

proximations can be very useful, even though the mathematical approximation of localizing the particles is not at all in accord with the real, very mobile molecular system. Of course, distinct from the binding question, the use of Ising methods to compute the electrostatic energy and other properties remains a valuable method of accounting for the discrete nature of the charges. The view proposed satisfies all the available criteria by which ion binding has been introduced: The high concentration in the "bound monolayer" insures very effective charge-charge shielding; the division in terms of the ionic distribution should, as in the case of simple electrolytes, be relatively field independent at low fields¹⁸ but yield a large Wien effect (as has been observed¹⁹); since we do not appeal to discrete ion-pair formation, it is clear that counterion binding and low counterion activity coefficients are but two descriptions of one phenomenon²⁰; we suggest that lattice gas calculations, which are in semiquantitative agreement with experiment, are useful mathematical approximations and that such a model should not be interpreted blindly in terms of pairs.

We now turn briefly to the possible extension of the models proposed herein to the case of coiled polyions. The results of Nagasawa and Rice⁶ indicated that the mean electrostatic field at a

(18) F. T. Wall, H. Terayama and S. Techakumpuch, *J. Polymer Sci.*, **20**, 477 (1956).

(19) F. E. Bailey, A. Patterson and R. M. Fuoss, *J. Am. Chem. Soc.*, **74**, 1845 (1952).

(20) M. Nagasawa, *ibid.*, **83**, 1026 (1961).

charged site inside a polyion had major contributions from both the near neighbor and the rest of the polyion. This suggests that we take the multiply charged linear model and imbed it inside a polyion. Such a model would correspond to choosing an electrostatic Kuhn element and surrounding this element with a more or less spherical charge distribution. Qualitatively, we expect the potential due to the rest of the ion to be approximately constant throughout the polymer domain.²¹ Thus, we would anticipate that the activity coefficient of the counterion would be further depressed (over that calculated herein for the small compounds) and that its value would be independent of molecular weight. While these qualitative features are easily seen to follow from the physical nature of the model, the mathematical formulation of this problem is fraught with difficulties, and more details will be presented in a subsequent paper.²²

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(21) J. Hermans and J. T. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1949).

(22) See, however, the related earlier calculation: F. E. Harris and S. A. Rice, *J. Chem. Phys.*, **25**, 955 (1956).

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Perfluoroalkyl and Perfluoroacyl Metal Carbonyls

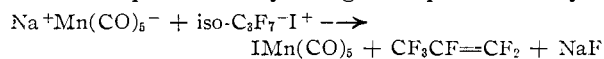
BY W. R. McCLELLAN

RECEIVED OCTOBER 19, 1960

Perfluoroacyl and perfluoroalkyl derivatives of manganese pentacarbonyl, $R_f\text{-CO-Mn(CO)}_5$ and $R_f\text{-Mn(CO)}_5$, respectively, where $R_f = \text{CF}_3$, $n\text{-C}_3\text{F}_7$ and $\text{iso-C}_3\text{F}_7$, and the perfluoromethyl-, -ethyl and -*n*-propyl derivatives of cobalt tetracarbonyl have been prepared by reaction of the appropriate perfluoroacyl halide with the lithium derivative of manganese or cobalt carbonyl hydride. The perfluoroalkylcobalt compounds have outstanding stability compared to their hydrocarbon analogs. The preparation of perfluoropropenylmanganese pentacarbonyl is also described.

Closson, Kozikowski and Coffield¹ have reported the preparation of alkyl- and acylmanganese pentacarbonyls by reaction of alkyl and acyl halides with sodium manganese pentacarbonyl. Certain of the acyl compounds lose the keto carbonyl on heating to give the corresponding alkyl derivatives and, in most cases, this reaction is reversed by carbon monoxide gas under high pressure.

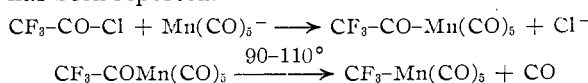
Because of the positive character of the halogen atom, reaction of perfluoroalkyl halides with sodium manganese pentacarbonyl does not provide a route to perfluoroalkylmanganese pentacarbonyls



The preparation of trifluoromethylmanganese pentacarbonyl, however, by thermal decarbonyla-

(1) R. D. Closson, J. Kozikowski and T. H. Coffield, *J. Org. Chem.*, **22**, 598 (1957).

tion of trifluoroacetylmanganese pentacarbonyl has been reported.²



We have used this route to prepare several other perfluoroacyl and perfluoroalkylmanganese pentacarbonyl derivatives described in Table I.

The only previously described cobalt tetracarbonyls have been the methyl,^{3,4} ethyl⁴ and benzyl derivatives which, because of their high degree of instability, have been prepared and isolated at sub-zero temperatures. We have prepared several

(2) T. H. Coffield, J. Kozikowski and R. D. Closson, International Conference on Coordination Chemistry (London, 1959), p. 126 (Abstract), Burlington House, London, 1959.

(3) W. Hieber, *Z. Naturforsch.*, **13b**, 192 (1958).

(4) D. S. Breslow and R. F. Heck, *Chem. and Ind. (London)*, 467 (1960).

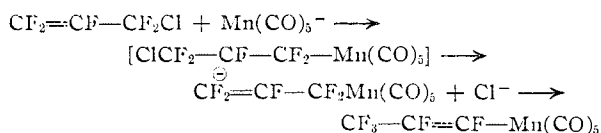
TABLE I
 PERFLUORO METAL CARBONYL DERIVATIVES

| Compound | Mode of preparation | Temp., °C. | Yield, % | Analytical | | | | Color | M.p., °C. | B.p., °C. (mm.) | Infrared data ^a | | F ¹⁹ magnetic resonance data ^b | |
|--|--|---------------|-------------|-------------|----------|-------|--------------|-------------|--------------|-----------------------|-------------------------------|------|---|-------------------------------------|
| | | | | C | H | Metal | Halo- gen | | | | (a) | (b) | Chemical shifts (p.p.m.) | In- tensity rela- tionship |
| CF ₃ -CO-Mn(CO) ₅ (I) | CF ₃ -CO-F, LiMn(CO) ₅ | 25 | 75 | Calcd. 28.8 | | 18.8 | 19.5 | Pale yellow | 55-56 | 55 (15) ^c | 6.15 | 4.65 | | |
| CF ₃ Mn(CO) ₅ (II) | From (I) | 110 | 92 | Found 28.7 | | 18.3 | 19.4 | White | 82-83 | 70 (20) ^c | .. | 4.64 | -85.8 (S) ^d | |
| | | | | Calcd. 27.3 | | 20.8 | 21.6 | | | | | | | |
| <i>iso</i> -C ₃ F ₇ -CO-Mn(CO) ₅ (IV) | <i>iso</i> -C ₃ F ₇ -CO-F, LiMn(CO) ₅ | -80 to 25 | 62 | Calcd. 27.6 | | 14.0 | 33.9 | Pale yellow | 34-37 | 58 (3) | 6.05 | 4.67 | | |
| | | | | Found 27.4 | | 15.3 | 32.4 | | | | | | | |
| <i>iso</i> -C ₃ F ₇ Mn(CO) ₅ | From (IV) | 110 | 90 | Calcd. 26.4 | | 15.1 | 36.5 | Colorless | 2 | 73 (17) | .. | 4.65 | -8.9 (S), ^e +87.1 (S) ^e | 6:1 |
| | | | | Found 26.9 | | 15.0 | 36.6 | | | | | | | |
| <i>n</i> -C ₃ F ₇ -CO-Mn(CO) ₅ (V) | <i>n</i> -C ₃ F ₇ -CO-Cl, LiMn(CO) ₅ | 25 | 83 | Calcd. 27.6 | | 14.0 | 33.9 | Pale yellow | | 56 (3) | 6.04 | 4.65 | | |
| | | | | Found 26.9 | | 14.7 | 35.1 | | | | | | | |
| <i>n</i> -C ₃ F ₇ Mn(CO) ₅ | From (V) | 105 | 90 | Calcd. 26.4 | | 15.1 | 36.5 | Colorless | | 66 (13) | .. | 4.67 | +0.45 (T), -11.3 (Q), +37.6 (S), J _{F-F} = 8 | 3:2:2 |
| | | | | Found 26.4 | | 14.6 | 36.4 | | | | | | | |
| Cl(CF ₂) ₄ -CO-Mn(CO) ₅ (VI) | Cl(CF ₂) ₄ -CO-Cl, LiMn(CO) ₅ | -15 to 25 | 75 | Calcd. 26.2 | 7.7 (Cl) | 12.0 | 33.2 | Pale yellow | 39-40 | 50 (2) ^c | 6.02 | 4.67 | | |
| | | | | Found 26.3 | 7.4 (Cl) | 12.4 | 29.8 | | | | | | | |
| Cl(CF ₂) ₄ -Mn(CO) ₅ | From (VI) | 90 | 90 | Calcd. 25.0 | 8.3 (Cl) | 12.8 | 35.3 | Pale yellow | | 58 (1) | .. | 4.68 | | |
| | | | | Found 25.9 | 7.9 (Cl) | 11.7 | 34.5 | | | | | | | |
| H(CF ₂) ₄ -CO-Mn(CO) ₅ (VII) | H(CF ₂) ₄ -CO-Cl, LiMn(CO) ₅ | -15 to 25 | 83 | Calcd. 28.3 | 0.25 | 13.0 | 35.9 | Pale yellow | 22-23 | 50 (13) ^c | 6.05 | 4.68 | +60.8 (D), +33.6 (S), +46.2 (S), +51.8 (S), J _{F-H} = 50 | 1:1:1:1 |
| | | | | Found 28.9 | 0.5 | 13.6 | 32.4 | | | | | | | |
| H(CF ₂) ₄ Mn(CO) ₅ | From (VII) | 90-95 | 76 | Calcd. 27.3 | 0.25 | 13.9 | 38.4 | Colorless | | 68 (2) | .. | 4.66 | | |
| | | | | Found 27.5 | 0.5 | 14.0 | 37.3 | | | | | | | |
| CF ₂ CF=CF-Mn(CO) ₅ (VIII) | CF ₂ =CF-CF ₂ Cl, LiMn(CO) ₅ | 25 | 30 | Calcd. 29.5 | | 16.8 | 29.2 | White | 76-76.5 | 42 (1) | | 4.66 | See Experimental | |
| | | | | Found 30.2 | | 16.4 | 28.9 | | | | | | | |
| CF ₃ Co(CO) ₄ | CF ₃ -CO-Cl, LiCo(CO) ₄ | -30 to 30 | Low | Calcd. 25.8 | | 24.5 | 23.8 | Lt. amber | 10.5-11 | 31 (28) | .. | 4.67 | -87 (S) | |
| | | | | Found 25.6 | | 23.4 | 24.1 | | | | | | | |
| C ₂ F ₅ Co(CO) ₄ | C ₂ F ₅ -CO-Cl, LiCo(CO) ₄ | -30 to 30 | Low | Calcd. 24.8 | | 20.3 | 32.8 | Lt. amber | | 32 (16) | .. | 4.68 | +6.0 (S), ^e -19.3 (S), ^e | 3.2 |
| | | | | Found 25.2 | | 20.5 | 32.7 | | | | | | | |
| <i>n</i> -C ₃ F ₇ Co(CO) ₄ (III) | <i>n</i> -C ₃ F ₇ -CO-Cl, LiCo(CO) ₄ | -15 to 30 | 37 | Calcd. 24.7 | | 17.3 | 39.1 | Lt. amber | | 44 (16) | .. | 4.69 | +2.0 (T), -25.5 (Q) +18.4 (S), J _{F-F} = 10 | 3:2:2 |
| | | | | Found 25.1 | | 17.3 | 38.9 | | | | | | | |

^a Listings of band(s) for keto-carbonyl are in column (a) and for terminal metal-carbonyl in column (b). ^b Trifluoroacetic acid in a capillary tube was used as a reference in this work. The letters, S, D, T and Q, refer to resonances that are singlet, doublet, triplet and quadruplet, respectively; the values given for chemical shifts were obtained by measuring from the centers of the multiplets. *J* is the coupling constant in c.p.s. In each listing, the first entry is the chemical shift figure for the F atoms on the terminal carbon atom and the last entry is for the F atoms on the carbon attached to metal. ^c Sublimation conditions. ^d 50% solution in tetrahydrofuran used in n.m.r. study. ^e Fine structure was not resolved.

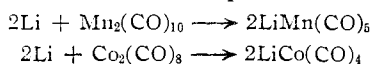
perfluoroalkylcobalt tetracarboxyls and, in contrast to the alkyl derivatives, the perfluoro compounds listed in Table I have excellent thermal and oxidative stability; the trifluoromethyl and pentafluoroethyl derivatives can be distilled (b.p. 91 and 110°, respectively) at atmospheric pressure with no decomposition. The intermediate acyl compounds, which decarbonylate at temperatures below 0°, were not isolated.

The behavior of the allylic halide, perfluoroallyl chloride, is different from that of the saturated perfluoro-isopropyl iodide in its reaction with lithium manganese pentacarbonyl. It appears that the $\text{Mn}(\text{CO})_5$ anion adds to the $>\text{CF}_2$ of 1,1-difluoro-3-halopropenes in a manner analogous to that observed for fluoride anion⁵



The perfluoroallylmanganese pentacarbonyl rearranges under surprisingly mild conditions to the more stable isomer, perfluoropropenylmanganese pentacarbonyl.

An improved method of preparing manganese pentacarbonyl and cobalt tetracarbonyl anions in tetrahydrofuran solution in high yield by reaction of lithium wire with the corresponding metal carbonyls is described in the Experimental section



Experimental

Lithium Manganese Pentacarbonyl.—A solution of 25 g. (0.064 mole) of dimanganese decacarbonyl in 250 ml. of anhydrous tetrahydrofuran containing 1.4 g. (0.2 mole) of short lengths of lithium wire was stirred with a high speed stirrer for 3 hr. During this time, the reaction mixture was blanketed with argon and a cooling bath was used to prevent the temperature from rising above 45–50°. A stirrer with loose wire ends was used to provide cutting action on the lithium. The deep green solution of lithium manganese pentacarbonyl was siphoned from the excess lithium. This solution was assumed to have a lithium manganese pentacarbonyl normality of 0.51.

Lithium Cobalt Tetracarbonyl.—A solution of 34.8 g. (0.10 mole) of dicobalt octacarbonyl in 350 ml. of anhydrous tetrahydrofuran containing 2.65 g. (0.38 mole) of short lengths of lithium wire was held in the temperature range of –10 to –20° while stirring with a high speed stirrer as described above. The initial vigorous reaction subsided in 20 to 30 minutes, and the solution then was warmed to room temperature while continuing the stirring. The excess lithium pieces were removed and the solution was considered to have a lithium cobalt tetracarbonyl normality of 0.58.

Typical conditions for preparing the perfluoro derivatives of manganese and cobalt carbonyls are described below. Analyses, yields and other details are given in Table I.

Trifluoroacetylmanganese Pentacarbonyl (I).—Over a period of 1 hr., 7.9 g. (0.068 mole) of trifluoroacetyl fluoride gas was bubbled into 120 ml. of a 0.51 *N* solution of lithium manganese pentacarbonyl in tetrahydrofuran under a nitrogen blanket. During this time the reaction mixture

was stirred and held at a temperature of 25°. After standing overnight at 0°, the solvent was removed at room temperature under reduced pressure. By sublimation of the residue at 50–55° (1.5 mm.), 13.3 g. of I was obtained as pale yellow crystals, m.p. 55–56°. Bands found in the infrared for a THF solution of I were at 8.12, 8.57, 8.83, 11.69, 13.95 and 14.57 μ . In addition to these, assignments for carbonyl bands are listed in Table I.

Trifluoromethylmanganese Pentacarbonyl (II).—On heating 10 g. (0.034 mole) of I at 110° at atmospheric pressure, 720 ml. (theory is 770 ml.) of carbon monoxide was collected in 100 minutes. By sublimation of the residue at 70° (20 min.), 8.3 g. of II was obtained as white crystals, m.p. 82–83°. Bands found in the infrared (solid state spectrum-KBr pellet) were at 9.47, 10.03 and 14.39 μ ; the carbonyl bands are listed in Table I.

Perfluoro-*n*-propylcobalt Tetracarbonyl (III).—Over a period of 15 minutes, 10.7 g. (0.046 mole) of perfluoro-*n*-butyryl chloride was added dropwise to 80 ml. of a 0.58 *N* solution of lithium cobalt tetracarbonyl in tetrahydrofuran under an atmosphere of nitrogen. The reaction mixture was stirred and held at a temperature of –25 to –20° during the dropwise addition of the acyl chloride. The solvent was removed under reduced pressure at a temperature of –15 to –20° with the use of a "Rinco" evaporator. In this temperature range, the evolution of gas from the reaction mixture was slow enough that no trouble was encountered with foaming during removal of solvent. The final residue was warmed to room temperature and held under a blanket of nitrogen until no further carbon monoxide was evolved. The residual product was extracted with pentane. After removal of solvent from the combined pentane extracts, 6.2 g. of III was distilled as a light amber liquid, b.p. 44° (16 mm). Bands found in the infrared for the pure liquid III were at 7.58, 8.15, 8.35, 8.54, 9.13, 9.62, 12.34 and 13.80 μ ; the carbonyl bands are listed in Table I.

Perfluoropropenylmanganese Pentacarbonyl (VIII).—At –5°, 4.8 g. (0.029 mole) of perfluoroallyl chloride was condensed into a flask under nitrogen, and then 53 ml. of a 0.44 *N* solution of lithium manganese pentacarbonyl in tetrahydrofuran was added with stirring. The reaction mixture was allowed to warm to room temperature. After holding at room temperature for 2 hr., it was stored overnight at 0°. The reaction mixture was filtered to remove the LiCl precipitate, and the solvent was then removed by distillation under reduced pressure at 25°. The dark residue was heated with an oil bath at 55° (1 mm.). When 0.35 g. of liquid had been collected, a white solid suddenly formed on the walls of the condenser and column of the distillation equipment. The 0.35 g. of liquid in the receiver changed to a mushy, low-melting solid. The infrared spectrum indicated that this mushy product was roughly 60% of VIII and 40% of a terminal CF_2 olefin product. It was assumed that this latter was perfluoroallylmanganese pentacarbonyl. Ether was added to dissolve the residual product in the distillation flask. Charcoal was added to the ether solution and it was then filtered. On cooling the filtrate to –15°, 2.15 g. of crystals with a light brown tinge, m.p. 69–73°, were obtained. By sublimation at 60° (3 mm.), 2.0 g. of VIII was obtained as white crystals, m.p. 76–76.5°.

Bands found in the infrared were at 6.09 μ (for internal $\text{C}=\text{C}$), 7.56, 8.42, 8.90, 9.67 and 12.35 μ ; carbonyl bands are listed in Table I. There was no 5.64 μ band for the $\text{CF}_2=\text{CF}$ function. The F^{19} magnetic resonance spectrum of 50% solution of VIII in tetrahydrofuran showed three different kinds of fluorine in an intensity ratio of 3:1:1. The CF_3 was a doublet split into doublets. The individual peaks were located at –11.7, –11.4, –11.1 and –10.8 p.p.m. (trifluoroacetic acid reference). Each of the olefinic CF 's was a doublet split into quadruplets. The chemical shifts were +16.8 p.p.m. for one CF and +89.4 p.p.m. for the other. The *J* value for the doublet separation was 135 c.p.s.

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(5) J. H. Fried and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **81**, 2078 (1959).