Communications TO THE EDITOR

Alkyl Derivatives of Manganese Carbonyl

Sir:

We wish to report the first alkyl derivatives of a metal carbonyl. Previous authors have reported the synthesis of cyclopentadienyl metal carbonyls[1] and alkyl derivatives thereof[2] as well as acetylene and allene complexes of metal carbonyls,[3,4] but we know of no previous report of stable alkyl metal carbonyls.

Manganese carbonyl dissolved in tetrahydrofuran was smoothly converted to a solution of $NaMn(CO)_5$ when treated with an excess of 1% sodium amalgam or finely divided sodium in an inert atmosphere. This solution, maintained in the inert atmosphere, was decanted from excess sodium and treated with dimethyl sulfate or methyl iodide. Removal of solvent and recrystallization from petroleum ether followed by sublimation gave colorless crystals of methyl manganese pentacarbonyl, m.p. 94.5–95° (uncorr.).

Anal. Calcd. for $C_6H_3MnO_5$: C, 34.3; H, 1.43; Mn, 26.2; mol. wt., 210. Found: C, 34.5; H, 1.37; Mn, 26.4; mol. wt., 207 (cryoscopic in benzene).

The crystalline compound is stable and volatilizes readily in a stream of air.

A corresponding benzyl derivative may be prepared using benzyl chloride. This material, m.p. 37.5–38.5° (uncorr.) is pale yellow and likewise stable to air in the solid form. It is somewhat less volatile than the methyl compound.

Anal. Calcd. for $C_{12}H_7MnO_5$: C, 50.4; H, 2.45; Mn, 19.3. Found: C, 49.7; H, 2.28; Mn, 19.6.

The infrared spectrum of the methyl compound dissolved in carbon disulfide shows bands at 3.5 μ (carbon-hydrogen stretching); 4.8 μ, 5.0 μ, and 5.1 μ in the metallocarbonyl region and a band at 8.5 μ.

This work will be more completely discussed in a forthcoming publication.

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(2) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(3) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **76**, 1457 (1954).

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Acyl Manganese Pentacarbonyl Compounds

Sir:

The synthesis of an alkyl metal carbonyl compound has been reported.[1] We now wish to report the first synthesis of acyl metal carbonyl compounds. On treatment of a tetrahydrofuran solution of sodium manganese pentacarbonyl with acetyl chloride, acetylmanganese pentacarbonyl, m.p. 54–55°, was obtained in 51% yield as a white, volatile, crystalline solid.

Anal. Calcd. for $C_7H_3O_6Mn$: C, 35.32; H, 1.27; Mn, 23.1. Found: C, 35.2; H, 1.28; Mn, 23.1.

A similar reaction using benzoyl chloride gave benzoylmanganese pentacarbonyl in 80% yield as a white, volatile, crystalline solid, m.p. 95–96°.

Anal. Calcd. for $C_{12}H_5O_6Mn$: C, 48.1; H, 1.68; Mn, 18.3. Found: C, 48.2; H, 2.03; Mn, 18.3.

The propionyl and isobutyryl compounds were also prepared.

The infrared spectrum of the acetyl compound showed a carbon hydrogen stretching band at 3.48 μ and bands at 4.75 μ, 4.9 μ, and 5.02 μ in the metallocarbonyl region. In addition, a ketonic carbonyl was noted at 6.08 μ. The benzoyl compound likewise showed bands at 3.28 μ, 4.7 μ, 4.85 μ, 4.9 μ, and 6.2 μ.

Pyrolysis of acetylmanganese pentacarbonyl gave a smooth evolution of carbon monoxide with the formation of methylmanganese pentacarbonyl. This decarbonylation was reversible with the methyl derivative being converted to the acetyl derivative at room temperature and 500 p.s.i.g. carbon monoxide.

Pyrolysis of the benzoyl product also proceeded with loss of carbon monoxide and formation of phenylmanganese pentacarbonyl, m.p. 52°, as a white volatile crystalline solid.

Anal. Calcd. for $C_{11}H_5O_5Mn$: C, 48.5; H, 1.85; Mn, 20.2. Found: C, 48.9; H, 1.95; Mn, 20.2.

The infrared spectrum of this compound showed no ketonic carbonyl band in the 6.0–6.2 μ region.

Bromination of the methyl and acetyl compounds gave methyl bromide and acetyl bromide, respectively, in addition to bromomanganese pentacarbonyl which has been obtained by direct bromination of manganese carbonyl. The reversible carbonylation and the bromination reactions and spectral data cited above support the conclusion that methyl and acetyl manganese bonds exist in these compounds.

A complete discussion of the above work including application of the reversible carbonylation to oxo-reaction mechanism will be reported in a future publication.

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