

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 d⁰ electronic configurations undergo hydrogen–fluorine exchange and metal reduction, while dⁿ species undergo chlorine–fluorine exchange.

Although the oxidative fluorination of organic compounds by medium oxidation state fluorides, such as CoF₃ or KCoF₄, 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. UF₆³ oxidatively fluorinates alcohols and aldehydes, MoF₆⁴ and WF₆⁵ have been used to fluorinate carbonyl groups in organic molecules, while, at low temperatures, VF₅⁶ fluorinates polyfluoroaromatics to fluorinated cyclohexadienes and cyclohexenes. The violent halogen-exchange reactions of VF₅⁷ and OsF₆⁸ with CCl₄ 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 C₁ and C₂ 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

VF₄, NbF₅, TaF₅, CrF₄ and MnF₃ did not dissolve or react with dichloromethane, while the monomeric MoF₆ and WF₆ dissolved without reaction. The weakly aggregated or monomeric d⁰ species VF₅, UF₆ and ReF₇ exhibit predominantly hydrogen–fluorine exchange with concomitant production of HF and reduction to VF₃, β-UF₅ and ReF₆, respectively. For ReF₆, OsF₆, IrF₆ and RuF₅, where d-electrons are present, predominantly chlorine–fluorine exchange is observed.† For ReF₆, after 5 days, the organic products contained only 50% of the available fluorine; the inorganic product, of average composition ReCl₃F₃, appeared to be a mixture of rhenium(vi) chloro-fluorides. For OsF₆, IrF₆ and RuF₅, 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 OsCl₅, IrCl₃ and RuCl₃, respectively. CrF₅ 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 d⁰ species, MoF₆ and WF₆, do not react with CH₂Cl₂, even though they undergo facile halogen exchange with inorganic chlorides (*e.g.* TiCl₄, BCl₃, Me₃SiCl) at room temp.¹⁰ For the remaining d⁰ binary fluorides, the series ReF₇, VF₅ and UF₆ react progressively more rapidly and more violently with both dichloromethane and inorganic chlorides (*e.g.* BCl₃, Me₃SiCl). The extreme reactivity of UF₆ and CH₂Cl₂ should be noted since it is reported³ that stable solutions of UF₆ 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 OsF₆ and IrF₆ 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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