

High Oxidation State Binary Transition Metal Fluorides as Selective Fluorinating Agents¹

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High oxidation state transition metal fluorides are selective fluorinating agents for dichloromethane; those with d^0 electronic configurations undergo hydrogen-fluorine exchange and metal reduction, while d^n species undergo chlorine-fluorine exchange.

Although the oxidative fluorination of organic compounds by medium oxidation state fluorides, such as CoF_3 or KCoF_4 , is a well established route to fluorocarbon species,² the use of higher oxidation state transition metal fluorides has received scant attention owing, in part, to the notorious reactivity of such compounds. UF_6 ³ oxidatively fluorinates alcohols and aldehydes, MoF_6 ⁴ and WF_6 ⁵ have been used to fluorinate carbonyl groups in organic molecules, while, at low temperatures, VF_5 ⁶ fluorinates polyfluoroaromatics to fluorinated cyclohexadienes and cyclohexenes. The violent halogen-exchange reactions of VF_5 ⁷ and OsF_6 ⁸ with CCl_4 have also been noted. We have recently completed the spectroscopic characterisation of many of the highest oxidation state transition metal fluorides,⁹ and have turned our attention to their reaction chemistry. The search for convenient synthetic routes to hydrofluorocarbons as chlorofluorocarbon replacements directed our attention to C_1 and C_2 chloroalkanes, and here we report our observations of the fluorinations of dichloromethane by high oxidation state transition metal fluorides.

In a typical experiment, the fluoride (*ca.* 0.1–0.3 mmol) was loaded, either in a dry-box for solid samples or by vacuum transfer for gases, into a pre-fluorinated FEP (polytetrafluoroethylene-perfluoropropylene copolymer) reactor (4 mm o.d., 1.5 cm³ total volume) fitted with a polytetrafluoroethylene valve. A large excess of dichloromethane (typically 0.4 cm³) was added by vacuum transfer, and the reaction tube allowed to warm slowly to room temp. On completion, the organic products were transferred to a second FEP tube, which was heat sealed under vacuum, and its contents investigated by ¹H and ¹⁹F NMR spectroscopy. The residual inorganic product was characterised by elemental analysis, IR spectroscopy and, where appropriate, X-ray powder diffraction. The results are summarised in Table 1.

Surprisingly, most of these aggressive inorganic fluorides reacted in a controlled, highly specific and predictable manner. Strongly fluorine-bridged polymeric species such as

VF_4 , NbF_5 , TaF_5 , CrF_4 and MnF_3 did not dissolve or react with dichloromethane, while the monomeric MoF_6 and WF_6 dissolved without reaction. The weakly aggregated or monomeric d^0 species VF_5 , UF_6 and ReF_7 exhibit predominantly hydrogen-fluorine exchange with concomitant production of HF and reduction to VF_3 , $\beta\text{-UF}_5$ and ReF_6 , respectively. For ReF_6 , OsF_6 , IrF_6 and RuF_5 , where d-electrons are present, predominantly chlorine-fluorine exchange is observed.† For ReF_6 , after 5 days, the organic products contained only 50% of the available fluorine; the inorganic product, of average composition ReCl_3F_3 , appeared to be a mixture of rhenium(vi) chloro-fluorides. For OsF_6 , IrF_6 and RuF_5 , all the available fluorine was utilised in the reaction. However, stable binary chlorides of Os^{VI} , Ir^{VI} and Ru^{V} are unknown and decomposition of the inorganic product gave chlorine plus OsCl_5 , IrCl_3 and RuCl_3 , respectively. CrF_5 did not dissolve or react with dichloromethane, but the addition of HF as a solvent for the binary fluoride resulted in a vigorous non-specific fluorination.

The absence or presence of d-electrons, therefore, has a marked influence on reactivity. The d^0 species, MoF_6 and WF_6 , do not react with CH_2Cl_2 , even though they undergo facile halogen exchange with inorganic chlorides (*e.g.* TiCl_4 , BCl_3 , Me_3SiCl) at room temp.¹⁰ For the remaining d^0 binary fluorides, the series ReF_7 , VF_5 and UF_6 react progressively more rapidly and more violently with both dichloromethane and inorganic chlorides (*e.g.* BCl_3 , Me_3SiCl). The extreme reactivity of UF_6 and CH_2Cl_2 should be noted since it is reported³ that stable solutions of UF_6 in chlorohydrocarbons are convenient reagents for the fluorination of organic substrates. When d-electrons are present reduction of binary fluorides by dichloromethane is much less likely to occur.

† CAUTION: The reactions with OsF_6 and IrF_6 can be extremely vigorous, and occasionally explode. This can be avoided by controlling the reactions with judicious cooling using liquid nitrogen.

Table 1 Products of the fluorination of CH₂Cl₂

	Mass of metal fluoride/g	Mass of CH ₂ Cl ₂ /g	Products ^b (mol%)									Inorganic residue
			CH ₂ ClF	CH ₂ F ₂	CHCl ₂ F	CHClF ₂	CHF ₃	CF ₂ Cl ₂	CF ₃ Cl	CF ₄	HF	
ReF ₇	0.2073	1.0613	1.40	—	48.66	0.64	—	—	—	—	49.30	ReF ₆
ReF ₆	0.0322	0.4757	82.44	3.32	3.98	3.14	—	—	—	—	7.12	'ReCl ₃ F ₃ '
OsF ₆	0.0379	0.2360	21.86	54.14	—	1.31	7.83	0.26	1.65	—	12.95	OsCl ₅
IrF ₆	0.0392	0.1896	32.63	22.77	8.62	7.93	5.75	—	—	—	22.30	'IrCl ₃ '
UF ₆	0.4150	1.3175	—	—	49.95	—	—	—	—	—	49.95	β-UF ₅
RuF ₅	0.0608	0.6472	36.18	57.09	1.62	1.12	0.62	—	—	—	3.36	'RuCl ₃ '
VF ₅	0.1905	0.9425	0.98	—	46.40	3.11	—	—	—	—	49.51	VF ₃
CrF ₅ ^a	0.2054	2.0868	27.84	2.58	8.17	27.54	3.02	2.00	2.38	4.42	—	CrF ₄

^a Reaction performed in HF (0.6858 g, 34.289 mmol) (see text). ^b Mol %.

Indeed, although ReF₇ undergoes relatively fast (*ca.* 4 h) hydrogen–fluorine exchange, ReF₆ (produced as the initial byproduct of the ReF₇ reduction) undergoes a slow (more than 5 days) chlorine–fluorine exchange. There is an increase in reactivity (ReF₆ < OsF₆ < IrF₆) for reactions with both dichloromethane and inorganic chlorides; the inorganic products are the same from both types of reaction. There is also a decrease in specificity for Cl–F exchange in this series as a consequence of the extreme reactivity of the Os^{VI} and Ir^{VI} species. The critical role of the metal *dⁿ* configuration and the mechanisms of these reactions are unclear at present. The absence of CHCl₃ and CCl₄ indicates that the reactions do not involve organic radicals and suggests a concerted mechanism with coordination of the dichloromethane to the very electron deficient metal centres. Further work into the mechanisms of these unusual reactions and the fluorination of other organic molecules by high oxidation state transition metal fluorides is in progress.

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