), 341 (0·073), 344 (0·060), 328 (0·050). Calc. for WF_5OMe: *M*, 310]. Tungsten was determined gravimetrically as WO_3. Trimethyl(pentafluorophenoxo)silane was prepared by a literature method.[8]

Preparation of Diethylamidotungsten(VI) *Fluorides*.—(*a*) $WF_2(NEt_2)_4$. Tungsten hexafluoride (8·1 mmol) and trimethylsilyldiethylamine (51·3 mmol) at 20 °C for 24 h gave a mixture (5·9 g; required for 1 : 4 reaction 5·7 g) of trimethylfluorosilane and unchanged Me_3SiNEt_2, which was not quantitatively separated, and a dark brown, sticky solid identified as *tetrakis*(*diethylamido*)*tungsten*(VI) *difluoride* [Found: C, 37·3; H, 7·7; F, 7·3; W, 36·7%; *M* (mol fraction in C_6F_6), 562 (0·152), 564 (0·117), 566 (0·075), 556 (0·065), 558 (0·052). Calc. for $C_{16}H_{40}F_2N_4W$: C, 37·7; H, 7·9; F, 7·5; W, 36·1%; *M*, 510]. Its i.r. spectrum [$\nu_{max.}$ (4000—400 cm^{-1}): 3215s, 3130sh, 2995s, 2945s, 2889m, 1590s, 1465sh, 1415s, 1381s, 1335m, 1312s, 1275sh, 1185s, 1145w, 1130s, 1090s, 1065s, 1020sh, 1002s, 895s, 800s, 695s, 600sbr, 465mbr, 420sh cm^{-1}] was similar to those of transition-metal diethylamides [9] and $MF_{5-n}(NEt_2)_n$ (M = Nb or Ta; *n* = 1 or 2) compounds,[4] but the presence of bands above 3000 cm^{-1} suggest that trace quantities of co-ordinated $NHEt_2$ could have been present.

The ^1H n.m.r. spectrum of $WF_2(NEt_2)_4$ in C_6F_6 or CS_2 contained signals (relative intensities 3 : 2) due to $-NEt_2$ groups at δ = 1·26 (partially resolved triplet) and 4·3 p.p.m. (broad featureless signal), and its ^{19}F spectrum consisted of two singlets, δ = –21 and –16 p.p.m. (relative intensity *ca.* 3 : 1).

(*b*) $WF_4(NEt_2)_2$. (i) WF_6 (14·5 mmol) and Me_3SiNEt_2 (29·1 mmol) at 20 °C for 12 h gave Me_3SiF (29·1 mmol) and a dark red, viscous liquid (Found: C, 23·8; H, 5·8; F, 18·7; N, 6·8; W, 45·5. Calc. for $C_8H_{20}F_4N_2W$: C, 23·8; H, 5·0; F, 18·8; N, 6·9; W, 45·5%). (ii) $WF_2(NEt_2)_4$ (2·9 mmol) and WF_6 (36·2 mmol) at 20 °C for two weeks gave unchanged WF_6 (32·8 mmol) and a dark red, viscous liquid (Found: C, 23·5; H, 4·8; F, 18·8; N, 7·1; W, 45·2%). Both liquids were spectroscopically identical. I.r. spectrum $\nu_{max.}$ (4000—400 cm^{-1}): 3150wbr, 2985s, 2942m, 2883m, 2500w, 1595wbr, 1530s, 1455s, 1378m, 1350m, 1310m, 1276w, 1190m, 1141m, 1130w, 1090m, 1065m, 1042w, 1012m, 992s, 908m, 895m, 795m, 661w, 640m, 600s, 555w, 508w, and 460w cm^{-1}. ^1H N.m.r. spectrum: two broad featureless signals at δ = 1·3 and 4·2 p.p.m. No ^{19}F spectra could be obtained, possibly owing to the high viscosity of the samples. The densities of both liquids were very similar: d_4^t/g cm^{-3} = 2·00 – 0·0014*t* and 2·13 – 0·0012*t* respectively in the range 20—50 °C. Both products were formulated as *bis*(*diethylamido*)*tungsten*(VI) *tetrafluoride*.

(*c*) *Attempted preparation of* $WF_3(NEt_2)_3$. WF_6 (6·1 mmol) and Me_3SiNEt_2 (18·4 mmol) at 20 °C for 48 h gave

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† No reprints available.

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Me_3SiF, unchanged Me_3SiNEt_2, and a dark red, viscous liquid (Found: C, 23·6; H, 4·9; F, 19·1; N, 6·8; W, 45·4. Calc. for $C_8N_{10}F_4N_2W$: C, 23·8; H, 5·0; F, 18·8; N, 6·9; W. 45·5%). Repetition of the reaction with longer times (up to 4 weeks) did not yield the hoped-for product.

Preparation of Pentafluorophenoxotungsten(VI) *Fluorides.*—(*a*) $WF_5OC_6F_5$. WF_6 (24·6 mmol) and trimethyl(pentafluorophenoxo)silane (15·6 mmol) at 0 °C for 0·5 h gave a mixture of Me_3SiF and unchanged WF_6 (3·9 g; required for 1 : 1 reaction 4·0 g) and a red liquid, slightly volatile at 20 °C, identified as *pentafluorophenoxotungsten*(VI) *pentafluoride* [Found: C, 15·8; F, 40·9; W, 40·2%; *M* (mol. fraction in C_6F_6): 518 (0·74), 501 (0·56), 496 (0·51), 491 (0·50), 479 (0·45). Calc. for $C_6F_{10}OW$: C, 15·6; F, 41·1; W, 39·8%; *M*, 462]. The vibrational spectrum of the liquid [Raman $\nu_{max.}$: 1633s, 1472vs, 1333s, 1198vs, 1051s, 767s, 724w, 498m, and 285w cm^{-1}; i.r. (2000—400 cm^{-1}) $\nu_{max.}$: 1624m, 1535sh, 1530s, 1515s, 1470sh, 1365m, 1332s, 1329sh, 1260w, 1192s, 1185sh, 1165sh, 1050s, 1010sh, 1001sh, 722s, 670s, 650sh, 635sh, 502w, and 455w cm^{-1}] indicated the presence of a C_6F_5 group.[10] Its ^{19}F n.m.r. spectrum consisted of an AB_4 signal due to the $-WF_5$ group (Table) and three signals at high field assigned to the C_6F_5 group. A full analysis of the latter could not be made owing to insufficient resolution, but a partial analysis, by comparison with related compounds,[11] gave $\delta(F_{ortho})$ −152, $\delta(F_{meta})$ −161, $\delta(F_{para})$ −151 p.p.m., and $^3J(F_{para}F_{meta})$ 20 Hz. $^4J(F_{ortho}F_{para})$ was not resolved although the 1 : 2 : 1 triplet due to F_{para} was broadened. The spectrum of $WF_5OC_6F_5$ reported previously[6] was recorded at a higher resonance frequency (84·67 MHz) than that used here, enabling better resolution to be obtained.

N.m.r. spectra (W–F region) of the products from reactions of WF_6 with $Me_3SiOC_6F_5$

Mol ratio $WF_6 : Me_3SiOC_6F_5$	Signal[a]	Chemical shifts[b] p.p.m.	Coupling constants/Hz	Assignments
1·6 : 1	AB_4; $J/\nu\delta = 0·31$	δ_A 141, δ_B 145	J_{AB} 70	$WF_5OC_6F_5$
1 : 2·1	AB_4	δ_A 138, δ_B 144		$WF_5OC_6F_5$
	A_2B_2; $J/\nu_0\delta = 0·35$	δ_A 122, δ_B 125	J_{AB} 65	*cis*-$WF_4(OC_6F_5)_2$
	Singlet	132		*trans*-$WF_4(OC_6F_5)_2$?[c]
	Doublet	114	59	*mer*-$WF_3(OC_6F_5)_3$?[d]
	Singlet	105		*fac*-$WF_3(OC_6F_5)_3$, *cis*- or *trans*-$WF_2(OC_6F_5)_4$ or $WF(OC_6F_5)_5$ are possible assignments
	Singlet	69		

[a] AB_4 and A_2B_2 spectra analysed according to R. K. Harris and K. J. Packer, *J. Chem. Soc.*, 1961, **4739** and to P. L. Corio *Chem. Rev.*, 1960, **395** respectively. Coupling of the C_6F_5 group assumed to be absent. [b] To low field of CCl_3F. [c] Tentative assignment by analogy with *cis*-isomer. [d] Expected triplet too weak to be observed.

(*b*) *Other members of the series* $WF_{6-n}(OC_6F_5)_n$. WF_6 (1·6 mmol) and $Me_3SiOC_6F_5$ (3·3 mmol) at 20 °C for 7 days gave Me_3SiF, and a red liquid slightly volatile at 20 °C. A similar product was formed from WF_6 (3·7 mmol) and $Me_3SiOC_6F_5$ (6·8 mmol). Analyses of the liquid corresponded to $WF_4(OC_6F_5)_2$ [Found: C, 22·6; F, 42·3; W, 29·7. Calc. for $C_{12}F_{14}O_2W$: C, 23·0; F, 42·5; W, 29·4%) but its ^{19}F n.m.r. spectrum indicated that several W–F species were present (Table). At least nine signals in the region −156 to −169 p.p.m. were observed, but their complexity prevented assignment of individual C_6F_5 groups.

RESULTS AND DISCUSSION

Diethylamido-compounds.—WF_6 reacts with a large excess of Me_3SiNEt_2 at room temperature to give tetrakis(diethylamido)tungsten(VI) difluoride according to equation (1). $WF_2(NEt_2)_4$ is a dark brown sticky solid,

$$WF_6 + 4Me_3SiNEt_2 \longrightarrow WF_2(NEt_2)_4 + 4Me_3SiF \quad (1)$$

involatile at 20 °C and rapidly hydrolysed in moist air. It is decomposed by most organic solvents but is soluble in C_6F_6 or CS_2 without reaction. Molecular weight determinations in C_6F_6 suggest that $WF_2(NEt_2)_4$ is monomeric. The two single-line resonances in its ^{19}F n.m.r. spectrum may mean that both *cis*- and *trans*-isomers are present but confirmatory evidence is not available from its ^1H spectrum as the two signals observed are broad. Steric factors favour the *trans*-isomer while W–N d_π–p_π bonding favours the *cis*, as is found in $WF_2(OMe)_4$.[2b,12] Attempts to prepare pure $WF_2(NMe_2)_4$ for comparison were unsuccessful.[13]

A dark red, viscous liquid which analyses as bis(diethylamido)tungsten(VI) tetrafluoride is formed according to equations (2) or (3). Its physical and chemical properties are similar to WF_5NEt_2 which, it has

$$WF_6 + 2Me_3SiNEt_2 \longrightarrow WF_4(NEt_2)_2 + 2Me_3SiF \quad (2)$$

$$WF_6 + WF_2(NEt_2)_4 \longrightarrow 2WF_4(NEt_2)_2 \quad (3)$$

been suggested, is polymeric *via* fluorine bridges.[3] Reactions designed to prepare $WF_3(NEt_2)_3$ were unsuccessful, either $WF_4(NEt_2)_2$ or a mixture, containing $WF_4(NEt_2)_2$ and $WF_2(NEt_2)_4$, being obtained. Although polymeric $WF_3(NEt_2)_3$ may not have been isolated owing to steric interaction between the three $-NEt_2$ groups in a structure where W is at least seven-co-ordinate, there is no obvious reason why monomeric $WF_3(NEt_2)_3$ should

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not exist. Increasing dialkylamido-for-halide substitution in titanium tetrahalides favours monomeric structures;[14] for example, $TiF(NEt_2)_3$ appears to be monomeric in solution.[15] The available evidence suggests that a similar situation obtains for WF_6.

It is of interest to compare the diethylamido-tungsten(VI) fluorides with the tellurium analogues as the two hexafluorides are of similar size.[16] The monomeric compounds TeF_5NR_2 ($R = Me$ or Et), *cis*-$TeF_4(NMe_2)_2$, and the unstable *cis*-$TeF_4(NMe_2)(NEt_2)$ are formed from TeF_6 and Me_3SiNR_2, but further substitution was not observed.[17] Evidently the Te–N bond energies in these compounds are insufficiently high to compensate for steric repulsions between $-NEt_2$ groups. In the tungsten series the formation of strong W–N bonds contributes to the stability of $WF_2(NEt_2)_4$ and it is noteworthy that monomeric $W(NMe_2)_6$ has been reported.[18]

Pentafluorophenoxo-compounds.—Pentafluorophenoxotungsten(VI) pentafluoride is formed from excess of WF_6 and $Me_3SiOC_6F_5$ at 0 °C. It is a red liquid, readily hydrolysed in moist air and slightly volatile at room temperature. Its n.m.r. spectrum (Table) and molecular weight determinations in C_6F_6 indicate that it is monomeric. Its colour is due to a strong broad band in its electronic spectrum, $\nu_{max.} = 28{,}600$ (in C_6F_6), 29,000 cm^{-1} in (Me_4Si), which tails into the visible region. The spectrum is similar to that of WF_5OPh, for which $\nu_{max.} = 27{,}800\ cm^{-1}$ (in C_6F_6 or Me_4Si),[19] and it is likely that in both cases the bands are due to intramolecular charge transfer.

The n.m.r. chemical shifts of the WF_5 group in $WF_5OC_6F_5$ occur to low field of those in WF_5OMe or WF_5OPh but in all three compounds F_t (*trans* to the $-OR$ group) is more shielded than F_c (*cis* to $-OR$). The increased shielding of F_t compared with F_c in the compounds $WF_{6-n}(OMe)_n$ ($n = 1$—5) and the upfield shifts of both F_c and F_t resonances that are observed as n increases, have been explained in terms of an increase in electron density at the W atom when an F atom is replaced by an $-OMe$ group. The $-OPh$ group has a similar, though smaller, effect.[12] The values of $\delta(F_t) - \delta(F_c)$ in WF_5OR are 4(C_6F_5), 14(Ph), and 29 p.p.m. (Me) indicating that replacement of F by OC_6F_5 has only a small net effect on the electron density at W.

Reactions between WF_6 and $Me_3SiOC_6F_5$ designed to prepare $WF_4(OC_6F_5)_2$ lead to a mixture of products, although the overall analysis of the red liquid product corresponds to disubstitution. Two of the species present in the liquid can be identified from its n.m.r. spectrum (Table) as $WF_5OC_6F_5$ and *cis*-$WF_4(OC_6F_5)_2$, these giving the most intense signals. Assuming that all the species present are monomeric, and by analogy with the ^{19}F chemical shifts of the series $WF_{6-n}(OMe)_n$,[2] we can make some very tentative assignments of the remaining three singlets (all of similar intensity) and the very weak doublet (Table). Apparently a redistribution equilibrium of the type indicated in equation (4) exists as the spectrum was unchanged after several weeks.

$$2WF_4(OC_6F_5)_2 \rightleftharpoons WF_5OC_6F_5 + WF_{6-n}(OC_6F_5)_n\ (n > 2) \qquad (4)$$

The compounds $WF_4(OR)_2$ ($R = Me$ or Ph) do not undergo redistribution reactions on standing and appear to exist exclusively in the *cis*-form,[2] but a mixture of *cis*- and *trans*-WF_4Cl_2 readily undergoes redistribution at room temperature.[1] Heats of hydrolysis measurements on $WF_{6-n}Cl_n$ and $WF_{6-n}(OMe)_n$ compounds suggest that the observed chemical differences between the two series have a thermochemical basis,[20] and the present work suggests that the $W-OC_6F_5$ bond is electronically more similar to W–Cl than to W–OMe. A possible reason for this is that p_π–d_π contributions to the W–O bands are more important in the methoxide series than in the pentafluorophenoxide series.

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