ELSEVIER

Journal of Fluorine Chemistry 91 (1998) 207–211

JOURNAL OF FLUORINE CHEMISTRY

Reactions of iridium and rhodium hydrides with anhydrous HF; crystal structure of $[Rh(CO)(PPh_3)_3][BF_4]\cdot thf$

Howard C.S. Clark, Karl S. Coleman, J. Fawcett, John H. Holloway, Eric G. Hope *, John Langer, Ian M. Smith

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

Received 8 April 1998; accepted 28 April 1998

Abstract

The reactions of $[MH(CO)(PPh_3)_3]$ (M = Rh or Ir) with anhydrous HF or $HBF_4\cdot Et_2O$ lead to completely different products. With an excess of acid, when M = Ir, oxidation gives $[IrH_2(CO)(PPh_3)_3][X]$ (X = HF_2, BF_4), whereas, when M = Rh, dissociation of a ligand and elimination of hydrogen gas gives a 1:1 mixture of $[Rh(CO)(PPh_3)_2(solv.)][X]$ and $[HPPh_3][X]$ (X = HF_2, BF_4). With a deficit of acid, $[Rh(CO)(PPh_3)_3][X]$ is also generated which, for X = BF_4, has been crystallographically characterised.

Keywords: Iridium; Rhodium; Anhydrous HF; NMR; Crystal structure

1. Introduction

As part of a study designed to produce low-valent transition metal compounds [1,2] we showed that anhydrous HF is not an inert solvent [3]. We have, since, demonstrated that it is a useful synthetic reagent which can introduce fluorine into metal–methyls with elimination of CH_4 [4] or into metal–hydrides with elimination of H_2 [5]. Here, we have extended the study of these exchange-type reactions to include five-coordinate Group 9 hydrides. Analysis of the products of these reactions, including an X-ray crystal structure of $[Rh(CO)(PPh_3)_3][BF_4]\cdot thf$, has shown that reactions with anhydrous HF are far from straightforward.

2. Experimental

^1H, ^{19}F and ^{31}P NMR spectroscopic studies were carried out on a Bruker ARX 250 spectrometer at 250.13, 235.34 and 101.26 MHz or a Bruker DPX 400 spectrometer at 400.13, 376.50 and 161.98 MHz, respectively in AHF or CD_2Cl_2. All chemical shifts are quoted in ppm using the high frequency positive convention; ^1H NMR spectra were referenced internally to tetramethylsilane, ^{19}F NMR spectra were referenced externally to $CFCl_3$ and ^{31}P NMR spectra were referenced externally to 85% H_3PO_4.

The complexes $[IrH(CO)(PPh_3)_3]$ and $[RhH(CO)(PPh_3)_3]$ were prepared by the literature route [6]. $HBF_4\cdot Et_2O$ (Aldrich) was used as supplied. Anhydrous HF (ICI) was purified by vacuum transfer, dried by repeated fluorination at room temperature and stored in Kel-F tubes over dry BiF_5 [7].

For the AHF reactions, the metal complex (0.1 mmol) was loaded in a dry box into a pre-passivated 4 mm or 6 mm o.d. FEP (perfluoroethylene–propylene copolymer) tube fitted with a PTFE valve. After evacuation on a metal vacuum line, anhydrous HF was transferred on to the metal complex at −196°C, and the mixture slowly allowed to warm to room temperature. At ca. −20°C, reaction ensued and the metal complexes dissolved to give yellow (Ir) or orange (Rh) solutions. For M = Rh, the reaction led to the generation of a non-condensable gas. The reaction vessels were then either heat-sealed for spectroscopic characterisation as described previously [8] or the solvent was removed in vacuo and the solids transferred to the dry box for further manipulation. For the HBF_4 reactions, the metal complex (0.1 mmol) was dissolved in the minimum quantity of solvent. The $HBF_4\cdot Et_2O$ was added by syringe in a dry box and, after reaction, the solvent was removed in vacuo and the solids transferred to the dry box for further manipulation. In both sets of reactions, the same cationic products were generated.

$[IrH_2(CO)(PPh_3)_3][X]$ (X = HF_2, BF_4). NMR (C_6D_6): ^1H, δ 7.2–7.8 (45H, unresolved multiplet, C_6H_5), −9.7 (1H,

* Corresponding author. Fax: +44-116-252-3789.

0022-1139/98/$ - see front matter
PII S0022-1139(98)00227-9

Table 1
X-ray crystal data collection, solution and refinement details for $[Rh(CO)(PPh_3)_3][BF_4]\cdot thf$

Formula	$C_{59}H_{53}BF_4O_2P_3Rh$
M	1076.64
Crystal size/mm	0.68×0.57×0.51
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.381 (2)
b (Å)	19.376 (3)
c (Å)	21.450 (3)
β (°)	91.49 (1)
U (Å^3)	5144.0 (14)
Z	4
D_c (g cm^{-3})	1.390
Absorption coefficient/mm^{-1}	0.483
$F(000)$	2216
T (K)	190 (2)
θ range (°)	2.67–25
ω-scan type, scan width (°)	0.80
Reflections collected	11068
Independent reflections	9054 (R_{int} = 0.0220)
Data, restraints, parameters	9050, 0, 631
Final $R1$ [b], $wR2$ [c] indices	0.0449, 0.1169
(all data)	0.0581, 0.1284
Difference map features (e Å^{-3})	1.050, −0.689

[a] Goodness of fit: $S=[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$, where n = number of reflections and p = total number of parameters refined.
[b] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[c] $wR2=[\Sigma(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

dtd, $^2J_{HP}$ 19, $^2J_{HP}$ 13, $^2J_{HH}$ 4, $H_{trans\text{-}CO}$), −11.5 (1H, dtd, $^2J_{HP}$ 115, $^2J_{HP}$ 19, $^2J_{HH}$ 4, $H_{trans\text{-}P}$); $^{31}P\{^1H\}$, δ 1.8 (2P, d, $^2J_{PP}$ 14, $P_{trans\text{-}P}$), −1.0 (1P, t, $^2J_{PP}$ 14, $P_{trans\text{-}H}$).

$[Rh(CO)(PPh_3)_2(solv.)][X]$. NMR(solv. = AHF; X = HF_2): $^{31}P\{^1H\}$, δ 45.1 (d, $^1J_{RhP}$ 179). NMR(solv. = CD_2Cl_2; X = BF_4): $^{31}P\{^1H\}$, δ 31.8 (d, $^1J_{RhP}$ 127). NMR(solv. = THF; X = BF_4): ^1H, δ 4.25 (2H, s, thf), 2.17 (2H, s, thf). $^{31}P\{^1H\}$, δ 30.6 (d, $^1J_{RhP}$ 125).

$[Rh(CO)(PPh_3)_3][BF_4]$. NMR(THF): $^{31}P\{^1H\}$, A_2BX, δ 27.3 (2P, $^1J_{RhP}$ -122, $^2J_{PP}$ 38, $P_{trans\text{-}P}$), 26.2 (1P, $^1J_{RhP}$ -130, $^2J_{pp}$ 38, $P_{trans\text{-}CO}$).

2.1. X-ray crystal structure determination

Crystals of $[Rh(CO)(PPh_3)_3][BF_4]\cdot thf$ were grown by slow evaporation from a thf solution. The crystal data and experimental parameters are given in Table 1. Data were collected using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). Unit cell parameters were obtained from the least squares fit of the setting angles of 27 automatically centred reflections. Intensity data were recorded using ω scans. Three check reflections monitored every 100 reflections showed no significant loss of intensity. The data were corrected for Lorentz and polarisation effects. A semi-empirical absorption correction based on psi scan data was applied, absorption T (max., min.) 0.778, 0.712. The structure was solved by Patterson methods using shelxtl-PC [9] and refined by full matrix least squares on F^2 using the program shelxl-93 [10]. Hydrogen atoms were included in calculated positions with C–H = 0.96 Å and final isotropic displacement parameter 0.08 Å^2. All non-hydrogen atoms were refined with anisotropic displacement parameters.

3. Results and discussion

The complexes $[MH(CO)(PPh_3)_3]$ (M = Rh and Ir) react readily with anhydrous HF to give yellow (Ir) and orange (Rh) products in solution for which ^{19}F NMR experiments, in marked contrast to those on the products obtained during the reaction of ruthenium and osmium hydrides with anhydrous HF [5], do not show any sign of metal-bound fluoride ligands, indicating that hydride–fluoride exchange reactions do not occur in these systems. The NMR spectra (vide infra) imply the formation of cationic metal complexes where the counterion is presumably HF_2^-. This counterion is readily replaced by anion exchange with, for example, $NaBF_4$. Alternatively, the tetrafluoroborate salts can be prepared more simply by direct reaction of the metal-containing starting materials with $HBF_4\cdot Et_2O$. These tetrafluoroborate salts are readily soluble in a range of organic solvents which has allowed confirmation of the nature of the products from the AHF reactions.

The products in all cases are readily identified from their ^1H and ^{31}P NMR spectra (Experimental). For M = Ir, the NMR spectral data are accounted for by the formation of the previously characterised cation, $[IrH_2(CO)(PPh_3)_3]^+$ (**I**). In particular, the ^1H NMR spectrum reveals, in addition to the resonances associated with the triphenylphosphine ligands, two mutually-coupled, doublets of doublets of triplets hydride resonances in a 1:1 ratio. The ^{31}P NMR spectrum shows two, mutually-coupled, resonances in a 2:1 ratio, both of which, from selective ^1H decoupling experiments, show coupling to both of the hydride resonances. Here, the anhydrous HF is acting purely as a very strong protic acid; the earlier preparations of this cation involved the reactions of $[IrH(CO)(PPh_3)_3]$ with other strong protic acids, e.g. sulphonic acids, RSO_3H (R = CF_3, CH_3, $C_6H_4CH_3$-*p*) [11] or fluorocarbon acids, $H_2C(SO_2CF_3)_2$, $PhCH(SO_2CF_3)_2$ and $HN(SO_2CF_3)_2$ [12].

For M = Rh, the NMR spectral data suggest that the product contains the novel cation $[Rh(CO)(PPh_3)_2(solv.)]^+$ (**II**). In particular, the ^1H NMR spectrum reveals only resonances associated with the triphenylphosphine ligands and the ^{31}P NMR spectra show two unrelated resonances. A singlet at δ 8.0, which reveals a large coupling ($^1J_{PH}$ = 510 Hz) when the decoupler is turned off, is readily assigned to $[HPPh_3]^+$ indicating that, during the reaction of $[RhH(CO)(PPh_3)_3]$ with AHF or HBF_4, triphenylphosphine is dissociated and then protonated. This prevents recoordination. We have proposed a similar ligand dissociation step in the reactions of $[MH_2(CO)(PPh_3)_3]$ (M = Ru, Os) with AHF [5] and it is well established that, in these ruthenium and osmium hydride complexes, the phosphine-*trans*-hydride is very labile in

solution. It is plausible, therefore, that the first step in the reaction of $[RhH(CO)(PPh_3)_3]$ is protonation to give the dihydride analogue of the iridium complex (**I**) but, when M = Rh, further reactions occur. The second resonance in the ^{31}P NMR spectrum is a wide doublet which is solvent dependent. In AHF, the peaks sharpen on cooling suggesting a fluxional process, but high temperature spectra are not accessible using AHF as solvent. When CD_2Cl_2 is used as the solvent for the reaction, the peaks are also broad at room temperature but, using THF as the solvent, the peaks are sharp and temperature independent. Following the loss of one triphenylphosphine ligand and the reductive elimination of H_2, a 14-electron species would be formed which, in the presence of a donor solvent such as THF, would formed the solvated (**II**). Additional evidence for solvent coordination arises from the THF reaction where the ^1H NMR spectrum recorded in CD_2Cl_2 clearly shows resonances broadened and shifted to higher frequency which are assigned to coordinated THF. The solvent can be displaced by the addition of a further equivalent of triphenylphosphine after the acid has been removed to give the previously characterised $[Rh(CO)(PPh_3)_3]^+$ (**III**) [12,13]. The ^{31}P NMR spectrum of (**III**) is a second-order A_2BX multiplet which may be simulated using the parameters detailed in the experimental (Fig. 1). These data are in close agreement with those reported earlier for (**III**) [12]. Hence, in contrast to the reaction of the iridium complex with AHF or HBF_4 which affords the same product as that obtained using other protic acids, the rhodium complex gives completely different products. In the reaction of $[RhH(CO)(PPh_3)_3]$ with fluorocarbon acids [12] no protonated phosphine is detected and a single product, $[Rh(CO)(PPh_3)_3]^+$ (**III**), is obtained. It is possible to obtain a mixture of (**III**) and (**II**) by the addition of a deficit of AHF or HBF_4 to the metal-containing starting material and it is also possible to identify the generation of small amounts of (**III**) from the observation of the most intense features of the second-order NMR spectrum in some of the other reactions. These results suggest that there are two possible reactions for $[RhH_2(CO)(PPh_3)_3]^+$; ligand dissociation/recombination and reductive elimination of hydrogen. The latter affords a stable, square planar, 16 electron complex which does not undergo further reaction, whilst in the former, which is the dominant reaction in the stronger protic acids AHF and HBF_4, the dissociated triphenylphosphine is protonated before re-combination to give the $[RhH_2(CO)(PPh_3)_2]^+$ which on reductive elimination of hydrogen affords the solvated (**II**).

The structure of $[Rh(CO)(PPh_3)_3][BF_4]\cdot thf$ is shown in Fig. 2 and selected bond lengths and angles are given in Table 2. Complex (**III**) exhibits slightly distorted square planar geometry about the rhodium atom. The metal, three phosphorus and carbonyl carbon atoms lie very close to the same plane (the dihedral angle between the planes containing P(1), P(3) and Rh(1) and C(1), P(2) and Rh(1) is only 4.0°) and the tetragonal distortion of the square-planar geometry common to neutral $[RhXL_3]$ complexes is not observed [14,15]. This presumably arises because the carbonyl ligand is small and some of the steric congestion behind the tetragonal distortion is relieved. Nevertheless, steric interactions between the bulky triphenylphosphine ligands causes significant asymmetry in the metal coordination sphere. Typically for $[RhXL_3]$ complexes, the Rh-P(*trans*-P) distances are very similar, e.g., 2.334(3) and 2.324(4) Å for the red-form of $[RhCl(PPh_3)_3]$ [15,16]. However, in (**III**), the Rh-P(1) distance at 2.328(1) Å is reasonable for a rhodium(I)-phosphine distance but is significantly shorter than Rh-P(2),

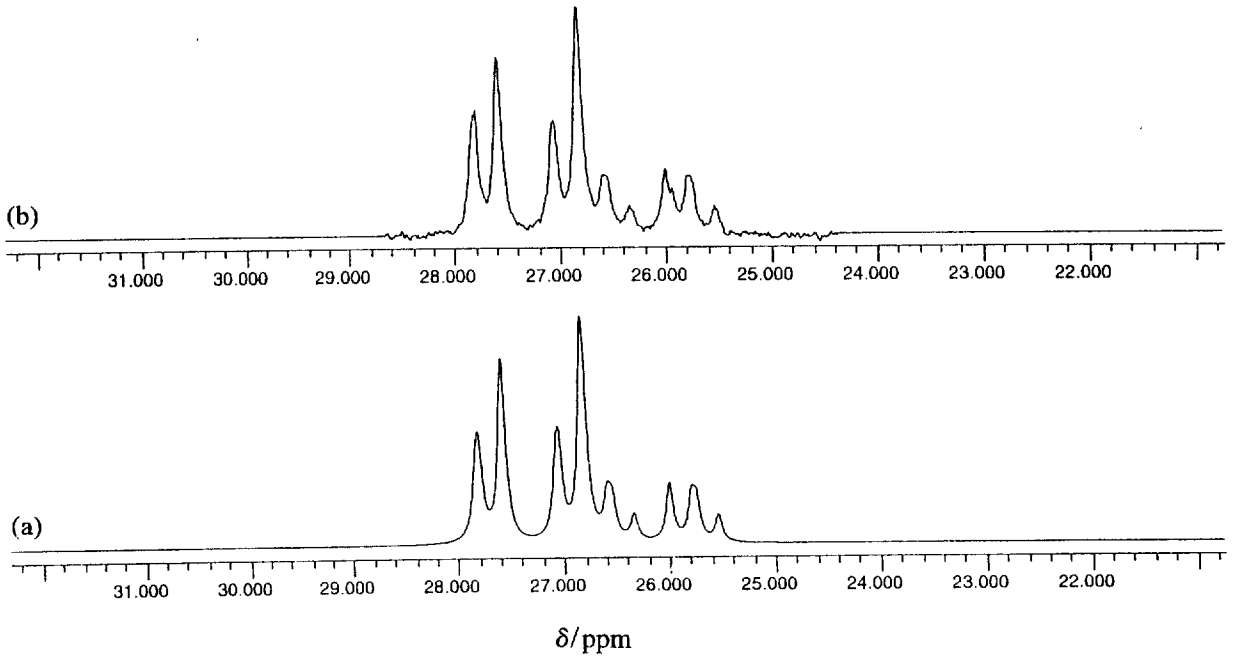


Fig. 1. Calculated (a) and experimental (b) 161.98 MHz $^{31}P\{^1H\}$ NMR Spectra of $[Rh(CO)(PPh_3)_3]^+$.

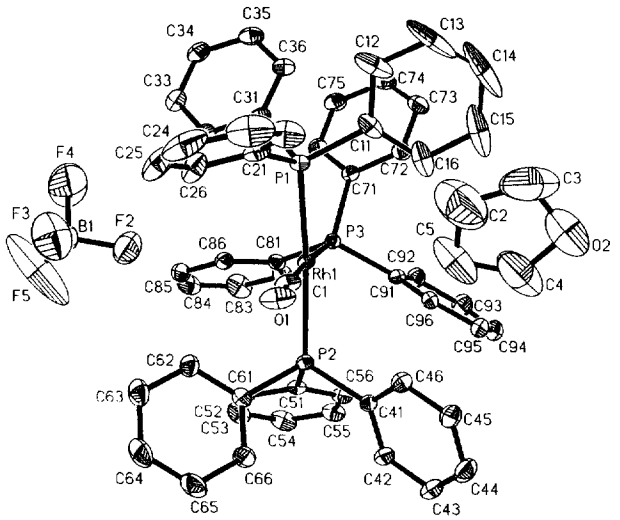
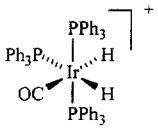
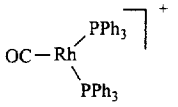


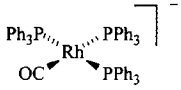
Fig. 2. Molecular structure of $[Rh(CO)(PPh_3)_3][BF_4]\cdot thf$. Displacement ellipsoids are shown at the 30% probability level.



(I)



(II)



(III)

2.380(1). Indeed Rh-P(2) (*trans*-P) is very similar to Rh-P(3) (*trans*-carbonyl) which is contrary to that which would be expected in view of the relative π-basicities of the *trans*-carbonyl and -phosphine ligands. It appears that the Rh-P(1) interaction dominates the metal coordination sphere. As a result of the short bond length, there is increased crowding in the plane resulting in the P(3)–Rh–C(1) axis (175.86(12)°) bending away from P(1), a compression of the P(2)–Rh–P(3) and P(2)–Rh–C(1) angles {92.37(3) and 84.96(12)°, respectively cf. P(1)–Rh–P(3) 95.90(3)° and P(1)–Rh–C(1) 86.91(12)°} and significant asymmetry in the geometries around P(2) and P(3). For P(1), the Rh–P(1)–C angles are very similar and show no obvious signs of crowding {115.6(2), 111.15(13) and 115.92(12)°}

Table 2
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[Rh(CO)(PPh_3)_3][BF_4]\cdot thf$

Rh(1)–C(1)	1.865(4)	Rh(1)–P(1)	2.3280(10)
Rh(1)–P(2)	2.3799(9)	Rh(1)–P(3)	2.3968(9)
P(1)–C(11)	1.812(4)	P(1)–C(31)	1.830(4)
P(1)–C(21)	1.846(4)	P(2)–C(51)	1.833(4)
P(2)–C(41)	1.835(4)	P(2)–C(61)	1.835(4)
P(3)–C(81)	1.827(4)	P(3)–C(91)	1.829(4)
P(3)–C(71)	1.834(3)	C(1)–O(1)	1.135(5)
C(1)–Rh(1)–P(1)	86.91(12)	C(1)–Rh(1)–P(2)	84.96(12)
P(1)–Rh(1)–P(2)	171.39(3)	C(1)–Rh(1)–P(3)	175.86(12)
P(1)–Rh(1)–P(3)	95.90(3)	P(2)–Rh(1)–P(3)	92.37(3)
C(11)–P(1)–C(31)	105.7(2)	C(11)–P(1)–C(21)	103.3(2)
C(31)–P(1)–C(21)	103.8(2)	C(11)–P(1)–Rh(1)	115.6(2)
C(31)–P(1)–Rh(1)	115.92(12)	C(21)–P(1)–Rh(1)	111.15(13)
C(51)–P(2)–C(41)	104.2(2)	C(51)–P(2)–C(61)	101.6(2)
C(41)–P(2)–C(61)	103.0(2)	C(51)–P(2)–Rh(1)	122.78(11)
C(41)–P(2)–Rh(1)	113.35(12)	C(61)–P(2)–Rh(1)	109.67(13)
C(81)–P(3)–C(91)	111.7(2)	C(81)–P(3)–C(71)	103.1(2)
C(91)–P(3)–C(71)	97.7(2)	C(81)–P(3)–Rh(1)	108.27(12)
C(91)–P(3)–Rh(1)	109.83(12)	C(71)–P(3)–Rh(1)	125.69(12)
O(1)–C(1)–Rh(1)	178.1(4)		

whilst for P(2) {109.67(13), 113.35(12) and 122.78(11)°} and P(3) {108.27(12), 109.83(12) and 125.69(12)°} steric crowding is relieved by bending two of the aryl rings away from the metal. This results in two short rhodium atom to *ortho*-hydrogen atom distances [Rh(1)...H(86A) 2.811 Å; Rh(1)...H(96A) 2.826 Å] suggestive of weak agostic interactions [17]; a similar (2.77 Å) interaction is found in the red form of $[RhCl(PPh_3)_3]$ [15].

4. Conclusions

Anhydrous HF readily protonates the metal complexes, $[MH(CO)(PPh_3)_3]$ (M = Rh or Ir), without the formation of a metal–fluoride bond, affording $[Rh(CO)(PPh_3)_2(solv.)]^+$ (**II**) and $[IrH_2(CO)(PPh_3)_3]^+$ (**I**) respectively, which have been characterised in solution by multinuclear NMR spectroscopies. Addition of triphenylphosphine to (**II**), or in the reaction of $[RhH(CO)(PPh_3)_3]$ with a deficit of acid, $[Rh(CO)(PPh_3)_3]^+$ (**III**) is formed which, as the tetrafluoroborate salt, has been structurally characterised to reveal a slightly distorted square planar geometry.

Acknowledgements

We would like to thank the EPSRC (HCSC, KSC) and the Royal Society (EGH) for financial support. Chemical Information File (CIF) for $[Rh(CO)(PPh_3)_3][BF_4]\cdot thf$ (**III**) has been deposited at the Cambridge Crystallographic Data Base Ref. No. 101474.

References

[1] S.A. Brewer, J.H. Holloway, E.G. Hope, J. Chem. Soc., Dalton Trans. (1994) 1067.

[2] S.A. Brewer, A.K. Brisdon, J.H. Holloway, E.G. Hope, L.A. Peck, P.G. Watson, J. Chem. Soc., Dalton Trans. (1995) 2945.

[3] S.A. Brewer, J.H. Holloway, E.G. Hope, J. Fluorine Chem. 70 (1995) 167.

[4] S.A. Brewer, L.A. Buggey, J.H. Holloway, E.G. Hope, J. Chem. Soc., Dalton Trans. (1995) 2941.

[5] K.S. Coleman, J.H. Holloway, E.G. Hope, J. Langer, J. Chem. Soc., Dalton Trans. (1997) 4555.

[6] N. Ahmed, S.D. Robinson, M.F. Uttley, J. Chem. Soc., Dalton Trans. (1972) 843.

[7] K.O. Christe, W.W. Wilson, C.J. Schack, J. Fluorine Chem. 11 (1971) 71.

[8] W.W. Dukat, J.H. Holloway, E.G. Hope, P.J. Townson, R.L. Powell, J. Fluorine Chem. 11 (1978) 293.

[9] G.M. Sheldrick, shelxtl PC Release 4.2, Siemens Analytical X-ray Instruments, Madison, WI, 1991.

[10] G.M. Sheldrick, shelxl-93, Program for Crystal Structure Refinement, University of Gottingen, Gottingen, Germany, 1993.

[11] P.A. Harding, S.D. Robinson, J. Chem. Soc., Dalton Trans. (1987) 947.

[12] A.R. Siedle, R.A. Newmark, R.D. Howells, Inorg. Chem. 27 (1988) 2473.

[13] M.J. Atherton, K.S. Coleman, J. Fawcett, J.H. Holloway, E.G. Hope, A. Karaçar, L.A. Peck, G.C. Saunders, J. Chem. Soc., Dalton Trans. (1995) 4029.

[14] M.J. Bennett, P.B. Donaldson, Inorg. Chem. 16 (1977) 655.

[15] P.B. Hitchcock, M. McPartlin, R. Mason, Chem. Commun. (1969) 1367.

[16] M. Brookhart, M.L.H. Green, L.-L. Wong, Prog. Inorg. Chem. 36 (1988) 1.

[17] L. Vaska, L.S. Chen, M.V. Miller, J. Am. Chem. Soc. 93 (1971) 6671.