Journal of Fluorine Chemistry, 66 (1994) 117–122

Radiotracers in fluorine chemistry. Part 17 [1]. Caesium and potassium fluorides supported on fluorinated γ-alumina

Thomas Baird, Abdallah Bendada, Geoffrey Webb and John M. Winfield*
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ (UK)

Abstract

Exhaustive fluorination of CsF or KF supported on γ-alumina, by SF_4 or OSF_2, nominally at room temperature, is an effective process for the removal of hydroxy groups and/or strongly bound H_2O from the surface of these materials. Anhydrous HF and OCF_2 are less effective reagents; the former can be used however if the surface is pretreated with SO_2. The physical properties of CsF and KF supported on fluorinated γ-alumina and the behaviour of these materials towards SF_4 and ClF, labelled with sulphur-35 and chlorine-36 respectively, indicates that the Lewis base character of the surfaces, which is ascribed to surface MF, M = Cs or K, particles, is retained after fluorination. Although the surface areas of the materials are reduced compared with their unfluorinated counterparts, they are greater than those for the unsupported fluorides.

Introduction

The utility of potassium fluoride supported on γ-alumina as a strongly basic reagent and catalyst in organic synthesis, for example [2–11], has led to considerable interest in determining the identity of the basic sites. The problem is not trivial, since during the impregnation of alumina by KF an additional reaction occurs giving K_3AlF_6 as the only identified Al–F species [12]. There is general agreement that at lower loadings (< 5.5 mmol g^{-1}) of MF (M = K or Cs), MF particles are a major component on the surface [12–16]. Formation of M_3AlF_6, M = K or Cs, becomes more important as the loading of MF is increased; in this situation the surface activity arising from MF decreases [16]. The species formed concomitantly with M_3AlF_6 was originally suggested to be free M^+OH^- [12], this being responsible in part [12, 17] or totally [18] for the basic properties of supported Group 1 fluorides under aqueous/organic conditions. In contrast, the behaviour of radiolabelled, volatile Lewis acids towards γ-alumina-supported CsF and KF over a range of compositions, provides no evidence for the presence of free MOH at high loadings but suggests that formation of M_3AlF_6 is accompanied by dehydroxylation of the γ-alumina surface to give H_2O and surface $[Al–O^-]M^+$ sites [16].

The hydroxylated nature of the MF/γ-alumina surface, and the probability that strongly bound water is present, makes these materials unsuitable for use in situations where anhydrous conditions must be maintained. During our radiotracer study [16], it became apparent that surface hydroxy groups and bound H_2O might be removed by fluorination of the surface without affecting the surface activity of MF particles. The hypothesis has been tested and the results are now reported. A preliminary account of some of this work has appeared [19].

Experimental

Except where described below, the methods used for the preparation of supported KF and CsF, for the preparation of radiolabelled compounds, for performing radiochemical experiments, and for physical and spectroscopic examinations were as previously described [16, 20, 21]. Chlorine monofluoride was prepared from $ClF_3 + Cl_2$ [22] and its purity checked by vapour pressure determination over a range of temperatures. Chlorine-36 labelled material was prepared similarly using $^{36}ClCl$; a linear relationship was established between the [^{36}Cl] count rate and pressure over the range 0–300 Torr using the Geiger–Müller direct monitoring cell described elsewhere [21].

Fluorination of supported Group I fluorides

A sample of MF/γ-alumina, M = Cs or K, was loaded into a Monel metal pressure vessel (139 cm^3) in a glove box, the vessel transferred to a vacuum line and evacuated for 1 h. A measured quantity of purified SF_4

---

*Author to whom correspondence should be addressed.

0022-1139/94/$07.00
SSDI 0022-1139(93)03006-8

was added and the mixture allowed to warm slowly to room temperature. The mixture was allowed to react for 6 h, volatile material (a mixture of SO_2, OSF_2 and unchanged SF_4) was removed and its composition determined by IR spectroscopy using experimentally determined calibration relationships. The procedure was repeated until the volatile material recovered showed no evidence for SO_2 nor OSF_2. The IR spectrum of the solid product contained bands attributable to $[SF_5]^-$ [23] and $[SO_2F]^-$ [24] anions. The solid was heated under dynamic vacuum at 433 K for 3 h then 523 K for 5 h. IR spectroscopic examination indicated that the sulphur-containing anions were no longer present.

Fluorinations of MF/γ-alumina samples with OSF_2 and OCF_2 were carried out in a similar manner, the volatile products being SO_2 and CO_2 and the anions formed $[SO_2F]^-$ and $[OCF_3]^-$ [25], respectively. The fluorination reactions were carried out using MF/γ-alumina compositions in the range 0.6–15.0 mmol MF (g γ-alumina)$^{-1}$, the materials being prepared by both aqueous and non-aqueous impregnation routes [16].

Fluorination of a CsF/γ-alumina sample (0.5 g) was carried out in an FEP tube ampoule attached to a Monel metal vacuum line. The solid was saturated with four HF aliquots, volatile material being removed between each addition; the sample was finally pumped for 2 h at room temperature. IR spectroscopic examination showed the presence of $[HF_2]^-$ and possibly other $[H_nF_{n+1}]^-$ anions [26], $\nu_{max.}$ 2043, 1843, 1468 and 1230 cm^{-1}. These bands were still present after the sample had been heated for periods up to 18 h at 673 K.

Formation of $[HF_2]^-$ was avoided by first allowing a sample of MF/γ-alumina (0.5 g) to react with SO_2 (MF/SO_2 mole ratio$<$1:1) at 253 K for 2 h. Removal of volatile material left a solid whose IR spectrum contained bands due to the $[SO_2F]^-$ anion [24]. The solid was allowed to react with HF as described above, then heated in a Monel metal vessel at 453 K for 5 h and then at 523 K for 5 h under dynamic vacuum conditions. The quantity of SO_2 collected during the first stage corresponded to an MF/SO_2 mole ratio of 1:1. The IR spectrum of the material finally isolated showed that $[SO_2F]^-$ and $[HF_2]^-$ were absent.

Results and discussion

Fluorination of γ-alumina-supported KF and CsF and the physical properties of the fluorinated materials

Fluorination of CsF or KF supported on γ-alumina can be achieved using sulphur tetrafluoride, thionyl fluoride or carbonyl fluoride. The reactions were carried out, nominally at room temperature, as described in the Experimental section and resulted in the formation of the expected hydrolysis products, OSF_2 and SO_2, SO_2 or CO_2, respectively, and the fluoro anions $[SF_5]^-$, $[SO_2F]^-$ and $[OCF_3]^-$. The latter were removed by subsequent thermal decomposition. The reactions were carried out using MF/γ-alumina samples prepared both by aqueous impregnation (loading in the range 0.6–15.0 mmol g^{-1}) and by impregnation using $M[OCF(CF_3)_2]$ in MeCN, followed by thermal decomposition of the supported alkoxide as described elsewhere [16] (loading in the range 0.6–10.0 mmol g^{-1}). For each reagent, the quantity required for complete reaction, estimated from the composition of the volatile products after reaction, depended on the identity of the Group I fluoride, its loading and the impregnation method. Representative results are given in Table 1. The overall pattern is consistent with our previous suggestion that the degree to which an MF/γ-alumina surface is dehydroxylated and dehydrated increases as the loading of MF, and consequently the formation of M_3AlF_6, increases. As expected, impregnation under non-aqueous conditions leads to materials that require less reagent for fluorination.

Multiple treatments with SF_4 or OSF_2 led to materials containing no hydroxy groups nor bound water, as judged by the lack of hydrolysis of SF_4 on contact with the fluorinated materials. Hydrolysis of SF_4 was observed to some extent, however, when the gas was exposed to materials that had been fluorinated with OCF_2. Evidently removal of surface hydroxy groups by OCF_2 under the conditions used was not complete; the fluorination of non-aqueous impregnated materials was not studied. Fluorination of MF/γ-alumina samples with anhydrous HF led to the formation of $[HF_2]^-$ on the solids which could not be removed by thermal decomposition at moderate temperatures. This problem was

TABLE 1. Fluorination of supported Group I fluorides

Reagent	Composition (mmol g^{-1})	Quantity of reagent reacted (mmol)			
		Aqueous impregnation		Non-aqueous impregnation[a]	
		CsF	KF	CsF	KF
SF_4	0.6	12.3	15.4	5.8	7.4
	5.5	8.7	10.4	4.0	5.0
	10.0	4.8	6.7	2.2	3.2
OSF_2	0.6	17.1	19.8	7.9	9.0
	5.5	13.6	16.5	6.4	7.8
	10.0	9.0	11.5	4.1	5.3
OCF_2	0.6	4.2	5.5		
	5.5	2.6	4.0		
	10.0	1.7	2.9		

[a] Using $M[OCF(CF_3)_2]$ in MeCN followed by thermal decomposition *in vacuo* [16].

avoided if the supported metal fluoride was first protected by treatment with SO_2. The $[SO_2F]^-$ anions so formed were unaffected by HF and could be decomposed after the HF treatment by thermal decomposition.

Examination of the fluorinated MF/γ-alumina samples by TEM, XRD, ^{27}Al MAS NMR and vibrational spectroscopy led to results that were identical to those reported previously for the unfluorinated materials [16]. Metal fluoride particles are present at low loading (for example at 4.4 mmol g^{-1}) and M_3AlF_6, M = Cs or K, at higher loadings. There was no evidence for the formation of AlF_3 nor other fluoroaluminate phases as a result of the fluorination reactions and the γ-alumina phase was present at all compositions studied. The quantities of SF_4, OSF_2 or OCF_2 estimated to have reacted with the supported metal fluorides (Table 1) were far greater than could be reasonably required to replace surface Al–OH groups by Al–F groups [27]. It is possible, therefore, that fluorine is also incorporated into the bulk material without apparent structural change to the γ-alumina. A similar effect has been reported very recently in the fluorination of cerium dioxide by F_2, where below 543 K fluorine is incorporated into the CeO_2 lattice without change in structure [28].

Fluorination of supported KF or CsF leads to decreases in their BET areas, particularly at low loading. Representative data are contained in Table 2; for comparison, BET areas of KF supported on γ-alumina range from 140–156 (1.1 mmol g^{-1}) to 29–39 $m^2\ g^{-1}$ (15.0 mmol g^{-1}) and the corresponding values for supported CsF are slightly smaller [16]. The three reagents SF_4, OSF_2 and SO_2/HF had an identical effect on the BET areas within experimental error. Data obtained for samples prepared by the non-aqueous impregnation route were identical to those in Table 2.

TABLE 2. BET areas

Composition (mmol g^{-1})	Fluorinating agent	BET area ($m^2\ g^{-1}$)[a]	
		CsF	KF
1.1	SF_4	32–36	36–44
	OSF_2	31–35	38–43
	SO_2/HF	33–37	40–46
4.4	SF_4	19–22	27–31
	OSF_2	20–23	27–32
	SO_2/HF	20–24	28–33
5.5	SF_4	17–20	26–29
	OSF_2	17–21	26–30
	SO_2/HF	18–22	26–31
15.0	SF_4	8–12	16–21
	OSF_2	8–11	15–20
	SO_2/HF	8–12	16–20

[a] Values quoted are the 95% confidence limits and refer to samples of supported fluoride prepared by aqueous impregnation.

The benefit of achieving an hydroxide-free surface is therefore off-set by a reduction in the surface area; however, the values in Table 2 are significantly greater than those for unsupported CsF even after the latter has been activated [20].

Reactions of [^{35}S]-labelled SF_4 and [^{36}Cl]-labelled ClF with supported KF and CsF

The reactions between [^{35}S]-labelled SF_4 and CsF, or KF supported on γ-alumina and then fluorinated with SF_4, were characterized by a rapid increase in the [^{35}S] activity on the surface of the solid (Fig. 1). For a given MF loading and initial pressure of $^{35}SF_4$, the saturation [^{35}S] surface count rate obtained from supported CsF was always slightly greater than that from KF, despite the greater BET areas of the latter materials. Removal of volatile material by condensation led to a rapid decrease in the [^{35}S] surface count rate, the final value obtained being *c.* 30% of the saturation value (Fig. 2). Repetition of this sequence led to an identical adsorption–desorption cycle. This behaviour is very similar to that reported for $^{35}SF_4$ on unfluorinated γ-alumina [16], except that in the present case no build-up of [^{35}S] was observed from repetitive reactions. There was no observable hydrolysis and the observations can be explained by the formation of weakly adsorbed SF_4 as the major surface species (70%) and permanently

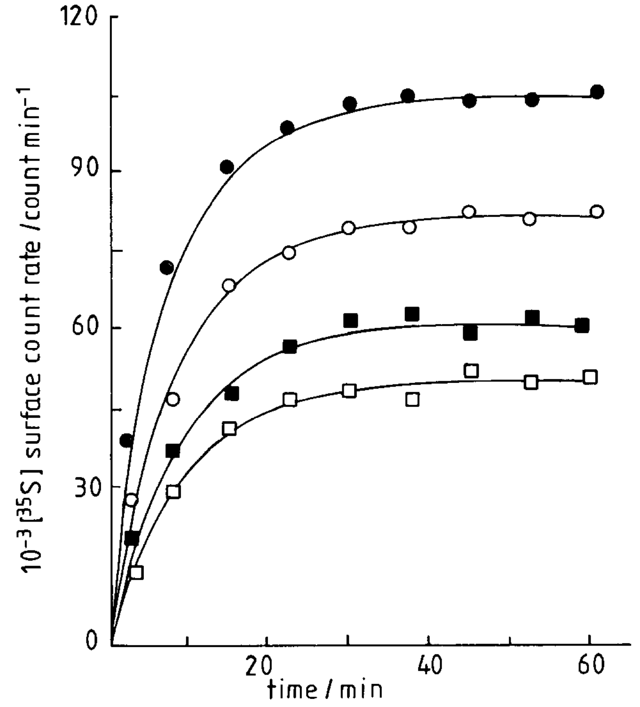

Fig. 1. Reaction of $^{35}SF_4$ (initial pressure = 300 Torr) with Group I fluorides supported on fluorinated γ-alumina (loading = 4.4 mmol g^{-1} in each case): ●, CsF on SF_4-fluorinated γ-alumina; ○, KF on SF_4-fluorinated γ-alumina; ■, CsF on HF-fluorinated γ-alumina; □, KF on HF-fluorinated γ-alumina.

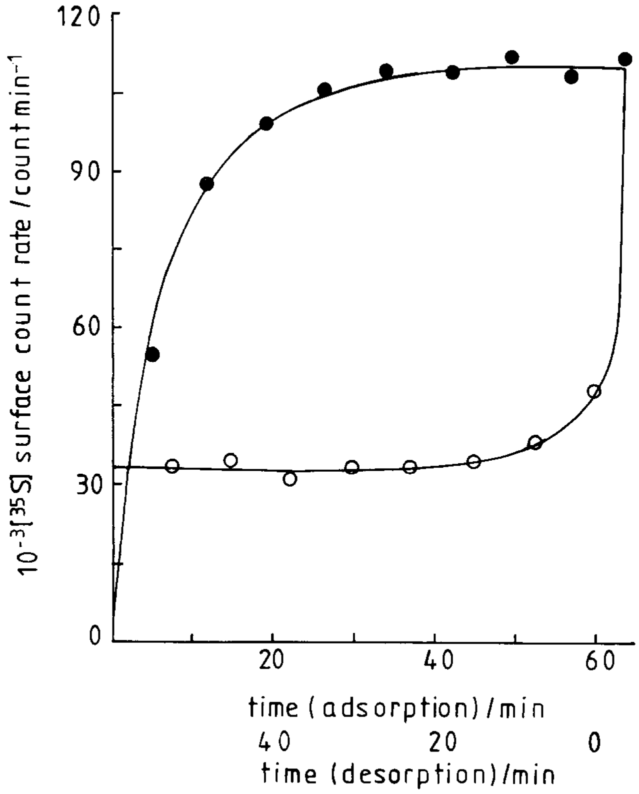

Fig. 2. Adsorption/desorption behaviour of $^{35}SF_4$ (initial pressure = 300 Torr) on CsF (loading = 4.4 mmol g^{-1}) supported on SF_4-fluorinated γ-alumina: ●, adsorption; ○, desorption.

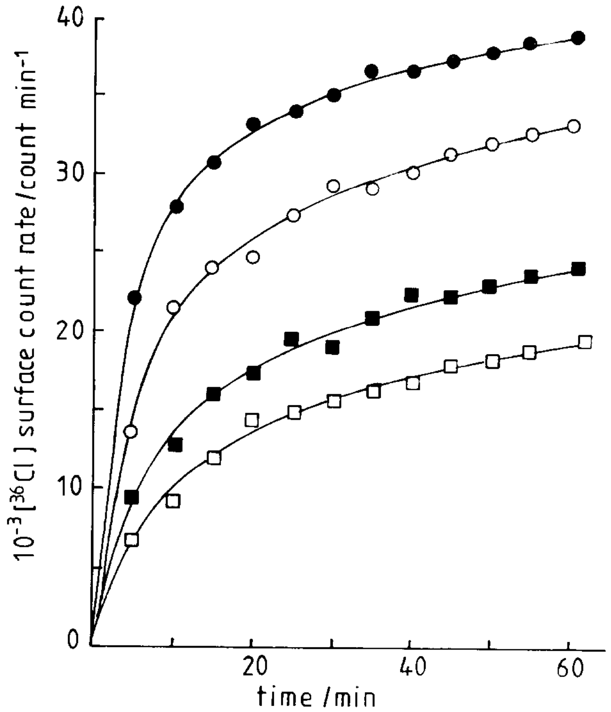

Fig. 3. Reaction of ^{36}ClF (initial pressure = 60 Torr) with Group I fluorides supported on fluorinated γ-alumina: ●, CsF (loading = 4.4 mmol g^{-1}) on SF_4-fluorinated γ-alumina; ○, KF (4.4 mmol g^{-1}) on OSF_2-fluorinated γ-alumina; ■, CsF (8.8 mmol g^{-1}) on OSF_2-fluorinated γ-alumina; □, KF (8.8 mmol g^{-1}) on SO_2 then HF-fluorinated γ-alumina.

retained $[SF_5]^-$ as the minor surface species. This is very similar to the situation encountered for unfluorinated MF/γ-alumina materials reacting with $^{35}SF_4$ [16]; for unsupported CsF, the proportions are 85% and 15%, respectively [20].

The [^{35}S] growth curves obtained from $^{35}SF_4$ reactions with materials fluorinated using OSF_2 or SO_2/HF were essentially identical to those for SF_4-fluorinated materials. Those obtained from HF-fluorinated materials indicated that $^{34}SF_4$ adsorption occurred to a smaller extent (Fig. 1) and OCF_2-fluorinated materials behaved similarly to those fluorinated with HF.

A more extensive study was made of the interactions between [^{36}Cl]-labelled chlorine monofluoride and fluorinated MF/γ-alumina samples since ClF had not been used in our previous study [16]. The behaviour of ClF was also studied using a conventional manometric method as a check on the radiochemical data. The results obtained from both techniques were identical. The supported Group I fluoride samples were fluorinated using SF_4, OSF_2 or SO_2/HF; the results in each case were identical for a given MF loading and a given initial pressure of ClF.

The [^{36}Cl] growth curves obtained when ^{36}ClF (initial pressure = 60 Torr) was allowed to react with CsF and KF supported on fluorinated γ-alumina (loadings = 4.4 or 8.8 mmol g^{-1}) are shown in Fig. 3. For a given loading, the extent of the interaction was greater for supported CsF and it was also greater at 4.4 mmol g^{-1}. Saturation count rates from the surface were not observed, in contrast to the $^{35}SF_4$ case. After 1 h reaction times, the [^{36}Cl] count rates from the surface and the total uptakes of ^{36}ClF (determined from the decrease in the gas-phase count rate) both varied linearly with pressure, for a given MF loading, over the range 0–300 Torr. In all cases, removal of volatile material produced no change in the [^{36}Cl] surface count rates; neither were they affected by pumping overnight.

The [^{36}Cl] surface count rates due to permanently retained species on supported CsF and KF showed a marked dependence on the loading of MF (Fig. 4). For all supported MF samples examined, the maximum [^{36}Cl] surface count rate was observed at a 5.5 mmol g^{-1} loading. Count rates for loadings of 20.0 mmol g^{-1} were identical with background count rates, indicating no interaction. The shapes of the [^{36}Cl] count rate versus loading curves are virtually identical to those observed when $^{35}SF_4$ or other radiolabelled, volatile Lewis acids were exposed to MF/γ-alumina samples [16]. For both unfluorinated and fluorinated supports, the curves are a measure of the effective surface con-

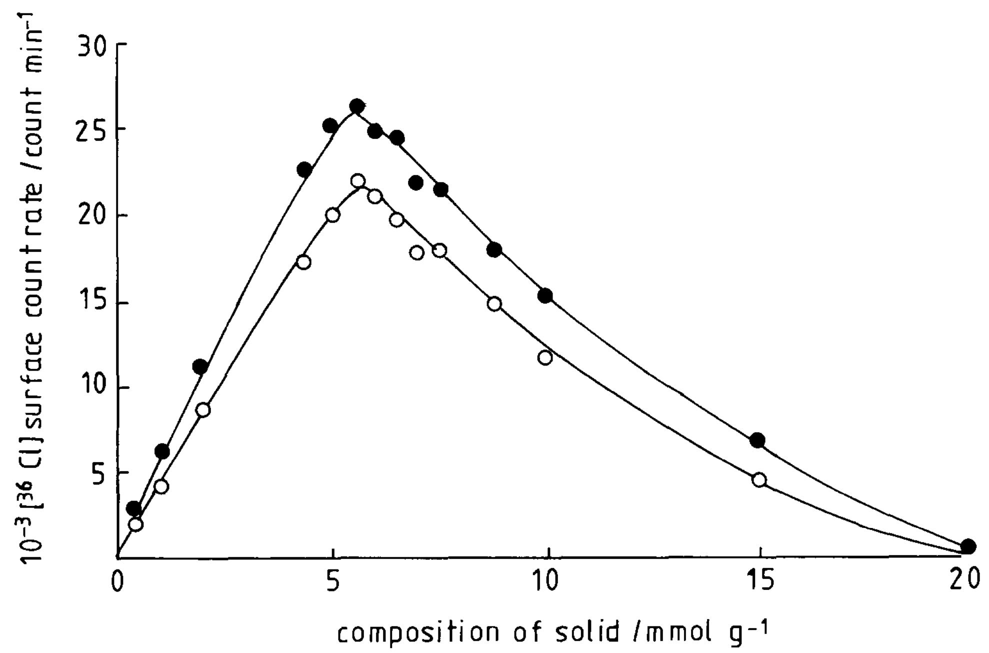

Fig. 4. Variation of ^{36}Cl surface count rate with composition: ●, CsF; ○, KF; in both cases supported on SF_4-fluorinated γ-alumina. Initial pressure of ClF = 300 Torr.

centrations of the F^- anion; in the present case, the reaction between ClF and F^- should produce the $[ClF_2]^-$ anion [29]. This was confirmed by the vibrational spectra of the materials, which after reaction with ClF contained bands, $\nu_{max.}$ 482 cm^{-1} (Raman) and 643, 502 and 483 cm^{-1} (IR), attributable to $[ClF_2]^-$ [29].

The results obtained in this study indicate that while hydroxy groups and bound water on the surface of γ-alumina-supported CsF and KF can be removed effectively by SF_4, OSF_2 or SO_2/HF, these treatments do not have any material effect on the metal fluoride particles. In particular, the results illustrated in Fig. 4 substantiate our earlier contention [16] that free, ionic metal hydroxides are not formed during the impregnation of γ-alumina by CsF or KF. It is expected that CsF or KF supported on fluorinated γ-alumina should be effective sources of F^- ion in catalytic applications. A study of the kinetics of the chlorofluorination of SF_4 by ClF in the presence of these materials has confirmed this expectation; the detailed results will be reported elsewhere.

Acknowledgements

We thank the SERC for financial support and the SERC solid-state NMR service (University of Durham) for the ^{27}Al NMR spectra.

References

1 Part 16: M.F. Ghorab and J.M. Winfield, *J. Fluorine Chem., 62* (1993) 101.
2 T. Ando, J. Yamawaki, T. Kawate, S. Sumi and T. Hanafusa, *Bull. Chem. Soc. Jpn., 55* (1982) 2504.
3 J.H. Clark, D.G. Cork and M.S. Robertson, *Chem. Lett.,* (1983) 1145.
4 J. Yamawaki, T. Kawate, T. Ando and T. Hanafusa, *Bull. Chem. Soc. Jpn., 56* (1983) 1885.
5 J.H. Clark, D.G. Cork and H.W. Gibbs, *J. Chem. Soc., Perkin Trans. 1,* (1983) 2253.
6 D. Villemin and M. Ricard, *Tetrahedron Lett., 25* (1984) 1059.
7 F. Texier-Boullet, D. Villermin, M. Ricard, H. Moison and A. Foucaud, *Tetrahedron, 41* (1985) 1259.
8 J.-M. Melot, F. Texier-Boullet and A. Foucaud, *Synthesis,* (1987) 364.
9 D.E. Bergbreiter and J.J. Lalonde, *J. Org. Chem., 52* (1987) 1601.
10 A.S. Radhakrishna, S.K. Suri, K.R.K.P. Rao, K. Sivaprakash and B.B. Singh, *Synth. Commun., 20* (1990) 345.
11 A.K.S.B. Rao, C.G. Rao and B.B. Singh, *J. Chem. Res. Synop.,* (1991) 350.
12 T. Ando, S.J. Brown, J.H. Clark, D.G. Cork, T. Hanafusa, J. Ichihara, J.M. Miller and M.S. Robertson, *J. Chem. Soc., Perkin Trans. 2,* (1986) 1133.
13 J.H. Clark, E.M. Goodman, D.K. Smith, S.J. Brown and J.M. Miller, *J. Chem. Soc., Chem. Commun.,* (1986) 657.
14 C.V.A. Duke, J.M. Miller, J.H. Clark and A.P. Kybett, *J. Mol. Catal., 62* (1990) 233.
15 S.J. Brown and J.M. Miller, *Can. J. Spectrosc., 34* (1989) 33.
16 T. Baird, A. Bendada, G. Webb and J.M. Winfield, *J. Mater Chem., 1* (1991) 1071.
17 T. Ando, J.H. Clark, D.G. Cork, T. Hanafusa, J. Ichihara and T. Kimura, *Tetrahedron Lett., 28* (1987) 1421.

18 L.M. Weinstock, J.M. Stevenson, S.A. Tomellini, S.-H. Pan, T.Utne, R.B. Jobson and D.F. Reinhold, *Tetrahedron Lett., 27* (1986) 3845.

19 T. Baird, A. Bendada, G. Webb and J.M. Winfield, *J. Fluorine Chem., 52* (1991) 245.

20 K.W. Dixon and J.M. Winfield, *J. Chem. Soc., Dalton Trans.,* (1989) 937.

21 K.W. Dixon, M.F. Ghorab and J.M. Winfield, *J. Fluorine Chem., 37* (1987) 357.

22 C.J. Schack and R.D. Wilson, *Synth. React. Inorg. Met.-Org. Chem., 3* (1973) 393.

23 L.F. Drullinger and J.E. Griffiths, *Spectrochim. Acta, Part A, 27* (1971) 1793; K.O. Christe, E.C. Curtis, C.J. Schack and D. Pilipovich, *Inorg. Chem., 11* (1972) 1679.

24 E.A. Robinson, D.S. Lavery and S. Weller, *Spectrochim. Acta, Part A, 25* (1969) 151; D.F. Burow, *Inorg. Chem., 11* (1972) 573; K. Garber and B.S. Ault, *Inorg. Chem., 22* (1983) 2509.

25 K.O. Christe, E.C. Curtis and C.J. Schack, *Spectrochim. Acta, Part A, 31* (1975) 1035.

26 S.D. Ross, *Inorganic Infrared and Raman Spectra,* McGraw-Hill, London, 1972; A. Azman, A. Ocvirk, D. Hadzi, P.A. Giguere and M. Schneider, *Can. J. Chem., 45* (1967) 1347.

27 See, for example, J.B. Peri, *J. Phys. Chem., 69* (1965) 211.

28 M. Takashima, S. Fukami, Y. Nosaka and T. Unishi, *J. Fluorine Chem., 57* (1992) 131.

29 K.O. Christe and J.P. Guertin, *Inorg. Chem., 4* (1965) 905, 1785.