Journal of Organometallic Chemistry, 65 (1974) 65—69

THE PREPARATION OF SOME GROUP VI FLUOROMETAL CARBONYL DERIVATIVES

W. DOUGLAS and J.K. RUFF

Department of Chemistry, University of Georgia, Athens, Georgia 30602 (U.S.A.)

(Received May 11th, 1973)

Summary

It has been found that fluoride ion can behave as a ligand towards the Group VI metal carbonyls. Thus the anions $Cr(CO)_5F^-$ and $W(CO)_5F^-$ were isolated and characterized. These products could be prepared by reaction of $[(C_6H_5)_3P]_2NF$ with the hexacarbonyls or by reaction of AgF with the dianions $M_2(CO)_{10}{}^{2-}$ (M = Cr or W). Their infrared spectra are discussed.

Introduction

Although a large number of bromo and iodo derivatives of the Group VI metal carbonyls are known where the metal is in the $0, +\frac{1}{2}, +1$ or $+2$ oxidation states (e.g. $M(CO)_5I^-$ [1], $Cr_2(CO)_{10}I$ [2], $Cr(CO)_5I$ [2], $[Mo(CO)_4I_2]_2$ [3,4] and $Mo(CO)_3I_3(C_6H_5)_3P^-$ [5] it was only recently that the first fluorocarbonyl derivative was reported [6]. The dimeric complex $[Mo(CO)_2F_4]_2$, prepared by reaction of $Mo(CO)_6$ and MoF_6, is highly reactive toward organic solvents and is unstable in glass [6]. (A similar reaction between ReF_6 and $Re_2(CO)_{10}$ produced monomeric $Re(CO)_3F_3$ [7].) The direct approach to the fluorocarbonyl derivatives via fluorination at low temperatures of the metal hexacarbonyls or $[C_5M_5M(CO)_3]_2$ dimers has not been successful [8].

Since bromide and iodide as well as pseudohalides are known to act as ligands towards the Group VI metal carbonyls [1,5] an attempt was made to utilize fluoride ion in this manner. Initial attempts to do this were unsuccessful and it was suggested that the products were too unstable at the temperature required for reaction to be isolated [1].

A recent report suggests the formation of a triply bridged fluoride derivative, $Mo_2(CO)_6F_3{}^{-3}$, but the material was also too unstable for complete characterization [9]. Two new routes to compounds of this type (e.g. $M(CO)_5X^-$ and $M_2(CO)_{10}X^-$) which may be run at or below room temperature have been developed [10,11]. These methods were applied to the preparation of $M(CO)_5F^-$ derivatives.

Experimental

All reactions were carried out under an inert atmosphere and all solvents were degassed prior to use. Analyses were performed by Meade Analytical Laboratories, Amherst, Massachusetts.

Preparation of $[(C_6H_5)_3P]_2NF\cdot CH_2Cl_2$

A 18.0 g (31.4 mmol) sample of $[(C_6H_5)_3P]_2NCl$, (hereafter abbreviated as PPNCl), in 50 ml of anhydrous CH_3OH was added to a suspension of 10.0 g (79.4 mmol) of AgF in 100 ml of anhydrous CH_3OH. The mixture was stirred for $\frac{1}{2}$ h before filtration. The filtrate was stripped and the residue dissolved in 250 ml of CH_2Cl_2. After filtering again, ether (≈ 400ml) was added to precipitate the product. The product was dried on the vacuum line for 1 h at 25°; 14.1 g (22.0 mmol, 70.4% yield) was obtained. Analysis found: C, 67.2; H, 4.54; Cl, 10.98. F, 2.87; N, 2.12; calcd: C, 69.4 H, 4.98; Cl 11.06; F, 2.96; N, 2.18%. Hydrolysable chlorine was found to be less than 0.05%. Thus little PPNCl was present. Attempted conversion of PPNCl to the fluoride using aqueous KF was not successful.

Preparation of PPN $M(CO)_5F$

Method A. A 2.5 g (1.72 mmol) sample of $(PPN)_2Cr_2(CO)_{10}$ was stirred with a suspension of 0.42 g (3.33 mmol) of AgF in 150 ml of THF for 5 h. The solvent was removed under vacuum and the residue extracted with 25 ml of CH_2Cl_2. After filtration, 100 ml of ether was added to the filtrate and it was allowed to stand for 1 h. The solution was filtered again and the filtrate stored at −10° for 10 h. The yellow crystals that formed were separated and then recrystallized from CH_2Cl_2 and ether. A 0.14 g (0.187 mmol) sample (5.5% yield) of $PPN[Cr(CO)_5F]$ was obtained; m.p. 165 - 167° (dec.). Analysis found: Cr, 7.01; F, 2.50; O, 10.7. Calcd: Cr, 7.23; F, 2.64; O, 11.1%. The preparation of $PPNW[(CO)_5F]$ was analogous. Reaction of 6.0 g (3.48 mmol) of $(PPN)_2W_2(CO)_{10}$ with 0.87 g (0.690 mmol) of AgF yielded 0.57 g (0.647 mmol) of $PPN[W(CO)_5F]$. Analysis found: F, 2.10; O, 9.10; W, 20.93. Calcd.: F, 2.16; O, 9.08; W, 20.89%. No hydrolysable chlorine, after degradation with dilute HNO_3, was present in either sample.

Method B. A mixture of 0.6 g (0.935 mmol) of $PPNF\cdot CH_2Cl_2$ and 1.0 g (4.55 mmol) of $Cr(CO)_6$ in 50 ml of CH_2Cl_2 was irradiated with a GE—AH4 floodlamp for 3 h. The solution was filtered and concentrated to ≈ 20 ml. Ether (60 ml) was added and the solution was allowed to stand for 1 h before being filtered. Pentane was added to the filtrate to precipitate 0.35 g (0.467 mmol, 50% yield) of $PPN[Cr(CO)_5F]$; m.p. 166 - 167°. Using 2.0 g (5.68 mmol) of $W(CO)_6$ and 0.6 g (0.935 mmol) of $PPNF\cdot CH_2Cl_2$ a yield of 0.21 g (0.238 mmol, 20%) of $PPN[W(CO)_5F]$ was obtained. Infrared spectra and mixed melting points proved that the products prepared by Methods A and B were identical.

Product characterization. Infared spectra of the two products were obtained on CH_2Cl_2 solutions using a Perkin—Elmer model 621 spectrometer which had been calibrated with indene. The infrared spectra of the other halocarbonyl derivatives (e. g. $PPN[W(CO)_5X]$ where X = Cl, Br and I) and on

PPN[Cr(CO)$_5$I] were obtained in an identical manner. The conductance of PPN[W(CO)$_5$F] as a function of concentration in nitromethane solution was determined using a Model 32 Conductivity Bridge from Yellow Springs Mfg. Co. The specific conductivity of the nitromethane was 4.2×10^{-7} ohm^{-1} and the cell constant was 0.1793 cm^{-1}. The molar concentration ($c \times 10^3$) and (equivalent conductance (cm^2 / ohm equiv)) of PPN[W(CO)$_5$F] are as follows: 3.060 (67.3); 1.530 (71.8); 0.765 (75.8), and 0.383 (80.8).

Discussion

The initial preparation of species of the type $M(CO)_5X^-$ (where M = Cr, Mo or W and X = Cl, Br or I) involved the reaction of the halide with the hexacarbonyl at elevated temperatures. Subsequently it was found that these compounds could be prepared at or below room temperature by (a) reaction of the dinuclear decacarbonyl anions $M_2(CO)_{10}{}^{2-}$ with a silver or mercury halide [11] or (b) by reaction of the halide ion with the photochemically produced $M(CO)_5$ moiety [10]. Both of these methods were successful when fluoride ion was employed.

$$M_2(CO)_{10}^{2-} + 2AgF \xrightarrow{THF} M(CO)_5F^- + 2Ag$$

$$M(CO)_6 + F^- \xrightarrow[h\nu]{CH_2Cl_2} M(CO)_5F^- + CO$$

Products could be isolated when either the chromium or tungsten carbonyl derivatives were used. Reaction occurred when the corresponding molybdenum derivatives were used but no product could be isolated. Although the yields in the photochemical reaction are much higher than in the redox reaction the source of the fluoride ion is important. The alkali metal fluorides and tetra-n-butylammonium fluoride did not work. This is perhaps due to a lack of solubility in CH_2Cl_2. Furthermore it was not possible to prepare the bridged fluoride derivatives under conditions where the bridged chloride, bromide or iodide compounds could be obtained. The products were isolated as light yellow crystalline solids which were sensitive to oxygen. Solutions of the products in CH_2Cl_2 or THF were not very stable and recrystallization led to loss of material.

The conductance of PPN[W(CO)$_5$F] was determined as a function of concentration and the resultant plot of $(\Lambda_\infty - \Lambda_c)$ vs. $\sqrt{c}$ yielded a slope of 258 which indicated the presence of a 1/1 electrolyte [13]. Attempts to obtain the ^{19}F NMR spectra of the anions $Cr(CO)_5F^-$ and $W(CO)_5F^-$ were unsuccessful due to the instability of the products in concentrated CH_2Cl_2 solutions.

The infrared spectra in the metal carbonyl stretching region for the $Cr(CO)_5F^-$ and $W(CO)_5F^-$ anions are given in Tables 1 and 2. Included are the spectra for the series $W(CO)_5X^-$ anions where X = Cl, Br and I. Probable assignments based on C_{4v} symmetry are also given. One notable aspect about the infrared spectra of the series $W(CO)_5X^-$ is that there is relatively little change in the $\nu(C{\equiv}O)$ frequencies even when the fluoride derivative is included. This suggests that the bonding between the metal and carbon is not appreciably

TABLE 1

ν(C≡O) FREQUENCIES (cm^{-1}) FOR PPN[W(CO)$_5$X]

	X			
	F	Cl	Br	I
A_1^1	2070w	2071w	2064w	2067w
B_1	1968w(sh)	1961w(sh)	1964w(sh)	1965w(sh)
E	1915s	1914s	1920s	1920s
A_1^2	1840m	1839m	1842m	1844m

TABLE 2

ν(C≡O) FREQUENCIES (cm^{-1}) FOR PPN[Cr(CO)$_5$X]

	X	
	F	I
A_1^1	2067w	2067w
B_1	1968w(sh)	1967w(sh)
E	1923s	1930s
A_1^2	1850m	1948m

affected by a change in the X group. Comparison of the infrared spectra of a number of other M(CO)$_5$L$^-$ derivatives, where L = SR [14], NCO, SCN [11] and CN [11], further demonstrates the insensitivity of the ν(C≡O) frequencies to substitution by anionic ligands.

The reason for the insensitivity of the ν(C≡O) frequencies upon different halide substitution in these anions is not known. The excess negative charge which tends to increase the electron density on the metal may override the effects of the substituent or the σ and π effects of the ligand may tend to cancel each other out. Recent studies of the infrared spectra of a series of compounds, Mn(CO)$_5$X, (where X = CH$_3$, Cl, Br and I) have attempted to correlate the ν(C≡O) frequencies with the σ and π bonding capabilities of the substituents [15]. Using CH$_3$Mn(CO)$_5$ as a reference it was found that the halides were better π acceptors than the CH$_3$ group and were also poorer σ donors. The σ acceptor strength decreased while the π donor ability increased with increasing electronegativity of the halide. Thus, fluoride would be expected to be a poorer σ donor than chloride but a better π acceptor. The combined effects on the metal halogen bond may tend to cancel each other.

Acknowledgement

The authors wish to acknowledge the support of the National Science Foundation under Grant No. GP11922.

References

1 E.W. Abel, I.S. Butler and J.G. Reid, J. Chem. Soc., (1963) 2068.
2 H. Behrens, Z. Naturforsch., B,19 (1964) 768.
3 R. Colton and I.B. Tomkins, Aust. J. Chem., 19 (1966) 1143.
4 R. Colton and I.B. Tomkins, Aust. J. Chem., 19 (1966) 1519.
5 W.S. Tsang, D.V. Meek and A. Wojcicki, Inorg. Chem., 7 (1968) 1263.
6 T.A. O'Donnell and K.A. Phillips, Inorg. Chem., 9 (1970) 2611.
7 T.A. O'Donnell and K.A. Phillips, Inorg. Chem., 11 (1972) 2563.

8 J.K. Ruff, unpublished results.
9 S.F. White and M.F. Farona, J. Organometal. Chem., 37 (1972) 119.
10 J.K. Ruff, Inorg. Chem., 7 (1968) 1921.
11 W.J. Schlientz and J.K. Ruff, Syn. Inorg. Metal.—Org. Chem., 1 (1971) 215.
12 J.K. Ruff and W.J. Schlientz, Inorg. Syn., 15 (1973) in press.
13 R.D. Feltham and R.G. Hayter. J. Chem. Soc., (1964) 4587.
14 W.J. Schlientz and J.K. Ruff, Inorg. Chem., 11 (1972) 2265.
15 W.A.G. Graham, Inorg. Chem., 7 (1968) 315.