Complexes Between Fluoro(ditertiary arsines) and Metal Tetrahalides

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The influence of incorporating fluorine atoms into ditertiary arsines on the reactions of the latter with metal halides has been investigated. The fluoroalicyclic-bridged ligands, 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene and 1,2-bis(dimethylarsino)-3,3,4,4,5,5-hexafluorocyclopentene, and the fluoroaromatic-bridged ligands, 1,2-bis(dimethylarsino)-3-fluorobenzene and 1,2-bis(dimethylarsino)-4-fluorobenzene, form six-co-ordinate complexes [MX_4(diarsine)] (M = Ti, V, Mo, Re, or Sn; X = Cl or Br). Eight-co-ordinate dodecahedral bis adducts are formed only with niobium tetrachloride and tetrabromide, and with the last three diarsine ligands. Complexes with nickel(II) and iron(II) confirm that these fluorodiarsines are weaker donors than are conventional diarsine ligands.

DITERTIARY arsines and phosphines form either six-co-ordinate, [MX_4(bidentate)], or eight-co-ordinate complexes, [MX_4(bidentate)$_2$], with metal tetrahalides depending on the choice of metal halide and ligand.[1] In this work the influence of incorporating fluorine atoms into the ditertiary arsines has been explored.[2]

Two types of ligand have been used, the fluoroaromatic-bridged 1,2-bis(dimethylarsino)-3-fluorobenzene and 1,2-bis(dimethylarsino)-4-fluorobenzene (3- and 4-Fpdma), and the fluoroalicyclic-bridged 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene (dtcb) and 1,2-bis(dimethylarsino)-3,3,4,4,5,5-hexafluorocyclopentene (dhcp). Apart from a description of the structure of [$ReCl_4$(dtcb)] prepared during this work,[3] there have been no reports of the reactions between fluoroarsines and metals in high oxidation states, in marked contrast to the extensive studies with metals in low oxidation states.[4]

RESULTS

The difficulty observed in forming complexes of the later transition-metal halides with dtcb [4,5] was not experienced in reactions with the early transition-metal halides. Like *o*-phenylenebis(dimethylarsine) (pdma), the ligand co-ordinated instantly to titanium tetrachloride, but the arsenic–metal bonds were not as strong as in the case of pdma. This is illustrated by the formation of [$TiCl_4$(pdma)] on mixing [$TiCl_4$(dtcb)] and pdma in acetonitrile. The ligands dtcb, dhcp, 3-Fpdma, and 4-Fpdma co-ordinated to $TiCl_4$, $TiBr_4$, and $SnCl_4$ in inert solvents to yield 1 : 1 adducts of the type [MX_4(diarsine)]. Vanadium tetrachloride formed a 1 : 1 adduct with 4-Fpdma. The magnetic moment of 1.76 B.M.† is similar to those of other vanadium(IV) complexes.[1,6] Dark green reduction products, the exact compositions of which are unknown, were formed with dtcb and dhcp. The complexes [$MoCl_4$(dtcb)] and [$MoCl_4$(dhcp)] were prepared by reaction of the ligand and the pentachloride in acetonitrile. The low yields were due to continued reduction to [$MoCl_3$(dhcp)].[7]

Similar reduction of rhenium pentachloride to adducts of rhenium tetrachloride is not uncommon.[8] Two complexes, [$ReCl_4$(dtcb)] and [$ReCl_4$(dhcp)], were prepared in this work by the reaction of dtcb and dhcp with $ReCl_5$ in carbon tetrachloride. These complexes are more stable than other complexes of the early transition-metal halides containing these ligands. Crystals of [$ReCl_4$(dtcb)] were obtained from nitromethane, and crystal-structure analysis [3] confirms a slightly distorted octahedral arrangement about the rhenium atom with dtcb acting as a chelating bidentate ligand. The room-temperature effective magnetic moments of 2.97 and 2.55 B.M. for [$ReCl_4$(dtcb)] and [$ReCl_4$(dhcp)], respectively, are lower than the values of *ca.* 3.4 B.M. generally reported for rhenium(IV) complexes.[8,9]

TABLE 1

Absorption maxima (10^3 cm^{-1}) in the diffuse-reflectance spectra, and magnetic data (room temperature), of niobium complexes

	$d_{xy} \rightarrow d_{z^2}$	$d_{xy} \rightarrow d_{xz}, d_{yx}$	$d_{xy} \rightarrow d_{x^2-y^2}$	$\mu_{eff.}$/B.M.
[$NbCl_4$(dhcp)$_2$]	9.8	13.3 (14.3) [a]	17.8	1.81
[$NbCl_4$(3-Fpdma)$_2$] [b]	11.0	13.9	17.3	1.90
[$NbCl_4$(4-Fpdma)$_2$]	10.5	13.7 (14.3) [a]	17.5	1.70
[$NbBr_4$(dhcp)$_2$]	9.7	13.7 [c]	16.75	1.72
[$NbBr_4$(3-Fpdma)$_2$] [b]	9.4	12.9 [c]	15.35	1.66
[$NbBr_4$(4-Fpdma)$_2$]	10.3	13.3 [c]	16.4	1.75

[a] Shoulder. [b] The data may be unreliable as magnetic or analytical data suggest the presence of impurities. [c] Indistinct shoulder.

All six complexes in the series [NbX_4L_2] (X = Cl or Br; L = dhcp, 3-Fpdma, or 4-Fpdma) were precipitated as air-unstable green solids from acetonitrile. The dhcp complexes were also prepared by the reaction of niobium pentahalides

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† 1 B.M. ≈ 9.27×10^{-24} A m^2; 1 mmHg ≈ 13.6×9.8 Pa.

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and ligand in sealed tubes at 80—100 °C. The room-temperature effective magnetic moment for all the niobium complexes (Table 1) of *ca.* 1.7 B.M. indicates the niobium atoms are in the oxidation state IV. The range of values obtained, and the observation that some are above the spin-only value for one unpaired electron, is not easily explained. The possibility of minute (1 in 10^6) amounts of ferromagnetic impurity exists,[10] in spite of improved preparative techniques. Three *d–d* bands were observed in the diffuse-reflectance spectra of all the complexes between 9 000 and 20 000 cm^{-1} (Table 1), with a shoulder appearing on the most intense (middle) band. The form of the spectra, and the assignments, are similar to Nb^{IV} complexes of other ditertiary arsines,[11] and clearly point to a dodecahedral stereochemistry with the arsenic atoms occupying the A sites and the halogen atoms the B sites. In agreement with these assignments, and with previous work,[11] it was again observed that the band at *ca.* 17 000 cm^{-1} changed most with changes in halogen atom, whereas the band of lowest energy was most dependent on the arsine ligand.

DISCUSSION

The results are contrary to what might be expected from the electroneutrality principle, which suggests that a metal atom may be able to accommodate additional ligands of weaker donor strength.

The four fluorodiarsines form only six-co-ordinate 1 : 1 adducts with TiCl_4. The non-existence of the eight-co-ordinate complexes, particularly $[\text{TiCl}_4(3\text{-Fpdma})_2]$ and $[\text{TiCl}_4(4\text{-Fpdma})_2]$, is unexpected, considering the steric similarity to pdma [12] and 1,2-bis(dimethylarsino)-4-methylbenzene (4-Mepdma) [13] which form 1 : 2 adducts. The difference in behaviour appears to arise from the fluorine atoms withdrawing electrons from the donor atoms, making these ligands weaker than pdma in terms of co-ordinating ability. Similarly eight-co-ordinate complexes could not be isolated with zirconium, hafnium, or vanadium tetrachlorides,[7] which form such complexes with pdma [12] and 4-Mepdma,[7] or with molybdenum or tin chlorides.

Niobium tetrachloride and tetrabromide form eight-co-ordinate $[\text{NbX}_4\text{L}_2]$ adducts with 3-Fpdma, 4-Fpdma, and dhcp. This is in contrast to the other metal tetrahalides; in particular, Zr^{IV} and Nb^{IV} are expected to be of similar size, although any metal-to-ligand π bonding from the d^1 Nb^{IV} ion is expected to be enhanced by the fluorine atom. The formation of eight-co-ordinate bis adducts with Nb^{IV} but only six-co-ordinate monoadducts with Ti^{IV} has previously been noted for *o*-phenylenebis(diethylarsine) [11,13,14] and *racemic-o*-phenylenebis(methylphenylarsine).[15] The ligand dtcb, which would be expected to have similar properties to dhcp, does not form eight-co-ordinate adducts, presumably because of the greater arsenic–arsenic distance.

The effect of the fluorine atoms on the ditertiary arsines is not reflected to any degree in the electronic spectra of the $[\text{TiCl}_4(\text{diarsine})]$ or $[\text{NbCl}_4(\text{diarsine})_2]$ complexes. Nevertheless the weaker co-ordinating ability of 4-Fpdma is confirmed by studies of $[\text{Ni}(4\text{-Fpdma})_2\text{Cl}_2]$, which is green and paramagnetic ($\mu_{\text{eff.}}$ 3.3 B.M.), in a similar manner to $[\text{Ni}\{\text{C}_6\text{F}_6(\text{AsMe}_2)_2\}_2\text{Cl}_2]$,[16] but in contrast to the diamagnetic brown complex $[\text{Ni}(\text{pdma})_2\text{Cl}_2]$.[17]

To gain further insight into the properties of these fluoro-ligands, $[\text{Fe}(4\text{-Fpdma})_3][\text{ClO}_4]_2$ was prepared and its electronic spectrum compared with that of $[\text{Fe}(\text{pdma})_3][\text{ClO}_4]_2$.[18] The fluorodiarsine complex showed absorption maxima at 13 700, 20 250, and 25 500 cm^{-1}, which correspond to the transitions ${}^1A_1 \rightarrow {}^3T_1$ (spin forbidden), ${}^1A_1 \rightarrow {}^1T_1$, and ${}^1A_1 \rightarrow {}^1T_2$ respectively. The bands of the pdma complex occur at 14 500, 21 400, and 26 600 cm^{-1} from which $10Dq$ was calculated to be 24 900 cm^{-1}.[18] A similar calculation using different energy expressions [19] reveals values of $10Dq = 24\,100$, $B = 350$, and $C = 3\,140\ \text{cm}^{-1}$, and, for $[\text{Fe}(4\text{-Fpdma})_3][\text{ClO}_4]_2$, $10Dq = 22\,500$, $B = 360$, and $C = 2\,740\ \text{cm}^{-1}$. Attempts to determine the ligand parameters of the fluoroaliphatic-bridged diarsines were unsuccessful, as the tris(diarsine) complexes of iron(II) could not be prepared.

The As–CH_3 stretching frequencies showed the typical shift of *ca.* 30 cm^{-1} on co-ordination, the shift being less for eight- than for six-co-ordination (Table 2). The As–CH_3 rocking mode, which normally shows a similar increase on co-ordination, could not always be unambiguously assigned in the case of the fluoroaliphatic ligands.

TABLE 2

Arsenic–methyl stretching bands (cm^{-1})

dtcb	578, 566	4-Fpdma	573, 566
$[\text{TiCl}_4(\text{dtcb})]$	623, 600	$[\text{TiCl}_4(4\text{-Fpdma})]$	614, 607
$[\text{SnCl}_4(\text{dtcb})]$	615, 585	$[\text{SnCl}_4(4\text{-Fpdma})]$	618, 591
dhcp	579, 565	$[\text{VCl}_4(4\text{-Fpdma})]$	620, 596
$[\text{TiCl}_4(\text{dhcp})]$	626, 598	$[\text{NbCl}_4(4\text{-Fpdma})_2]$	609, 587
$[\text{SnCl}_4(\text{dhcp})]$	610, 584		
$[\text{NbCl}_4(\text{dhcp})_2]$	602, 588		

EXPERIMENTAL

1,2-*Bis(dimethylarsino)-4-fluorobenzene* (4-Fpdma).—The method of preparation used was similar to that for *o*-phenylenebis(dimethylarsine),[20] using 1,2-dichloro-4-fluorobenzene in place of *o*-dichlorobenzene. The addition of

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NaAsMe$_2$ was carried out *after* the removal of the unchanged sodium metal. An excess of dichlorofluorobenzene was necessary to prevent formation of the triarsine, 1,3,4-tris-(dimethylarsino)benzene. One of the by-products of the reaction had a b.p. very close to that of the fluorodiarsine, which necessitated the use of spinning-band distillation methods. A colourless liquid was obtained, b.p. 145 °C at 12 mmHg (Found: C, 39.8; H, 4.8; F, 6.2. Calc. for $C_{10}H_{15}As_2F$: C, 39.5; H, 5.0; F, 6.3%).

1,2-*Bis(dimethylarsino)-3-fluorobenzene* (3-Fpdma).—This ligand was prepared from 2,3-dichlorofluorobenzene in a similar manner to the method described for 4-Fpdma. The resulting liquid was identified by comparison of mass-spectral data with those of 4-Fpdma.[21]

TABLE 3

Analytical data (%)

	Found						Calc.					
	C	H	Cl, Br	F	As	M	C	H	Cl, Br	F	As	M
[TiCl$_4$(dtcb)]	18.0	2.7	26.7	14.2	28.3	10.3	18.3	2.3	26.9	13.8	28.7	9.2
[TiCl$_4$(dhcp)]	18.9	2.5	24.5	20.0	25.9	8.9	18.8	2.1	24.7	19.9	26.1	8.4
[TiCl$_4$(3-Fpdma)]	23.9	3.2	28.9			10.5	24.2	3.0	28.6			9.7
[TiCl$_4$(4-Fpdma)]	24.1	3.4	28.8	3.6	30.0	10.1	24.2	3.0	28.6	3.8	30.2	9.7
[TiBr$_4$(dtcb)]	13.9	2.3	46.3	10.9	21.6	7.6	13.7	1.7	45.4	10.8	21.3	6.7
[TiBr$_4$(dhcp)]	14.5	1.8	42.4	14.9	19.7	6.3	14.4	1.6	42.4	15.2	19.8	6.4
[TiBr$_4$(4-Fpdma)]	17.8	2.4	47.7	2.7		7.3	17.9	2.2	47.5	2.8		7.1
[SnCl$_4$(dtcb)]	16.0	2.5	23.5	12.6	24.3		16.2	2.2	23.9	12.8	25.2	
[SnCl$_4$(dhcp)]	16.8	2.0	22.2	17.6	23.2		16.8	1.9	22.0	17.7	23.3	
[SnCl$_4$(4-Fpdma)]	21.7	2.9	28.7	3.0			21.3	2.7	25.0	3.4		
[VCl$_4$(dtcb)] *	17.4	2.4	25.7	13.7			18.2	2.3	26.9	14.5		
[VCl$_4$(dhcp)] *	19.8	2.3	23.4				18.7	2.1	24.6			
[VCl$_4$(4-Fpdma)]	23.8	3.1	28.5	3.7			24.0	3.0	28.6	3.8		
[MoCl$_4$(dtcb)]	17.2	2.3	25.5				16.8	2.1	24.8			
[MoCl$_4$(dhcp)]	17.7	2.2	23.7				17.4	1.9	22.8			
[ReCl$_4$(dtcb)]	14.6	2.0	21.7	11.3			14.5	1.8	21.4	11.5		
[ReCl$_4$(dhcp)]	14.9	1.7	19.8	15.8	20.6		15.2	1.7	19.9	16.0	21.1	
[NbCl$_4$(dhcp)$_2$]	22.6	2.4	14.0	22.5	29.6		21.5	2.4	14.1	22.7	29.8	
[NbCl$_4$(3-Fpdma)$_2$]	28.7	3.7	16.9	4.4		11.1	28.5	3.6	16.9	4.5		11.0
[NbCl$_4$(4-Fpdma)$_2$]	28.2	3.6	16.9				28.5	3.6	16.9			
[NbBr$_4$(dhcp)$_2$]	18.4	2.1	27.1			7.8	18.3	2.0	27.0			7.9
[NbBr$_4$(3-Fpdma)$_2$]	23.4	3.1	34.1			10.2	23.6	2.9	31.3			9.1
[NbBr$_4$(4-Fpdma)$_2$]	23.6	2.8	31.7			9.4	23.6	2.9	31.3			9.1

* Physical properties indicated that some reduction had occurred.

The titanium, vanadium, and tin complexes were precipitated from carbon tetrachloride solutions. The metal tetrahalide (0.2—0.5 g) was dissolved and an equimolar amount of the ditertiary arsine ligand was syringed into the stirring solution. The resulting solid was washed several times with cold carbon tetrachloride, in which it was slightly soluble, and dried *in vacuo*. Analytical data are given in Table 3. All the complexes are non-electrolytes in acetonitrile and are diamagnetic. The diffuse-reflectance and solution spectra showed the usual four charge-transfer bands between 15 000 and 50 000 cm^{-1}.[7] The molecular weight of [TiCl$_4$(4-Fpdma)] in boiling acetonitrile showed it to be monomeric (Found: 520 ± 30. Calc.: 523).

Bis[1,2-*bis(dimethylarsino)*-3,3,4,4,5,5-*hexafluorocyclopentene*]*tetrachloroniobium*(IV).—A solution of niobium tetrachloride (0.3 g) in acetonitrile (50 cm^3) was slowly filtered into a stirring solution of the ligand (dhcp, 1.0 g) [22] in acetonitrile (10 cm^3). A red solution formed immediately, and a green solid slowly precipitated, which was filtered off, washed several times with acetonitrile, and stored *in vacuo*.

The other niobium complexes were prepared in a similar manner, with a two-fold excess of ligand being added in each case.

[1,2-*Bis(dimethylarsino)*-3,3,4,4-*tetrafluorocyclobutene*]-*tetrachloromolybdenum*(IV).—The ligand dtcb (1.0 g) [23] in acetonitrile (5 cm^3) was slowly added to a solution of molybdenum pentachloride (0.73 g) in acetonitrile (30 cm^3). A green-brown solution produced a light brown solid on heating and removal of excess of solvent. The solid was filtered off and washed with small amounts of cold acetonitrile. The yield was very low.

The corresponding dhcp complex was prepared similarly.

[1,2-*Bis(dimethylarsino)*-3,3,4,4,5,5-*hexafluorocyclopentene*]*tetrachlororhenium*(IV).—A green product was isolated from carbon tetrachloride by reacting rhenium pentachloride (1.0 g) and dhcp (0.7 g) as described previously for [ReCl$_4$(dtcb)].[3]

Bis[1,2-*bis(dimethylarsino)*-4-*fluorobenzene*]*dichloronickel*(II).—Nickel dichloride hexahydrate (0.3 g) in ethanol (6 cm^3) and 4-Fpdma (0.44 g) in ethanol (4 cm^3) were mixed to yield a red-brown solution. On removal of some ethanol *in vacuo*, a green solid precipitated, and was filtered off, washed with cold ethanol, and dried *in vacuo* (Found: C, 31.9; H, 3.5. Calc. for $C_{20}H_{30}As_4Cl_2F_2Ni$: C, 32.5; H, 4.1%).

Tris[1,2-*bis(dimethylarsino)*-4-*fluorobenzene*]*iron*(II) *Perchlorate*.—This complex was prepared as described for the pdma analogue [18] (Found: C, 29.5; H, 3.5. Calc. for $C_{30}H_{45}As_6Cl_2F_6FeO_8$: C, 30.9; H, 3.9%).

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