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Hexafluoroacetylacetonato Derivative of Manganese Carbonyl[1]

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The reaction of metal carbonyls with 1,3-diketones was initially studied by Hieber,[2] who reported the formation of tris(acetylacetonato)iron(III) from iron pentacarbonyl and 2,4-pentanedione. Using the iron tetracarbonyl halides, Hieber and Bader[3] were able also to prepare the complexes formulated as $FeBr_2 \cdot 2$-acac[4] and $2FeCl_2 \cdot 3$acac. More recently, Dunne and Cotton[5] prepared, in good yields, the compounds Mo(acac)$_3$, Mo(tfac)$_3$,[4] Cr(acac)$_3$, and Cr(tfac)$_3$ by refluxing the hexacarbonyls with 2,4-pentanedione and 1,1,1-trifluoropentane-2,4-dione. The chelate Mo(acac)$_3$ was also obtained from essentially the same reaction by Larson and Moore.[6] Later, Goan, *et al.*,[7] discovered that the conditions of this reaction and that of various diketones with the carbonyls of iron and chromium could be moderated when the mixtures are irradiated with ultraviolet light.

Thus, the above reactions of the metal carbonyls and their derivatives proceed to the simple chelates, and no intermediate mixed carbonyl acetylacetonates had been obtained despite some efforts of synthesis.[7]

Consideration of relative stabilities of low-valent transition metal complexes with hydrogen- and fluorine-containing ligands[8] prompted us to explore possible syntheses of such acetylacetonato compounds using highly fluorinated pentanediones. Described here is the first successful preparation of a 1,3-diketone derivative of manganese carbonyl, Mn(CO)$_4$(hfac).[4] Almost concurrently with the submission of this paper for publication, Bonati and Wilkinson[9] reported the synthesis of several rhodium(I) pentanedionato carbonyl complexes from rhodium(I) carbonyl chloride and β-diketones.

Experimental

Dimanganese decacarbonyl was purchased from the Ethyl Corporation. Hexafluoroacetylacetone, obtained from Columbia Organic Chemicals Co., was distilled before use. All solvents were dried over P_4O_{10} and fractionally distilled.

The proton magnetic resonance spectrum of the complex in $CDCl_3$ solution was recorded on a Varian A 60 instrument using tetramethylsilane as an internal reference. The molar conductivity of a nitromethane solution of Mn(CO)$_4$(hfac) was measured with a Model RC 16B2 conductivity bridge (Industrial Instruments, Inc.). The molecular weight (1.7–1.8×10^{-2} *M* solution in $CHCl_3$) was determined using a Mechrolab osmometer. Analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of Mn(CO)$_4$(hfac).—In a typical preparation, chloropentacarbonylmanganese(I) (2.70 g., 12 mmoles), synthesized by the method of Abel and Wilkinson,[10] was dissolved in acetonitrile (250 ml.) to produce a clear pale yellow solution. Hexafluoroacetylacetone (2.55 g., 12 mmoles), also in acetonitrile (10 ml.), was added and the stirred mixture kept at 25° under a nitrogen atmosphere. Slow evolution of gas occurred over about 6 hr., during which time the color of the solution changed to dark amber. After allowing a total reaction time of 12 hr., the solution was evaporated to dryness (25°, ~20 mm.). The resulting bright yellow solid was extracted with 30–60° petroleum ether (six 100-ml. portions), and the combined extracts were evaporated (25°, ~20 mm.). The solid was then washed with two 2-ml. portions of petroleum ether and sublimed (55°, 0.01 mm.). The yield of the bright yellow Mn(CO)$_4$(hfac) (m.p. 99–100° dec.) was 0.63 g. (14%).

Anal. Calcd. for $C_9HO_6F_6Mn$: C, 28.9; H, 0.3; F, 30.5; Mn, 14.7; mol. wt., 374. Found: C, 28.9; H, 1.0[11]; F, 30.1; Mn, 14.8; mol. wt., 367, 365. The n.m.r. spectrum showed a single proton signal at τ 3.84.

The residue from the initial petroleum ether extractions of the product has not yet been fully characterized, although analyses indicate the empirical formula $C_9H_9O_6N_2Cl_2Mn_2$. Preliminary studies show this metal carbonyl derivative to have very low solubility in the majority of organic solvents, to be nonvolatile, and to decompose (80°, 0.01 mm.) to yield $Mn_2(CO)_{10}$.

The reaction of $Mn(CO)_5Cl$ with hexafluoroacetylacetone was also carried out in acetonitrile using excess quantities of the diketone (from 1:1 to 2:1). In all cases, the same two products were obtained. However, when a large excess of the diketone (5:1) and small volume of the solvent (acetonitrile, *ca.* 50 ml.) were employed, a white precipitate, later shown to be Mn(hfac)$_2$-$(H_2O)_2$[12] (infrared spectrum), was also isolated from the reaction mixture.

Infrared Spectrum of Mn(CO)$_4$(hfac).—Metal carbonyl stretching frequencies were observed at 2123 (w), 2055 (s), 1973 (s), and 1950 (s) cm.$^{-1}$ (Beckman IR-9; chloroform solution); the ketonic carbonyl stretching frequency at 1635 (s) cm.$^{-1}$ (KBr pellet); the C–H in-plane bend at 1142 (s) cm.$^{-1}$ (KBr pellet); other bands at 3155 (w), 3019 (w), 2952 (w), 2300 (w), 1603 (m), 1570 (sh), 1565 (sh), 1557 (m), 1531 (m), 1469 (s), 1465 (sh), 1373 (w), 1353 (m), 1268 (s), 1254 (s), 1240 (s), 1215 (s), 1107 (sh), 1039 (w), 957 (w), 817 (w), 801 (s), 770 (w), 746 (m), 703 (sh), 683 (s), 668 (w), 636 (sh), 627 (s), 597 (s), 528 (s), 518 (s), 464 (m), and 451 (m) cm.$^{-1}$ (KBr pellet).

Results and Discussion

Hexafluoroacetylacetonatotetracarbonylmanganese(I), stable over long periods of time in air, is a nonelectrolyte in nitromethane. It is readily soluble in chloroform, acetonitrile, ether, and methyl alcohol; sparingly soluble in hexane and carbon tetrachloride; and insoluble in water. The proton magnetic resonance spectrum of the complex consists of a single signal at τ 3.84; the position of the peak supports a chelate attachment of the hexafluoroacetylacetonato group,[13] and

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[1] Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 3, 1964.

[2] W. Hieber, *Sitzungsber. Heidelberg Akad. Wiss.*, **3**, 3 (1929); *Chem. Zentr.*, **1**, 2029 (1929).

[3] W. Hieber and G. Bader, *Z. anorg. allgem. Chem.*, **190**, 193 (1930).

[4] acac = anion of pentane-2,4-dione; tfac = anion of 1,1,1-trifluoropentane-2,4-dione; hfac = anion of 1,1,1,5,5,5-hexafluoropentane-2,4-dione.

[5] T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, **2**, 263 (1963).

[6] M. L. Larson and F. W. Moore, *ibid.*, **1**, 856 (1962).

[7] J. C. Goan, C. H. Huether, and H. E. Podall, *ibid.*, **2**, 1078 (1963).

[8] See, for example, R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 38 (1964), and references therein; also, R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964), and quoted references.

[9] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

[10] E. W. Abel and G. Wilkinson, *ibid.*, 1501 (1959).

[11] It has been our experience that chemical analyses of fluorine-containing compounds often give high hydrogen contents.

[12] M. L. Morris, R. W. Moshier, and R. E. Sievers, *Inorg. Chem.*, **2**, 411 (1963).

[13] J. P. Collman, Advances in Chemistry Series, No. 37, American Chemical Society Washington, D. C., 1963, p. 78.

the sharpness of the signal indicates that the compound is diamagnetic.

The infrared spectrum of the derivative (chloroform solution) in the metal carbonyl stretching frequency region consists of one weak (2123 cm.$^{-1}$) and three strong bands (2055, 1973, 1950 cm.$^{-1}$). The number of bands and their relative frequencies and intensities are in accord with the pattern predicted for a complex of the type *cis*-$M(CO)_4X_2$[14] (molecular symmetry C_{2v}) on the basis of symmetry and group theoretical considerations.[15]

Examination of the complete infrared spectrum of $Mn(CO)_4$(hfac) in a KBr pellet lends support to the bonding of the hexafluoroacetylacetonato group to the manganese in the usual bidentate manner, through the two equivalent oxygen atoms. Both the ketonic carbonyl stretching (1635 cm.$^{-1}$) and the C–H in-plane bending frequency (1142 cm.$^{-1}$) occur in the same regions as for the known bis- and tris(hexafluoroacetylacetonato) complexes.[12]

The attempted preparation of acetylacetonatotetracarbonylmanganese(I) from 2,4-pentanedione and chloropentacarbonylmanganese(I) yielded an unstable yellow solid. The infrared spectrum of this solid was in good agreement with that expected for the desired product; however, instability of the compound precluded consistent analytical data.

It is of interest to note that relative stabilities of the acetylacetonato- and hexafluoroacetylacetonatotetracarbonylmanganese(I) complexes parallel those of the alkyl and perfluoroalkyl metal carbonyls.[8] Greater stability of the fluorinated derivatives is most probably due to a high electronegativity of the trifluoromethyl group[16] which facilitates removal of the negative charge from a low-valent metal.

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[14] M = metal; X = unidentate ligand.

[15] See L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962); also, F. A. Cotton, *ibid.*, **3**, 702 (1964), and previous papers with C. S. Kraihanzel.

[16] W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectry.*, **5**, 118 (1960), and references therein.

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The Synthesis of Tin(II) Heterocycles Directly from Stannous Oxide[1a]

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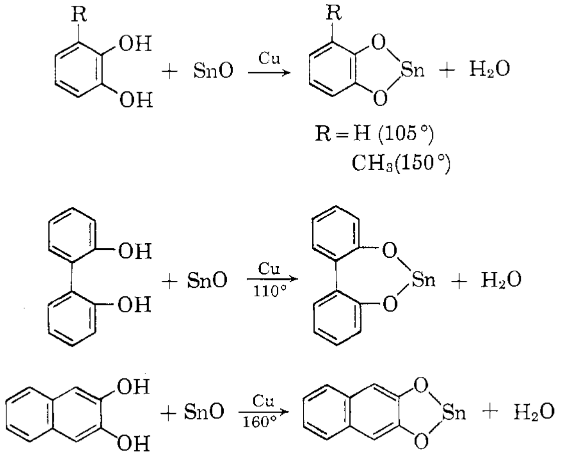
Dihydric phenols react directly with tin metal in the presence of copper as a catalyst to give tin(II) heterocycles. These cyclic esters of tin(II) are notable chiefly for their low volatility and very high thermal stability (*e.g.*, in air to *ca.* 500°).[2] They can also be obtained by reaction of dihydric phenols with a slurry of stannous chloride and sodamide powders in ether. Derivatives containing methyl and *n*-butyl groups attached to tin have been prepared, and these tin(IV) heterocycles exhibit similar properties.[3] It has been recently reported that stannous oxide reacts with methyl chloride to give dimethyltin dichloride.[4] Reaction conditions are said to be milder for this synthesis than for the direct synthesis of organotin halides from tin metal.[5] This paper describes the reaction of dihydric phenols with stannous oxide.

Dihydric phenols react with stannous oxide at pressures varying from 1500 p.s.i. of nitrogen gas to partial vacuum according to the following schemes.



A temperature high enough to melt the diol is sufficient to bring about reaction. Copper metal powder acts as a catalyst. The previously synthesized compounds *o*-phenylenedioxytin(II) and 2,2′-diphenylenedioxytin(II) were prepared by this new route, along with the novel compounds 3-methyl-1,2-phenylenedioxytin(II) and 2,3-naphthalenedioxytin(II). The reaction can also be carried out by refluxing a solution of the diol in an inert organic solvent in the presence of stannous oxide and copper powders. In addition, polymeric systems were produced when resorcinol and hydroquinone were employed as starting materials.

The cyclic tin(II) esters are white crystalline solids which possess high thermal and hydrolytic stability, especially when compared to the tin(IV) alkoxides[6] or with the recently reported tin(II) alkoxides.[7] They are insoluble in common organic solvents, but have some solubility in pyridine, triethylamine, and dimethyl sulfoxide from which they can be recovered unchanged. Because of their limited solubility, only the molecular weight of 3-methyl-1,2-phenylenedioxytin(II) could be determined ebullioscopically in pyri-

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[1] (a) Portions of this investigation were reported at the XIXth IUPAC Meeting, London, July 1963. (b) To whom all inquiries should be addressed.

[2] J. J. Zuckerman, *J. Chem. Soc.*, 1322 (1963).

[3] H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.*, **1**, 328 (1964).

[4] K. A. Andrianov, T. V. Vasil'eva, Z. N. Nudel'man, L. M. Khanashivili, A. S. Kochetkova, A. G. Cherednikova, *J. Gen. Chem. USSR*, **32**, 2275 (1962).

[5] J. J. Zuckerman, *Advan. Inorg. Chem. Radiochem.*, **6**, 383 (1964).

[6] J.-Cl. Maire, *Ann. Chim.* (Paris), **6**, 969 (1961).

[7] E. Amberger and M.-R. Kula, *Chem. Ber.*, **96**, 2562 (1963).