Chemistry of the Metal Carbonyls VIII

Perfluoroacetyl and Perfluoroalkyl Derivatives of Manganese and Rhenium

By H. D. Kaesz, R. B. King, and F. G. A. Stone

Mallinkrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts, U.S.A.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution 4.0 International License.

Many compounds are known wherein a perfluoroalkyl group is bonded to a non-metal or metalloid, but only a few perfluoroalkyl metal compounds have been described, and these involve metals of the main groups of the Periodic Table. However, there appears to be no valid reason why certain perfluoroalkyl transition metal derivatives should not exist. Indeed, the relatively high electronegativity of perfluoroalkyl groups, compared with alkyl groups, should favor formation of stable σ-bonds with transition metals. This note reports the synthesis of new perfluoroalkylmanganese- and perfluoroalkylrhenium-pentacarbonyl compounds by decarboxylation of the perfluoroacetyl derivatives \( \text{C}_n\text{F}_{2n+1}\text{COMe}(\text{CO})_5 \) \( [\text{Me} = \text{Mn}, \text{Re}] \). The latter substances are also new, and may be obtained by treating tetrahydrofuran solutions of the salts \( \text{NaMn}(\text{CO})_5 \) or \( \text{NaRe}(\text{CO})_5 \) with perfluoroacetyl halides. This route to organometallics of the type \( \text{C}_n\text{F}_{2n+1}\text{Me}(\text{CO})_5 \) \( [\text{Me} = \text{Mn}, \text{Re}] \) was suggested by the previous discovery that acylmanganese- and acylrhenium-pentacarbonyl compounds may be decarboxylated to give a variety of organonitrogenous and organonitrogenous pentacarbonyl compounds.

The perfluoroacetyl derivatives of general formula \( \text{C}_n\text{F}_{2n+1}\text{COMe}(\text{CO})_5 \) (Table 1) are air stable, very volatile, white to pale-yellow crystalline solids, which may be converted in about 80—100% yield into the corresponding perfluoroalkyl derivatives by heating in an evacuated bulb to 80° in the case of the manganese compounds, and to 120—150° in the case of the rhenium compounds. The perfluoroalkyl compounds (Table 1) are like the perfluoroacetyl derivatives in being completely air-stable and very volatile. The vapor pressures of liquid \( \text{C}_n\text{F}_{2n}(\text{CO})_5 \) studied over the range 80—120° correspond to the equation \( \log_{10} P_{\text{mm}} = 9.100 - 2662 T^{-1} \), implying an extrapolated boiling point of 155°. No evidence of thermal decomposition was observed up to 120° but above this temperature the compound began to react with the mercury in the vapor pressure apparatus, forming a white solid.

The F{sup 19} n.m.r. spectra of the compounds listed in Table 1 are currently under study. In the spectrum of the compound \( \text{C}_5\text{F}_{13}\text{Mn}(\text{CO})_5 \), the resonance due to the CF{sub 3} group is at 84 p.p.m. \({\text{10}}\) and that of the CF{sub 2} group at 69 p.p.m. However, in the spectrum of the acyl compound \( \text{C}_5\text{F}_{13}\text{COMn}(\text{CO})_5 \) while the resonance due to the CF{sub 3} group is at 80 p.p.m., that due to the CF{sub 2} group is at 115 p.p.m. The great difference in the positions of the F{sup 19} resonances in the CF{sub 2} groups of the two compounds.

---

1. For part VII of this series see J. Amer. chem. Soc. 82, December [1960].
2. Present address: Department of Chemistry, University of California, Los Angeles, California.
5. During the early part of our work the existence of the two compounds \( \text{CF}_3\text{COMn}(\text{CO})_5 \) and \( \text{CF}_2\text{Mn}(\text{CO})_5 \) was reported by T. H. Coffield, J. Kozirowski and R. D. Cluson, Abstract of the International Conference on Coordination Chemistry, London, April, 1959, p. 126.
10. Chemical shifts given are relative to CCl{sub 4}F used as an internal standard, and are measured in dilute CCl{sub 4}F solutions. The spectra were taken at 40 mc. on a Varian Model 4300 B high resolution spectrometer.
is undoubtedly a consequence of the fact that in C$_2$F$_5$Mn(CO)$_5$ the CF$_2$ group is bonded directly to manganese whereas in C$_2$F$_5$COMn(CO)$_5$ the CF$_2$ group is separated from manganese by a carbonyl group.

The infrared spectra of the perfluoroacyl manganese and rhenium compounds show a strong band near 1650 cm$^{-1}$ (e.g. in C$_2$F$_5$CORE(CO)$_5$ (CCl$_2$ : CCl$_4$ solution) at 1646 cm$^{-1}$) due to the acyl carbonyl group. This band is of course absent in the perfluoroalkyl compounds. All the compounds listed in Table 1 have in their infrared spectra bands near 2000 cm$^{-1}$ due to the carbonyl groups of the Me(CO)$_5$ [Me = Mn, Re] moieties, and bands in the region 1000 – 1300 cm$^{-1}$ due to the C–F bonds of the fluorocarbon groups. All these bands are very strong and in, for example, C$_2$F$_5$Mn(CO)$_5$ (CCl$_2$ : CCl$_4$ solution, CaF$_2$ prism) appear at 2130 (w), 2072 (w), 2038 (v.s.), 2023 (s), 2002 (v.w.) and 1983 (v.v.) cm$^{-1}$ for the carbonyl region, while the C–F bands (NaCl optics) appear at 1296 (s), 1268 (v.v.), 1178 (v.s.), 1031 (v.s.), 1008 (v.s.) and 906 (v.s.) cm$^{-1}$.

Current interest in π-allyl metal compounds prompted us to study the reaction between perfluoroalkyl chloride and NaMn(CO)$_5$ in tetrahydrofuran. From the reaction mixture a white crystalline volatile solid (m.p. 71 – 72$^\circ$) was isolated of composition C$_3$F$_5$Mn(CO)$_5$ [Calcd. for C$_3$F$_5$O$_5$Mn: C, 29.5; F, 29.1; Mn, 16.9. Found: C, 29.3; F, 28.9; Mn, 17.0]. Unlike α-allylmanganese pentacarbonyl, the new compound C$_3$F$_5$Mn(CO)$_5$ is stable in air even over a period of months, and moreover, when heated to 120$^\circ$ in an evacuated bulb did not release carbon monoxide. Furthermore, the $^19$F n.m.r. spectrum of C$_3$F$_5$Mn(CO)$_5$ does not show a 2 : 2 : 1 ratio of peaks intensities like the $^1$H spectrum of π-allylmanganese tetracarbonyl, but shows a 3 : 1 : 1 ratio of peaks. Of the latter, the most intense occurs as a quadruplet at 67 p.p.m., while the two weaker ones occur at 95 p.p.m. and 164 p.p.m. as doubles of quadruplets. These properties indicate that the compound C$_3$F$_5$Mn(CO)$_5$ is α-perfluoropropenylmanganese pentacarbonyl rather than α-perfluoroallylmanganese pentacarbonyl.

Reaction between the acid chloride C$_3$F$_5$COCl and the salt C$_3$H$_5$Mo(CO)$_3$Na in tetrahydrofuran afforded the new compound C$_3$H$_5$Mo(CO)$_3$(CO$_3$F$_3$) in 8% yield [calcd. for C$_3$H$_5$F$_3$O$_4$Mo : C, 32.6; H, 1.1. Found: C, 32.6; H, 1.0%]. This perfluoroacetyl molybdenum compound is a yellow solid melting at about room temperature. It is somewhat air-sensitive turning blue on exposure to air for several hours. It darkens on prolonged storage at room temperature even under nitrogen but seems to be stable when stored under nitrogen below 0$^\circ$. Even though this perfluoroacetyl molybdenum compound is much less stable than the perfluoroacyl manganese and perfluoroacyl rhenium compounds reported above, it is apparently more stable than analogous compounds derived from non-fluorinated acyl groups which are described as being too unstable for isolation in the pure state.

We are indebted to the Ethyl Corporation for a gift of manganese carbonyl. This research was supported by the United States Air Force under Contract No. AF 49(638)-518, monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.