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Preliminary communication

The preparation of pentacarbonyl heptafluoro-1-methylpropenyl metallate ions of chromium, molybdenum and tungsten

W. JOSEPH SCHLIENTZ and JOHN K. RUFF*
Department of Chemistry, University of Georgia, Athens, Georgia 30601 (U.S.A.)

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Although several examples are known in which a perfluoropropenyl group is bonded to a metal carbonyl derivative, no anionic derivatives have been reported[1]. The general preparative procedure employed for the known compounds is the reaction of perfluoroallyl chloride with metal carbonyl anions such as $Mn(CO)_5^-$ [2] or $Fe(CO)_2C_5H_5^-$ [3]. We wish to report the preparation of pentacarbonylheptafluoro-1-methylpropenyl metallate anions of the type $M(CO)_5C_4F_7^-$ (M = Cr, Mo or W). The synthesis of the pentacarbonyl perfluoro-1-methylpropenyl metallate anions employed the recently discovered redox reaction[4] which occurs between silver salts and the dinuclear metal carbonyl anions[5], $M_2(CO)_{10}^{2-}$ (where M = Cr, Mo or W). The reaction between the dianion and *trans*-perfluoro-1-methylpropenylsilver[6] occurs according to the following stoichiometry:

$$M_2(CO)_{10}^{2-} + 2AgC_4F_7 \longrightarrow 2M(CO)_5C_4F_7^- + 2Ag$$

The anions of the three Group VI metals were isolated using the bis(triphenylphosphine)iminium[7] cation, $[Ph_3PNHPPh_3]_2^+$ as the counterion (here after abbreviated as PPN). For example reaction of 1.8 g (1.1 mmole) of $[PPN]_2[W_2(CO)_{10}]$ with 0.58 g (2.0 mmole) of AgC_4F_7 in 25 ml of THF led to the immediate formation of metallic silver. After addition of 100 ml of diethyl ether and approximately 1 g of Celite Filter Aid the solution was allowed to stand at −10° for 0.5 h. The solution was then filtered and the solvent was removed under vacuum. The residue was redissolved in diethyl ether and the product was crystallized by addition of pentane to yield 1.3 g (63% yield) of $[PPN][W(CO)_5C_4F_7]$. The molybdenum and chromium compounds were prepared in an analogous fashion. (Yield Cr, 34%; Yield Mo, 26%). Analyses and melting points are listed in Table 1.

The salts are slowly oxidized by air but they can be stored under nitrogen at −10° for several weeks. They are soluble in polar organic solvents such as dichloromethane, tetrahydrofuran and diethyl ether but are insoluble in benzene and pentane. The tungsten salt in nitromethane was shown to be a 1/1 electrolyte by the study of its conductance as a function of concentration. A plot of $\Lambda_{00}-\Lambda_c$ *vs.* $\sqrt{c}$ gave a slope of 282, within the expected range[8]. The chromium and molybdenum salts were not sufficiently stable in solution to allow measurements.

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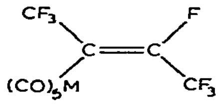
*Alfred P. Sloan Fellow 1960–1971.

TABLE 1
PROPERTIES OF THE [PPN] [$M(CO)_5C_4F_7$] SALTS

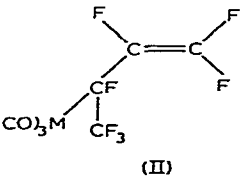
Metal	M.p. (°C)	Color	Analysis: Found (calcd.) C	H	F	M
Cr	113-116	white	59.4	3.2	14.4	
			(59.3)	(3.3)	(14.6)	
Mo	123-125	white	56.7	3.3	14.0	10.1
			(56.5)	(3.1)	(13.9)	(10.1)
W	127-130	pale yellow	51.9	2.8	12.8	17.8
			(51.9)	(2.8)	(12.8)	(17.6)

The infrared spectra of the three salts in THF solution show only three absorptions in the $\nu(C{\equiv}O)$ region (see Table 2). This is consistent with C_{4v} site symmetry for the metal ($2A_1 + E$)[9]. The frequency assigned to the two A_1 modes and the E mode (*e.g.* 2061 and 1872 cm^{-1} for the A_1 modes and 1913 for the E mode in the tungsten salt) are close to those $\nu(C{\equiv}O)$ modes observed for other $M(CO)_5X^-$ anions[10,11]. No bands occurred in the region from 1570 cm^{-1} to the lowest $A_1\,\nu(C{\equiv}O)$. Thus the $\nu(C{\equiv}C)$ stretching frequency in the propenyl group was not observed, either because of interference with the absorption at 1570 cm^{-1} (due to the cation) or because of its inherently low extinction coefficient.

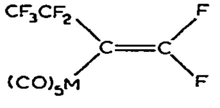
Since the electronegativities of several perfluoroalkyl groups have been estimated to lie between chlorine and bromine[12], it is tempting to consider the formation of the complex anions as rising from the displacement of THF in the neutral $M(CO)_5THF$ species which is generated during the redox reaction★. Displacement of THF from the photochemically produced $M(CO)_5THF$ moiety is well known to occur in the presence of numerous bases such as halide ions or phosphines[10,11,12]. However, it is not possible to determine whether the C_4F_7 group retains its *trans* configuration or even its identity when bonded to the Group VI metal from the infrared spectra.



(I)



(II)



(III)

The ^{19}F NMR spectra of all three complex anions ($M(CO)_5C_4F_7^-$) are essentially identical (see Table 2) and consist of two doublets and a multiplet (relative areas 3/3/1). Since the spectra are also nearly identical to that reported for *trans*-AgC_4F_7, it is likely that the *trans* configuration of the propenyl group was retained (structure I) and that fluorine migration to form an allylic system did not occur (structures II and III). The

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★Evidence for the formation of $M(CO)_5THF$ during reaction of the $M_2(CO)_{10}^{2-}$ anions with $HgCl_2$ was obtained by isolating, $M(CO)_5PF_2N(C_2H_5)_2$ in moderate yield when the reaction was carried out in the presence of the fluorophosphine. No reaction occurs between the fluorophosphine and the dianions under similar conditions[14].

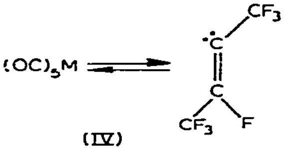
TABLE 2

INFRARED AND ^{19}F NMR DATA FOR THE [PPN] [$M(CO)_5C_4F_7$] SALTS

M	ν(C≡O)	^{19}F NMR^a(CH_2Cl_2), ppm from $CFCl_3$
Cr	2048 w, 1920 s, 1872 m	47.5 d (*J* 20 Hz), 62.5 d (*J* 9 Hz), 88.6 m
Mo	2059 w, 1923 s, 1872 m	47.8 d (*J* 21 Hz), 62.9 d (*J* 9 Hz), 88.6 m
W	2061 w, 1913 s, 1863 m	47.6 d (*J* 20 Hz), 62.6 d (*J* 10 Hz), 88.2 m

^{a}d, doublet; m, unresolved multiplet. Coupling constants in parentheses.

latter two structures are unlikely since perfluorovinyl groups bonded to transition metals are more stable than the isomeric allylic systems[1]. The possibility that the carbon–carbon double bond is perpendicular to the metal, as is found in Zeise's salt and many other olefin complexes, is unlikely but not inconsistent with the ^{19}F NMR (structure IV).



(IV)

This type of configuration has not been definitely established for perfluorocarbon–olefin complexes. Furthermore, olefins bound to transition metals in this manner are easily displaced by stronger bases. No such displacement was observed when [PPN] [$W(CO)_5$-C_4F_7] was treated with $(C_6H_5)_3P$ in THF under ambient conditions. Thus it is concluded that like most of the other known examples of perfluorovinylmetalcarbonyl complexes the bonding in structure I is the correct one.

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