Chemistry of the Metal Carbylons VIII
Perfluoroacyl and Perfluoroalkyl Derivatives of Manganese and Rhenium

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Perfluoracylchloride reagieren mit Lösungen von Mn(CO)₅Na und Re(CO)₅Na nach
RfCOCl + Me(CO)₅Na → RfCOMe(CO)₅ + NaCl
zu Perfluoracyl-Derivaten von Mangan und Rhenium. Durch Decarboxylierung dieser Perfluoracyl-
Verbindungen erhält man die entsprechenden Perfluorallymangan- und Perfluorallyrhenium-
verbündungen, RfMe(CO)₅.

Many compounds are known wherein a perfluoro-
alkyl group is bonded to a non-metal or metalloid,¹ but only a few perfluoralkyl metal compounds have been described, and these involve metals of the main groups of the Periodic Table.² However, there appears to be no valid reason why certain per-
fluoralkyl transition metal derivatives should not exist. Indeed, the relatively high electronegativity of perfluoralkyl groups, compared with alkyl groups, should favor formation of stable σ-bonds with transition metals. This note reports the synthe-
thesis of new perfluoralkylmanganese- and perfluoro-
alkylrhenium-pentacarbonyl compounds by dec-
carboxylation of the perfluoracyl derivatives C₅F₈n+₁COMe(CO)₅ (Me = Mn, Re). The latter substances are also new,³ and may be obtained by treating tetrahydrofuran solutions of the salts NaMn(CO)₅ or NaRe(CO)₅ with perfluoracyl halides. This route to organometallics of the type C₅F₈n+₁Me(CO)₅ (Me = Mn, Re) was suggested by the previous discovery that acylmanganese- and acylrhenium-pentacarbonyl compounds may be de-
carboxylated to give a variety of organomanganese and organorhenium pentacarbonyl compounds.⁴ ⁵ ⁶ ⁷

The perfluoracyl derivatives of general formula C₅F₈n+₁COMe(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 perfluoralkyl derivatives by heating in an evacuated bulb to 80⁰ in the case of the man-
ganeses compounds, and to 120 — 150° in the case of the rhenium compounds. The perfluoralkyl compounds (Table 1) are like the perfluoracetyl derivatives in being completely air-stable and very volatile. The vapor pressures of liquid CF₃F₂Mn(CO)₅ studied over the range 80 — 120⁰ correspond to the equation log₁₀ P 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,⁸ forming a white solid.

The F¹⁹ n.m.r. spectra of the compounds listed in Table 1 are currently under study.⁹ In the spectrum of the compound CF₃F₂Mn(CO)₅, the resonance due to the CF₃ group is at 84 p.p.m.¹⁰ and that of the CF₃ group at 69 p.p.m. However, in the spectrum of the acyl compound CF₅COM(CO)₅, while the resonance due to the CF₃ group is at 80 p.p.m., that due to the CF₃ group is at 115 p.p.m. The great difference in the positions of the F¹⁹ reso-
nces in the CF₃ groups of the two compounds

¹ For part VII of this series see J. Amer. chem. Soc. 82, December [1960].
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⁵ During the early part of our work the existence of the two compounds CF₅COM(CO)₅ and CF₃Mn(CO)₅, was reported by T. H. Coffield, J. Koszowki and R. D. Closson, Abstracts of the International Conference on Coordination Chemistry, London, April, 1959, p. 126.
⁹ E. Pitcher and F. G. A. Stone, unpublished observations.
¹⁰ Chemical shifts given are relative to CF₅CF₃F used as an internal standard, and are measured in dilute CF₅CF₃F solutions. The spectra were taken at 40 mc. on a Varian Model 4300 B high resolution spectrometer.
Table 1. Some perfluoroacetyl and perfluoroalkyl manganese and rhenium pentacarbonyl compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>M. p.</th>
<th>Analysis [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[°C]</td>
<td>Carbon</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Required</td>
</tr>
<tr>
<td>C₂F₅COMn(CO)₅</td>
<td>49—50</td>
<td>28.1</td>
</tr>
<tr>
<td>C₂F₅COMn(CO)₅</td>
<td>38—40</td>
<td>27.6</td>
</tr>
<tr>
<td>C₂F₅CORe(CO)₅</td>
<td>81—83</td>
<td>20.3</td>
</tr>
<tr>
<td>C₂F₅CORe(CO)₅</td>
<td>54</td>
<td>20.7</td>
</tr>
<tr>
<td>C₂F₅Mn(CO)₅</td>
<td>15—17</td>
<td>26.8</td>
</tr>
<tr>
<td>C₂F₅Mn(CO)₅</td>
<td>~ 0°</td>
<td>26.4</td>
</tr>
<tr>
<td>C₂F₅Re(CO)₅</td>
<td>30—40</td>
<td>18.9</td>
</tr>
<tr>
<td>C₂F₅Re(CO)₅</td>
<td>~ 27°</td>
<td>19.4</td>
</tr>
</tbody>
</table>

is undoubtedly a consequence of the fact that in C₂F₅Mn(CO)₅ the CF₂ group is bonded directly to manganese whereas in C₂F₅COMn(CO)₅ the CF₂ group is separated from manganese by a carbonyl group.

The infrared spectra of the perfluoroacetyl manganese and rhenium compounds show a strong band near 1650 cm⁻¹ (e.g. in C₂F₅CORe(CO)₅ (CCl₂ : CCl₄ 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, C₂F₅Mn(CO)₅ (CCl₂ : CCl₄ solution, CaF₂ 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 ¹¹—¹³ prompted us to study the reaction between perfluoroalkyl chloride and NaN₅(CO)₅ in tetrahydrofuran. From the reaction mixture a white crystalline volatile solid (m.p. 71 — 72°) was isolated of composition C₃F₅Mn(CO)₅ [Calc. for C₃F₅O₅Mn : C, 29.5; F, 29.1; Mn, 16.9. Found: C, 29.3; F, 28.9; Mn, 17.0]. Unlike α-allylmanganese pentacarbonyl ¹³, the new compound C₃F₅Mn(CO)₅ is stable in air even over a period of months, and moreover, when heated to 120° in an evacuated bulb did not release carbon monoxide. Furthermore, the F¹⁹ n.m.r. spectrum of C₃F₅Mn(CO)₅ does not show a 2 : 2 : 1 ratio of peak intensities like the H¹ spectrum of π-allylmanganese tetracarbonyl ¹³, 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 C₃F₅Mn(CO)₅ is α-perfluoropropenylmanganese pentacarbonyl rather than α-perfluoroallylmanganese pentacarbonyl.

Reaction between the acid chloride C₅F₅COCl and the salt C₅H₅Mo(CO)₃Na ¹⁴ in tetrahydrofuran afforded the new compound C₅H₅Mo(CO)₃(CO₅F₅) in 8% yield [Calc. for C₁₂H₅F₇O₄Mo : 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°. Even though this perfluoroacetyl molybdenum compound is much less stable than the perfluoroacetyl manganese and perfluoroacetyl rhenium compounds reported above, it is apparently more stable than analogous compounds derived from non-fluorinated acyl groups which are described ¹⁸ as being too unstable for isolation in the pure state.

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