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Amine Acyl Manganese Tetracarbonyl Complexes

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RECEIVED JANUARY 15, 1960

Alkyl manganese pentacarbonyls reacted with certain primary and secondary amines producing a new type of manganese complex $RCOMn(CO)_4NHR'R''$; no carbon monoxide escaped in the reactions. New compounds included $CH_3COMn(CO)_4NH_2C_6H_{11}$, $CH_3COMn(CO)_4NH_3$, $CH_3COMn(CO)_4NH(CH_3)C_6H_{11}$, $CH_3COMn(CO)_4NH_2C_6H_5$, $C_6H_5COMn(CO)_4NH_2C_6H_{11}$ and $C_6H_5COMn(CO)_4NH_2C_6H_5$. There is a discussion of configurations and possible paths of reactions.

Recently Closson, Coffield and Kozikowski reported the synthesis of alkyl[2] and acyl[3] manganese pentacarbonyls. With the exception of the reversible carbonylation,[3,4] the chemistry of these compounds has not yet been investigated. We wish now to report the reaction of alkyl manganese pentacarbonyls with amines and a synthesis of a new group of amine acyl manganese carbonyl complexes.

Methylmanganese pentacarbonyl reacted smoothly with cyclohexylamine in tetrahydrofuran forming an air-stable, yellow, crystalline compound (I) melting at 97.0–97.5° with decomposition. Since no carbon monoxide was evolved during the reaction, it appeared that I was not a simple displacement product of the type $RMn(CO)_{5-x}(R'NH_2)_x$. This assumption was supported by analytical data which showed that the empirical formula of I was $C_{12}H_{16}MnNO_5$. Cryoscopic molecular weight determination showed that I was monomeric. Thus I must contain one methyl, one cyclohexylamine and five carbonyl groups per molecule.

Among a number of structures compatible with both the analytical results and the inert gas theory, two were considered as being most probable. If I resulted from an amine cleavage of the methylmanganese bond, followed by salt formation, structure A might be expected. On the other hand, structure B might be visualized if I was formed by an amine displacement of carbon monoxide and then carbonylation to the acetyl complex.

$$[CH_3(C_6H_{11})NH_2]^{\oplus}\ [Mn(CO)_5]^{\ominus}$$

A

$$CH_3COMn(CO)_4NH_2C_6H_{11}$$

B

Structure A was discarded on the basis of the following results. Manganese pentacarbonyl salts are known to liberate manganese carbonyl hydride when treated with mineral acids.[5] However, when a diglyme[6] solution of I was treated with sulfuric acid, no hydride was produced, and only the presence of methylmanganese pentacarbonyl was indicated. Similarly, the reaction of I with anhydrous hydrogen chloride gave only methylmanganese pentacarbonyl and cyclohexylammonium chloride. Finally, if I possessed structure A, then I should be formed by a reaction between sodium manganese pentacarbonyl and N-methyl-cyclohexylammonium chloride. However, this reaction produced no compound similar

$$[CH_3(C_6H_{11})NH_2]^{\oplus}Cl^{\ominus} + NaMn(CO)_5 \longrightarrow A + NaCl$$

to I. Instead, some manganese carbonyl hydride was obtained, apparently arising from a disproportionation of the alkyl ammonium salt. The

$$[CH_3(C_6H_{11})NH_2]^{\oplus}[Mn(CO)_5]^{\ominus} \rightleftarrows HMn(CO_5) + CH_3(C_6H_{11})NH$$

experimental evidence showed that I was not an ionic compound of structure A.

Structure B was favored by infrared evidence. I showed five absorption bands in the metallocarbonyl region (4.8, 4.95, 5.05 and 5.15μ), whereas methyl manganese pentacarbonyl exhibits only three bands. Thus I must possess a lower degree of symmetry, which may be expected if the amine ligand is coördinated with manganese as in structure B. In addition I showed a band at 6.2μ which may be attributed to a metallo-acyl group.[3]

If I possessed structure B it is possible that an amine displacement on acetylmanganese pentacarbonyl would also give I. The reaction in this case would be accompanied by a loss of carbon monoxide, analogous to the behavior of the halomanganese pentacarbonyls with amine reagents.[7] Indeed, the slow reaction between acetylmanganese pentacarbonyl and cyclohexylamine gave I in small yield. This, however, may not be considered as a conclusive structure proof. It is known[4] that acetylmanganese pentacarbonyl will decarbonylate spontaneously in ether solution slowly forming methylmanganese pentacarbonyl. Thus, it is possible that in the above reaction I was formed by the reaction of the amine with methyl, rather than with acetylmanganese pentacarbonyl.

The configuration of I was definitely established as cyclohexylamine acetylmanganese tetracarbonyl (B) by the cleavage of the acetyl–manganese bond. The reaction of *I* with sodium methoxide in methanol gave methyl acetate in 69% yield.

$$CH_3COMn(CO)_4NH_2C_6H_{11} + NaOCH_3 \longrightarrow CH_3COOCH_3 + [NaMn(CO)_4(NH_2C_6H_{11})]$$

II

The acetate fragment was identified through conversion to N-benzylacetamide. In an attempt to identify the other cleavage product (II) the

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(1) Department of Chemistry, Purdue University, Lafayette, Indiana.

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

(3) T. H. Coffield, J. Kozikowski and R. D. Closson, *ibid.*, **22**, 598 (1957).

(4) T. H. Coffield, J. Kozikowski and R. D. Closson, *Abstracts of Conference Papers*, International Conference on Coördination Chemistry, London, April 6–11, 1959, Paper No. 26.

(5) W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 339 (1958).

(6) Dimethyl ether of diethylene glycol.

(7) (a) T. H. Coffield and N. Hebert, U. S. Patent 2,902,489, September 1, 1959. (b) W. Hieber and W. Schrapp, *ibid.*, **14b**, 460 (1959).

reaction mixture was treated with an excess of methyl iodide. This gave some methylmanganese pentacarbonyl and bis-cyclohexylamine iodomanganese tricarbonyl, indicating a complex disproportionation of II.

In order to investigate the scope and limitations of the amine displacement of alkyl manganese carbonyls, several alkyl manganese complexes were reacted with a number of amines.

Methylmanganese pentacarbonyl gave the expected tetracarbonyl complexes with ammonia, N-methylcyclohexylamine and aniline but not with pyridine and trimethylamine. The reaction with aniline was considerably slower than with the other amines.

Phenylmanganese pentacarbonyl gave the benzoyl tetracarbonyl complexes with cyclohexylamine and aniline. However, these reactions were not as smooth as in the case of the methyl analog. The yields of the expected tetracarbonyl compounds were low due either to a slow reaction accompanied by decomposition, as in the case of aniline, or to side reactions as in the case of cyclohexylamine.

No cyclohexylamine phenylacetylmanganese tetracarbonyl could be isolated from the reaction between benzylmanganese pentacarbonyl and cyclohexylamine, although the infrared spectrum of the crude recovered starting material showed several weak bands which might be attributed to traces of the expected tetracarbonyl complex.

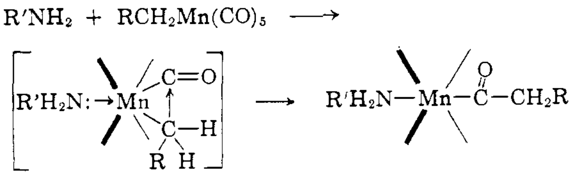
These experimental data show that the reaction between alkyl manganese carbonyls and amines depends both on the alkyl group and on the nature of the amine. Methylmanganese pentacarbonyl forms the amine-tetracarbonyl complexes much more readily than do the phenyl and benzyl analogs. Primary and secondary aliphatic amines react with methyl- and phenylmanganese pentacarbonyls more readily than do the aromatic amines, all forming the expected tetracarbonyl complexes. The tertiary amines also react with alkyl manganese carbonyls but do not form the acyl-tetracarbonyl complexes.

Several reaction paths are possible for the formation of the amine acyl manganese tetracarbonyl complexes. One possibility is an amine displacement of one carbon monoxide ligand with subsequent carbonylation of the intermediate. However, this two step sequence does not seem probable. It is known[4] that the carbonylation of alkyl manganese carbonyls is a reversible process and proceeds only slowly at atmospheric pressure. Thus, if the reaction proceeded by the above two step mechanism it might be expected that some carbon monoxide would be lost during the reaction. Consequently the reaction should give a mixture of both the acyl- and the alkyl amine tetracarbonyl complexes. However, no evolution of carbon monoxide was observed in any of these reactions, and only the acetyl complexes have been isolated, usually in good yields.

$$\mathrm{RMn(CO)_5 + R'NH_2 \longrightarrow RMn(CO)_4NH_2R' + CO} \quad (1)$$

$$\mathrm{RMn(CO)_4NH_2R' + CO \longrightarrow RCOMn(CO)_4NH_2R'} \quad (2)$$

A more plausible reaction path would be one involving an amine displacement of the alkyl group followed by the attack of the alkyl carbon on one of the metallo-carbonyl ligands.



Although the possibility that a free carbanion is generated cannot be excluded definitely, a concerted mechanism, where manganese–carbon bond breakage and carbon–carbon bond formation occurs simultaneously, is preferred. In this respect, the mechanism resembles that proposed for the carbonylation of alkyl manganese pentacarbonyls.[4]

Experimental

Reagents.—Alkyl and acyl manganese pentacarbonyls used in this work were prepared by literature methods.[2,3] Phenylmanganese pentacarbonyl was prepared from the benzoyl compound by decarbonylation in refluxing ether. All amines were fractionated before use. Tetrahydrofuran was distilled from sodium and benzophenone. Petroleum ether (b.p. 38–42°) was used for all recrystallizations requiring a hydrocarbon solvent. All melting points are uncorrected.

Cyclohexylamine Acetylmanganese Tetracarbonyl.—Methylmanganese pentacarbonyl (2.1 g., 0.010 mole) and cyclohexylamine (1.48 g., 0.015 mole) were dissolved in 70 ml. of tetrahydrofuran. The solution was stirred in a nitrogen atmosphere at room temperature for 4 hr. No gas evolution was observed. The reaction mixture was poured into 750 ml. of ice water and the resulting yellow precipitate (2.9 g., 93%) was filtered off, washed with water and dried. The product, recrystallized from ether, melted at 97.0–97.5° with gas evolution. It was soluble in carbon tetrachloride, chloroform, benzene and sparingly soluble in isoöctane and methanol. The infrared spectrum (carbon tetrachloride solution) showed bands at 4.8, 4.95, 5.05 and 5.15 μ in the metallo-carbonyl region and a band at 6.2 μ. Molecular weight was determined cryoscopically.

Anal. Calcd. for: $C_{12}H_{16}MnNO_5$: C, 46.6; H, 5.21; Mn, 17.8; N, 4.53; mol. wt., 309. Found: C, 46.6; H, 5.37; Mn, 17.9; N, 4.23; mol. wt., 295.

Action of Hydrogen Chloride on Cyclohexylamine Acetylmanganese Tetracarbonyl.—A solution of 2.0 g. (0.006 mole) of cyclohexylamine acetylmanganese tetracarbonyl in 40 ml. of ether was treated with 2.8 g. of ether saturated with anhydrous hydrogen chloride. A white precipitate formed immediately. After stirring for 20 minutes the mixture was filtered giving cyclohexylammonium chloride (0.44 g., 54%) melting at 202–203°. The filtrate was evaporated to dryness and the residue was sublimed at room temperature giving methyl manganese pentacarbonyl (0.27 g., 31%), which was identified by infrared. Sublimation residues were recrystallized from ether giving the starting material (0.76 g., 38% recovery).

Reaction of Acetylmanganese Pentacarbonyl with Cyclohexylamine.—Acetylmanganese pentacarbonyl (3.0 g., 0.013 mole) and cyclohexylamine (6.5 g., 0.025 mole) were dissolved in 90 ml. of tetrahydrofuran and stirred in a nitrogen atmosphere at room temperature for 24 hr. The solvent was evaporated *in vacuo* and the residues were dissolved in ether. Cooling gave 0.31 g. of yellow crystals, melting at 56–57°, identified as the starting material (10% recovery). The mother liquor was evaporated to dryness. Recrystallization of the brown tacky residue from petroleum ether gave yellow crystals (0.58 g., 15%) melting at 96.2–97.0°. The infrared spectrum of this product was identical with that of cyclohexylamine acetylmanganese tetracarbonyl.

Anal. Calcd. for: $C_{12}H_{16}MnNO_5$: C, 46.6; H, 5.21; Mn, 17.8. Found: C, 46.6; H, 5.45; Mn, 17.2.

Structure Proof of Cyclohexylamine Acetylmanganese Tetracarbonyl.—To cyclohexylamine acetyl manganese tetracarbonyl (10.0 g., 0.032 mole) dissolved in 300 ml. of methanol there was added dropwise a solution of sodium methoxide (1.75 g., 0.032 mole) with ice cooling. After the addition the solution was stirred at room temperature for 2.5 hr. Approximately 100 ml. of solvent was distilled off *in vacuo* at 20–25°. Fractionation of this distillate afforded six fractions collected in the range of 53.2–63.9°. The infrared examination showed that the product was identical to authentic methanol–methyl acetate azeotrope. The refractive index data showed that the product contained 1.6 g. of methyl acetate (69% of theoret). Twelve ml. of the azeotrope was refluxed with 4 ml. of benzylamine and 1.0 g. of ammonium chloride for 42 hr. Methanol then was distilled off, and the residue neutralized with aqueous HCl. Ether extraction and evaporation gave white crystals which melted at 63–64° after recrystallization from *n*-hexane–ether. No melting point depression was observed with an authentic sample of N-benzylacetamide.

The reaction mixture remaining after the first distillation was treated with methyl iodide (13.6 g., 0.096 mole) and stirred at room temperature for 2.5 hr. The solvent was evaporated *in vacuo*, leaving 60 ml. of a brown solution. Methyl manganese pentacarbonyl (0.48 g.) sublimed out of the reaction mixture during the evaporation. Yellow-brown flakes, presumably bis-cyclohexylamine iodomanganese tricarbonyl, crystallized out of the brown solution after standing overnight. After recrystallization from chloroform the solid melted at 192.0–192.5° with decomposition.

Anal. Calcd. for $C_{15}H_{26}IMnN_2O_3$: C, 38.8; H, 5.65; I, 27.4; Mn, 11.9, N, 6.04. Found: C, 39.3; H, 5.89; I, 27.9; Mn, 11.6; N, 6.03.

Ammonia Acetylmanganese Tetracarbonyl.—A mixture of methylmanganese pentacarbonyl (4.0 g., 0.019 mole) and liquid ammonia (200 ml.) was refluxed with stirring for 2 hr. Excess ammonia was allowed to evaporate slowly. A greenish-yellow solid (4.11 g., 95%) remained in the reaction vessel. Recrystallization from ether gave 3.65 g. of ammonia acetylmanganese tetracarbonyl, light yellow crystals, melting at 95.5–96.0° with decomposition.

Anal. Calcd. for $C_6H_6MnNO_5$: C, 31.8; H, 2.69; Mn, 24.2; N, 6.17. Found: C, 32.4; 2.70; Mn, 24.4; N, 6.16.

N-Methylcyclohexylamine Acetylmanganese Tetracarbonyl.—Methylmanganese pentacarbonyl (5.0 g., 0.024 mole) and N-methylcyclohexylamine (4.0 g., 0.036 mole) were dissolved in 50 ml. of tetrahydrofuran and stirred at room temperature for 2 hr. Excess solvent was evaporated *in vacuo*. The residues were cooled in Dry Ice giving 3.1 g. (40%) of yellow crystals. The product, recrystallized from petroleum ether (b.p. 38–42°), melted at 73–74°.

Anal. Calcd. for $C_{13}H_{18}MnNO_5$: C, 48.3; H, 5.60; Mn, 17.0; N, 4.33. Found: C, 48.3; H, 5.58; Mn, 17.4; N, 4.44.

Aniline Acetylmanganese Tetracarbonyl.—Methylmanganese pentacarbonyl (3.0 g., 0.014 mole) and aniline (2.0 g.. 0.022 mole) were dissolved in 50 ml. of tetrahydrofuran and kept under nitrogen at room temperature for 75 hr. Then the solution was poured into 400 ml. of ice water, giving a yellow precipitate, which after washing and drying weighed 1.72 g. (38%). Recrystallization from ether gave yellow crystals, melting at 83–84°.

Anal. Calcd. for $C_{12}H_{10}MnNO_5$: C, 47.6; H, 33.3; Mn, 18.1; N, 4.62. Found: C, 46.6, H, 33.3; Mn, 17.8; N, 4.70.

Cyclohexylamine Benzoylmanganese Tetracarbonyl.—Phenylmanganese pentacarbonyl (2.0 g., 0.0074 mole) and cyclohexylamine (0.80 g., 0.0081 mole) were dissolved in 35 ml. of ether and stirred at room temperature for 1.5 hr. The resulting orange solution was cooled in Dry Ice giving 0.25 g. (12% recovery) of phenylmanganese pentacarbonyl. The mother liquor was concentrated, cooled in Dry Ice and filtered, giving 0.87 g. of an orange, heterogeneous, solid mass. Infrared examination suggested the presence of starting materials; however, no definite products could be isolated. The orange-brown viscous filtrate was dried over potassium hydroxide pellets and paraffin flakes, giving 0.70 g. of a tacky, brown solid. Repeated extraction with petroleum ether, concentration of extracts and cooling gave 0.23 g. (10% yield) of crude cyclohexylamine benzoylmanganese tetracarbonyl. Recrystallization from petroleum ether gave a yellow solid, melting at 75–78°.

Anal. Calcd. for $C_{17}H_{18}MnNO_5$: C, 55.0; H, 4.89; Mn, 14.8. Found: C, 54.8; H, 5.90; Mn, 14.7.

Aniline Benzoylmanganese Tetracarbonyl.—Phenylmanganese pentacarbonyl (2.72 g., 0.010 mole) and aniline (1.02 g., 0.011 mole) were dissolved in 30 ml. of ether and allowed to stand at room temperature under nitrogen for 163 hr. The resulting yellow-brown solution was filtered and cooled in Dry Ice giving 0.83 g. of yellow crystals. Fractional crystallization from petroleum ether gave 0.22 g. of benzoylmanganese pentacarbonyl and 0.61 g. of starting material. The mother liquor was concentrated and cooled giving 0.50 g. of starting material (total recovery of 41%). After further concentration the mother liquor was treated with isoöctane precipitating a dark yellow solid (0.23 g., 10%). The crude product melted at 78–79°.

Anal. Calcd. for: $C_{17}H_{12}MnNO_5$: C, 55.9; H, 3.13; Mn, 15.0. Found: C, 55.9; H, 3.62; Mn, 15.8.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY AND BRANDEIS UNIVERSITY, WALTHAM, MASSACHUSETTS]

Oxidation Potentials of Arylferrocenes[1]

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RECEIVED JANUARY 22, 1960

Formal oxidation potentials for several *para* substituted phenylferrocenes have been determined in aqueous acetic acid by potentiometric titration. Differences between the oxidation potential of phenylferrocene and the arylferrocenes exhibit a linear correlation with the Hammett σ constant for the *para* substituent. A value of -2.41 for the reaction constant is calculated from the data.

The reversible oxidation of ferrocene to the singly charged ferricinium cation is the simplest and perhaps the most characteristic reaction exhibited by this unique organometallic substance. This transformation, which may be effected anodically as well as by a variety of chemical oxidants,[2a] is by no means confined to ferrocene and its derivatives but occurs with bis-cyclopentadienyl complexes involving other transition metals as well. Reversible polarographic oxidation potentials have been reported by Wilkinson and co-workers for bis-cyclopentadienyl compounds of cobalt(II),[2a] nickel (II),[2b] vanadium(III)[2c] and titanium(III),[2c] and for bis-indenyl cobalt(II).[2d] In all cases, the

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[1] Presented in part before the Division of Inorganic Chemistry, 136th National Meeting, American Chemical Society, Atlantic City, N. J., September, 1959.

[2] (a) J. A. Page and G. Wilkinson, THIS JOURNAL, **74**, 6149 (1952). G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *ibid.*, **74**, 2125 (1952). (b) G. Wilkinson, P. L. Pauson and F. A. Cotton, *ibid.*, **76**, 1970 (1954). (c) G. Wilkinson and J. M. Birmingham, *ibid.*, **76**, 4281 (1954). (d) P. L. Pauson and G. Wilkinson, *ibid.*, **76**, 2024 (1954).