O(3) and O(4), distorted out of the *mean* croconate carbon plane. The hydrogen-bonding network presumably responsible for this and other small but significant chain deformations is analogous to those previously discussed in detail for the $C_5O_5Cu(H_2O)_3$ and $C_5O_5Zn(H_2O)_3$ compounds. The magnitudes of the closest intra- and interchain nonbonding distances in manganese(II) croconate closely parallel those in zinc(II) croconate.[12]

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[12] The transformations in Table V of ref. 2 should be corrected as follows. IV: $-1/2 + x, y, 1/2 - z$. VI: $x, 1/2 - y, -1/2 + z$.

CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH, PENNSYLVANIA

Organonitrogen Derivatives of Metal Carbonyls. I. Reactions between Metal Carbonyl Anions and Haloalkyl Amines[1]

BY R. B. KING AND M. B. BISNETTE

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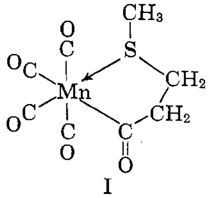
2-Chloroethyldimethylamine reacts with $NaMn(CO)_5$ to give the yellow crystalline cyclic acyl derivative $(CH_3)_2NCH_2CH_2COMn(CO)_4$. Similarly, 2-chloroethyldimethylamine reacts with $NaFe(CO)_2C_5H_5$ to give the dark red crystalline cyclic acyl derivative $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ and the yellow-orange salt $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$. N-2-Chloroethylpiperidine reacts with $NaFe(CO)_2C_5H_5$ to give the yellow-orange compound $C_5H_{10}NCH_2CH_2Fe(CO)_2C_5H_5$ with an iron–carbon σ bond. Reaction of 2-chloromethylpyridine with $NaFe(CO)_2C_5H_5$ or $NaW(CO)_3C_5H_5$ gives yellow-orange $NC_5H_4CH_2Fe(CO)_2C_5H_5$ or yellow $NC_5H_4CH_2W(CO)_3C_5H_5$, respectively, with metal–carbon σ bonds. However, reaction of 2-chloromethylpyridine with $NaMn(CO)_5$ or $NaMo(CO)_3C_5H_5$ gives pale yellow $NC_5H_4CH_2COMn(CO)_4$ or yellow $NC_5H_4CH_2COMo(CO)_2C_5H_5$, respectively, with a five-membered heterocyclic ring containing the metal atom, an acyl carbonyl group, a CH_2 group, and one carbon and one nitrogen atom of the pyridine system. Spectroscopic evidence for the proposed structures of these new complexes is presented and discussed.

Introduction

Recently we reported some reactions between metal carbonyl anions and haloalkyl sulfides such as $ClCH_2SCH_3$ and $ClCH_2CH_2SCH_3$.[2,3] In the case of 2-chloroethyl methyl sulfide, $ClCH_2CH_2SCH_3$, these studies led to the discovery of a novel type of heterocyclic acyl derivative exemplified by the manganese carbonyl complex $CH_3SCH_2CH_2COMn(CO)_4$ (I).[4] Characteristic of the structure of the new manganese complex I is the presence of a five-membered chelate-type heterocyclic ring containing the manganese atom, an acyl carbonyl group, two other carbon atoms, and a CH_3S group. One lone pair of the sulfur atom of the CH_3S group is coordinated to the manganese atom.

It appeared reasonable to us that the CH_3S group in the heterocyclic ring of $CH_3SCH_2CH_2COMn(CO)_4$ (I) could be replaced by other groups containing a free electron pair capable of being coordinated to a metal atom and so located such that coordination to the metal atom will result in a five- or six-membered ring. One category of such groups are those containing tertiary aminoid nitrogen (*e.g.*, $(CH_3)_2N$) with a lone pair readily capable of coordinating with a transition metal atom. Accordingly, we have investigated reactions between carbonyl anions and chloromethyl and 2-chloroethyl tertiary amines with the haloalkyl groups situated with respect to the nitrogen atom to permit formation of an acyl derivative with a five-membered heterocyclic ring containing the metal atom, an acyl carbonyl group, the amine nitrogen atom, and two other carbon atoms. In this paper, the first of a new series from our laboratory discussing unusual compounds obtained from metal carbonyl derivatives (especially anions) and various organonitrogen compounds such as amines, isocyanates, diazonium salts, etc., we describe compounds prepared from metal carbonyl anions and the three haloalkylamines: (a) 2-chloroethyldi-


I

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[1] Some of this work was presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; Abstracts, p. 43M.

[2] R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 1267 (1964).

[3] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965).

[4] Strictly speaking, an arrow should be drawn from the sulfur atom to the manganese atom in order to indicate the manganese–sulfur bond. This bond is omitted for formulas in the text for I and related compounds for ease in printing the running text.

methylamine, $ClCH_2CH_2N(CH_3)_2$; (b) N-2-chloroethylpiperidine, $ClCH_2CH_2NC_5H_{10}$; (c) 2-chloromethylpyridine, $NC_5H_4CH_2Cl$.

Experimental Section

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition the metal carbonyl regions of many compounds (Table I) were taken in either dilute cyclohexane solution or a halocarbon oil mull and recorded on a Beckman IR-9 spectrometer with grating optics and using a scale expanded by a factor of 2.5 relative to the normal scale. Proton n.m.r. spectra were taken in the indicated solvents (carbon disulfide, chloroform, or acetone-d_6) and recorded on a Varian A-60 spectrometer. Ultraviolet spectra were taken in cyclohexane or dioxane solutions and recorded on a Cary Model 14 spectrometer. Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., with the Mechrolab vapor pressure osmometer using benzene solutions.

Tetrahydrofuran and 1,2-dimethoxyethane were distilled over lithium aluminum hydride immediately before use. A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions with organometallic compounds, (b) admitting to evacuated flasks and other vessels, and (c) handling filtered solutions of organometallic compounds. Chromatographic separations were carried out on 80–200 mesh adsorption alumina (Fisher Scientific Co., No. A-540).

The hydrochlorides of the chloroalkyl amines used in this work were commercial samples.[5] The free amines were liberated from their hydrochlorides with aqueous base (sodium hydroxide for 2-chloroethyldimethylamine and 2-chloroethylpiperidine; sodium carbonate for 2-chloromethylpyridine). After extraction from the aqueous solutions with diethyl ether, the chloroalkyl amines were distilled giving products with the following boiling points: 2-chloroethyldimethylamine, 109–111° (740 mm.); 2-chloroethylpiperidine, 47° (0.25 mm.); and 2-chloromethylpyridine, 72° (5 mm.) or 46° (0.5 mm.). Storage of the free amines at low temperatures ($-10°$ or preferably $-78°$) is recommended since on standing they deposit solid salts due to self-quaternization. Qualitative observations suggest the stability of the chloroalkyl amines to *in*crease in the series 2-chloroethyldimethylamine < 2-chloromethylpyridine ≪ N-2-chloroethylpiperidine.

The nature of the chloroalkyl amines was confirmed by their proton n.m.r. spectra taken as neat liquids: (A) $(CH_3)_2NCH_2CH_2Cl$: Resonances at τ 6.48 (triplet, $J = 7.5 \pm 0.2$ c.p.s.), τ 7.44 (triplet, $J = 7.5 \pm 0.2$ c.p.s.), and τ 7.77 (singlet) of approximate relative intensities 2:2:6 corresponding to the two methylene protons bonded to the carbon atom to which the chlorine atom is bonded, the two methylene protons bonded to the carbon atom to which the nitrogen atom is bonded, and the six methyl protons, respectively. (B) $C_5H_{10}NCH_2CH_2Cl$: Resonances at τ 6.50 (triplet, $J = 7.5 \pm 0.2$ c.p.s.), τ 7.41 (triplet, $J = 7.5 \pm 0.2$ c.p.s.), τ 7.6 (two peaks, separation 5 c.p.s., besides the τ 7.41 triplet), and τ 8.55 (one peak, width at half-height 7 c.p.s.) of approximate relative intensities 2:2:4:6 corresponding to the two methylene protons bonded to the carbon atom to which the chlorine atom is bonded, the two other methylene protons of the 2-chloroethyl group, the four other methylene protons bonded to the carbon atom to which the nitrogen atom is bonded, and the remaining six methylene protons, respectively. (C) $NC_5H_4CH_2Cl$: See Table II.

The metal carbonyl derivatives required for this work were ultimately obtained from commercial samples of the "pure" metal carbonyls pentacarbonyliron (Antara Division of General Aniline and Film, New York, N. Y.), decacarbonyldimanganese, hexacarbonylmolybdenum (Climax Molybdenum Co., New York, N. Y.), and hexacarbonyltungsten (Climax Molybdenum Co. or Pressure Chemical Co., Pittsburgh, Pa.). Treatment of $Fe(CO)_5$ or $Mo(CO)_6$ with dicyclopentadiene at the dedimerization temperature by well-established procedures[6] gave the cyclopentadienylmetal carbonyls $[C_5H_5Fe(CO)_2]_2$ or $[C_5H_5Mo(CO)_3]_2$, respectively. Reduction of the dimeric metal carbonyl derivatives $Mn_2(CO)_{10}$, $[C_5H_5Mo(CO)_3]_2$, or $[C_5H_5Fe(CO)_2]_2$ with ~1% sodium amalgam in tetrahydrofuran solution at room temperature by well-established procedures[6,7] gave solutions of the sodium salts $NaMn(CO)_5$, $NaMo(CO)_3C_5H_5$, or $NaFe(CO)_2C_5H_5$, respectively.[8] A solution of $NaW(CO)_3C_5H_5$ was obtained by boiling hexacarbonyltungsten with sodium cyclopentadienide in 1,2-dimethoxyethane under reflux.[7]

Reaction between $NaMn(CO)_5$ and 2-Chloroethyldimethylamine.—A solution of 10 mmoles of $NaMn(CO)_5$ in 150 ml. of tetrahydrofuran was treated with 1.0 g. (9.3 mmoles) of 2-chloroethyldimethylamine and the resulting mixture boiled under reflux for 16 hr. After cooling to room temperature solvent was removed at ~25° (30 mm.). The residue was extracted with three 50-ml. portions of dichloromethane, and solvent was removed from the filtered dichloromethane extracts at ~25° (30 mm.). A filtered solution of the residue in ~75 ml. of diethyl ether was chromatographed on a 2 × 50 cm. alumina column and the chromatogram developed with diethyl ether. Two yellow bands were observed which were eluted with diethyl ether. Evaporation of the filtered eluate from the second of these bands gave 0.46 g. (19% yield based on $Mn_2(CO)_{10}$) of yellow crystals purified further by pentane washing and/or sublimation at 75° (0.1 mm.). The yellow air-stable product, resembling $Mn_2(CO)_{10}$ very much in general appearance, melted sharply at 126–126.5°.

Anal. Calcd. for $C_9H_{10}MnNO_5$: C, 40.4; H, 3.7; N, 5.2; Mn, 20.6; O, 30.0; mol. wt., 267. Found: C, 40.5; H, 3.7; N, 5.0; Mn, 20.7; O, 30.2; mol. wt., 290.

Infrared Spectrum.—ν_{CH} at 2970 (sh), 2950 (sh), 2910 (sh), and 2860 (m) cm.$^{-1}$. See Table I for ν_{CO}; other bands at 1470 (sh), 1465 (s), 1450 (m), 1435 (m), 1410 (m), 1295 (w), 1247 (w), 1233 (vw), 1210 (vw), 1173 (vw), 1111 (w), 1100 (vw), 1040 (vw), 1004 (s), 980 (m), 938 (m), 842 (m), and 768 (s) cm.$^{-1}$.

Proton N.m.r. Spectrum ($CHCl_3$ Solution).—Resonance at τ 7.14 (singlet) and 7.38 (complex but symmetrical well-defined pattern of at least four lines) of relative intensities 6:4 arising from the six methyl and four methylene (CH_2) protons, respectively.

Reaction between $NaFe(CO)_2C_5H_5$ and 2-Chloroethyldimethylamine.—Owing to the unexpected and unprecedented formation of an ionic product, the reaction between $NaFe(CO)_2C_5H_5$ and 2-chloroethyldimethylamine was carried out numerous times. Significant variations were made in the use or nonuse of ultraviolet irradiation[9] to effect formation of the cyclic acyl derivative $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ and in the product isolation, separation, and purification. Space does not permit detailed description of all of the procedures used to study this reaction. The procedure given below was selected to give useful quantities (not necessarily optimum or maximum yields) of reasonably pure samples of $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ and $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$ with a minimum of manipulations.

A solution of 50 mmoles of $NaFe(CO)_2C_5H_5$ in 150 ml. of tetra-

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[5] (a) The 2-chloroethyldimethylamine hydrochloride was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisc. Conversion of this salt to the free amine is described by E. Baer and S. K. Pavanaram, *J. Biol. Chem.*, **236**, 2410 (1961). (b) The 2-chloroethylpiperidine hydrochloride was purchased from Columbia Organic Chemicals Co., Inc., Columbia, S. C., and from Aldrich Chemical Co., Inc., Milwaukee, Wisc. (c) The 2-chloromethylpyridine hydrochloride was purchased from City Chemical Corp., New York, N. Y.

[6] These procedures have recently been discussed by R. B. King in "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, pp. 109, 114.

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

[8] Our techniques for preparing and handling some of these sodium salts are discussed in R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964) (see especially p. 24 of this article).

[9] In the preparation of the analogous $CH_3SCH_2CH_2COFeCOC_5H_5$ from $NaFe(CO)_2C_5H_5$ and 2-chloroethyl methyl sulfide[2,3] ultraviolet irradiation was necessary.

hydrofuran was stirred ~16 hr. with 5.4 g. (50 mmoles) of 2-chloroethyldimethylamine at room temperature. Solvent was removed from the brown reaction mixture at ~25° (30 mm.). The brown residue was extracted with three 100-ml. portions of dichloromethane. Solvent was removed from the filtered[10] extracts again at ~25° (30 mm.) leaving an orange-brown partially solid residue which was kept ~72 hr. under nitrogen.[11]

This residue was washed with ~125 ml. of pentane in four portions. These pentane washings appeared to contain varying amounts of a yellow-orange to yellow-brown liquid iron complex which was unstable and air-sensitive. Attempts to isolate this liquid, possibly $(CH_3)_2NCH_2CH_2Fe(CO)_2C_5H_5$ isomeric with $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ described below, in sufficient quantity and quality for adequate characterization were unsatisfactory, apparently due to the limited stability of this material.

The rather lumpy dirty brown residue from the pentane washings was next triturated on the filter with 150 ml. of pure benzene in six portions. This dissolved out the $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$. Solvent was removed from the air-sensitive filtered benzene solution at ~25° (30 mm.), leaving a red-black viscous liquid which soon crystallized. After washing with diethyl ether, the dark red crystals were sublimed at 80° (0.1 mm.) for 16 hr. to give 0.315 g. (2.5% yield) of dark red rather air-sensitive crystalline $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$, m.p. 108–111° dec., sparingly soluble in pentane or diethyl ether but soluble in benzene or dichloromethane.

The residue from the benzene washings was extracted with four ~15-ml. portions of dichloromethane. The filtered orange solution was treated with hexane and solvent was removed at ~25° (30 mm.). The resulting orange crystals were washed with three portions of benzene, two portions of diethyl ether, and one portion of pentane to give, after drying, 1.714 g. (14% yield) of yellow-orange crystalline $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]]_2Cl\cdot H_2O$, m.p. 112–114° dec. Upon heating under vacuum (0.25 mm.) $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$ decomposed at 90°, giving a dark brown residue and a small quantity of a purple sublimate of $[C_5H_5Fe(CO)_2]_2$.

Properties of $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$.—*Anal.* Calcd. for $C_{11}H_{15}FeNO_2$: C, 53.0; H, 6.0; N, 5.6; Fe, 22.5; O, 12.9. Found: C, 52.9; H, 5.7; N, 5.7; Fe, 21.7; O, 13.5.

Infrared Spectrum.—ν_{CH} at 2850 (w) cm.$^{-1}$; ν_{CO} at 1890 (s) [metal] and 1590 (s) [acyl] cm.$^{-1}$; other bands at 1460 (w), 1395 (vw), 1348 (vw), 1157 (vw), 1014 (w), 1003 (w), 986 (vw), 974 (w), 936 (w), 847 (w), 832 (vw), 820 (m), 809 (sh), and 770 (w) cm.$^{-1}$.

Proton N.m.r. Spectrum ($CHCl_3$ Solution).—Apparent singlet resonances at τ 5.54, 7.16, and 7.59 of approximate relative intensities 5:3:7 due to the five π-cyclopentadienyl protons, the three protons of one methyl group, and the seven protons with coincidentally identical chemical shifts including the three protons of the remaining methyl group and the four protons of the two methylene groups.

Properties of $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$.—*Anal.* Calcd. for $C_{18}H_{22}ClFe_2NO_5$: C, 45.1; H, 4.6; N, 2.9; O, 16.7; Fe, 23.4; Cl, 7.4. Found: C, 46.5, 46.4; H, 5.1, 5.0; N, 2.9, 2.6; O, 16.3, 16.2; Fe, 21.8, 22.2; Cl, 7.4, 7.2.

Infrared Spectrum.—ν_{CH} at 3040 (vw), 3015 (vw), and 2900 (m); see Table I for ν_{CO}; other bands at 2650 (m), 2600 (m), 2475 (w), 2450 (w), 1625 (w), 1475 (m), 1425 (m), 1405 (m), 1368 (vw), 1345 (vw), 1320 (vw), 1230 (vw), 1180 (vw), 1168 (vw), 1130 (vw), 1100 (vw), 1055 (vw), 1030 (vw), 1012 (w), 995 (w), 960 (vw), 925 (w), 900 (vw), 878 (w), 845 (s), and 832 (s) cm.$^{-1}$.

Proton N.m.r. Spectrum ($CHCl_3$ Solution).[12]—Singlet resonances at τ 4.95 and 5.04 of approximately equal relative intensities each due to the five protons of a π-cyclopentadienyl group. Other resonances were observed at τ 5.20 (partially occluded by the cyclopentadienyl resonances), ~6.5 (very broad), 7.03 (apparent singlet), 7.24 (singlet), and 8.78 (complex). Difficulties in integration prevent assignment of relative intensities to these resonances.

Reaction between $NaFe(CO)_2C_5H_5$ and 2-Chloroethylpiperidine.—A solution of 40 mmoles of $NaFe(CO)_2C_5H_5$ in 250 ml. of tetrahydrofuran was stirred with 6.0 g. (40.6 mmoles) of N-2-chloroethylpiperidine. After 16 hr. solvent was removed at ~25° (30 mm.) and the residue extracted with ~150 ml. of dichloromethane in three portions. Removal of solvent from the filtered extracts also at ~25° (30 mm.) left a liquid. This liquid was extracted with 50 ml. of pentane in three portions. Cooling these filtered pentane extracts several hours in a −78° bath precipitated orange crystals of the product. These were filtered and similarly recrystallized two additional times from pentane to give 4.467 g. (39% yield) of yellow-orange crystalline $C_5H_{10}NCH_2CH_2Fe(CO)_2C_5H_5$, m.p. 38–39°.

Anal. Calcd. for $C_{14}H_{19}NFeO_2$: C, 58.1; H, 6.6; N, 4.8; O, 11.1; Fe, 19.4. Found: C, 57.5; H, 7.1; N, 5.1; O, 11.5; Fe, 18.7.

Infrared Spectrum.—ν_{CH} at 3020 (vw), 2910 (m), 2840 (w), 2775 (w), and 2740 (w) cm.$^{-1}$; see Table I for ν_{CO}; other bands at 1467 (w), 1451 (w), 1437 (w), 1410 (w), 1334 (vw), 1320 (vw), 1303 (vw), 1295 (sh), 1265 (vw), 1252 (vw), 1225 (vw), 1144 (w), 1121 (vw), 1090 (m), 1061 (w), 1038 (vw), 1013 (vw), 996 (vw), 974 (w), 874 (vw), 855 (w), 852 (sh), 843 (m), 834 (sh), 830 (m), and 781 (w) cm.$^{-1}$.

Proton N.m.r. Spectrum (CS_2 Solution).—Resonances at τ 5.38 (singlet), 7.73 (complex with three discernible peaks), 8.44 (apparent singlet), and 8.57 (broad apparent singlet) of estimated relative intensities 5:6:2:6 which may be tentatively[13] assigned to the five protons of the π-cyclopentadienyl group, the six protons of the three methylene groups in α positions relative to the nitrogen atom, the two protons of the single methylene group in a γ position relative to the nitrogen atom, and the six protons of the three methylene groups in β positions relative to the nitrogen atom.

Ultraviolet Spectrum.—Maximum at 348 mμ (ϵ 1410) in cyclohexane solution.

Reaction between $NaFe(CO)_2C_5H_5$ and 2-Chloromethylpyridine.—A solution of 30 mmoles of $NaFe(CO)_2C_5H_5$ in 150 ml. of tetrahydrofuran was stirred 16 hr. at room temperature with 3.82 g. (30 mmoles) of 2-chloromethylpyridine. Solvent was then removed at 25° (30 mm.). The residue was extracted with three 75-ml. portions of dichloromethane. Solvent was removed from the filtered extracts at ~25° (30 mm.), leaving a mixture of orange-brown solid and liquid.

A filtered solution of this product in 50 ml. of diethyl ether was chromatographed on a 2 × 50 cm. alumina column. The chromatogram was developed with diethyl ether. After a minor pale orange band the characteristic brown-violet band of $[C_5H_5Fe(CO)_2]_2$ was observed followed by a yellow-brown band of $NC_5H_4CH_2Fe(CO)_2C_5H_5$. These bands were eluted with diethyl ether. Solvent was removed from the eluate from the yellow-brown band, leaving a yellow-brown liquid which was purified by three low-temperature recrystallizations from ~50 ml. of pentane to give 1.0–2.0 g. (12.5–25% yield) of yellow-orange $NC_5H_4CH_2Fe(CO)_2C_5H_5$, m.p. 42–44°.

Anal. Calcd. for $C_{13}H_{11}FeNO_2$: C, 58.0; H, 4.1; N, 5.2; O, 11.9. Found: C, 57.8; H, 4.4; N, 5.2; O, 11.9.

Infrared Spectrum.—ν_{CH} at 3040 (w), 2950 (vw), and 2900 (vw) cm.$^{-1}$; see Table I for ν_{CO} bands; other bands at 1577 (m), 1548 (w), 1464 (s), 1428 (m), 1410 (m), 1351 (vw), 1294 (w), 1235 (m), 1146 (m), 1107 (vw), 1059 (vw), 1045 (w), 1015 (vw), 996 (vw), 981 (vw), 950 (vw), 884–872 (vw, br), 841 (m), 834 (m), 827 (sh), 778 (m), and 741 (m) cm.$^{-1}$.

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(10) If the dichloromethane extracts are filtered through alumina, *no* $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$ can be isolated from the filtrate. This ionic material is either destroyed by or completely adsorbed on the alumina.

(11) Formation of the $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ appears to occur during this standing at room temperature.

(12) The frequent presence of paramagnetic impurities in samples of this compound (at least in solution) prevented us from obtaining satisfactory n.m.r. spectra on many of our samples. Data from the best of our spectra are reported.

(13) The detailed assignments of these resonances arising from the $C_5H_{10}NCH_2CH_2$ group are uncertain.

TABLE I

INFRARED SPECTRA IN THE METAL AND ACYL CARBONYL REGIONS[a]

Compound	Medium[b]	ν_{CO}(metal),[c] cm.$^{-1}$	ν_{CO}(acyl),[c] cm.$^{-1}$
$[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl \cdot H_2O$	HC	2015 s, 2004 s, 1999 s, 1955 sh, 1937 vs	None
$C_5H_{10}NCH_2CH_2Fe(CO)_2C_5H_5$	CH	2015 s, 1960 s	None
$NC_5H_4CH_2Fe(CO)_2C_5H_5$	CH	2025 s, 2020 sh, 1970 vs, 1933 w	None
$CH_3SCH_2CH_2COMn(CO)_4$[d]	CH	2083 m, 2001 s, 1977 vs, 1951 w	1660 w
$(CH_3)_2NCH_2CH_2COMn(CO)_4$	CH	2069 m, 1986 s, 1967 vs, 1958 sh, 1940 w	1660 w
$NC_5H_4CH_2COMn(CO)_4$	CH	2078 w, 1994 m, 1985 m, 1958 m	1668 w
$NC_5H_4CH_2COMo(CO)_2C_5H_5$	HC	1946 s, 1934 vs, 1854 vs	1624 s
$NC_5H_4CH_2W(CO)_3C_5H_5$	CH	2023 m, 1937 vs	None

[a] Beckman IR-9 spectrometer with grating optics. [b] CH = cyclohexane solution, HC = halocarbon oil mull. [c] In general most of these bands are of relative intensity s or vs when observed on the general spectra of the 4000–700 cm.$^{-1}$ region taken in KBr pellets described elsewhere in the Experimental Section. More dilute samples were used to obtain the spectra listed in this table. [d] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965).

TABLE II

PROTON N.M.R. SPECTRA OF $NC_5H_4CH_2Y$ DERIVATIVES, τ

		C_5H_4 protons[a,b]				
Compound	Solvent	*ortho* [1]	*meta* [2]	*para* [1]	CH_2 protons	π-C_5H_5 protons
$NC_5H_4CH_2Cl$	$NC_5H_4CH_2Cl$	1.44 (5)[c]	~2.4	2.87 (5, 2)	5.29[e]	...
$NC_5H_4CH_2Fe(CO)_2C_5H_5$	CS_2	1.72 (4)[c]	3.10	2.68 (~8)[d]	7.45[e]	5.29[e]
$NC_5H_4CH_2W(CO)_3C_5H_5$	CS_2	1.71 (~4)[c]	3.11 (~8)[d]	2.61 (~8)[d]	7.09[e]	4.51[e]
$NC_5H_4CH_2COMo(CO)_2C_5H_5$	$(CD_3)_2CO$	1.04 (7)[c]	2.29 (~7)	2.71 (7, 2)[f]	6.00[e]	4.62[e]
$NC_5H_4CH_2COMn(CO)_4$	$(CD_3)_2CO$	1.01 (7)[c]	2.37 (7)	1.95 (7, 2)[f]	6.00[e]	...

[a] Position given relative to nitrogen atom of ring. Number of protons of each type given in brackets. [b] Largest splitting in c.p.s. given in parentheses. [c] Apparent doublet with additional fine structure. [d] Apparent triplet with additional fine structure. [e] Singlet. [f] Triple doublet with the two indicated coupling constants.

Ultraviolet Spectrum.—Maximum at 315 mμ (ϵ 10,650) in cyclohexane solution.

Reaction between $NaW(CO)_3C_5H_5$ and 2-Chloromethylpyridine.—A solution of 20 mmoles of $NaW(CO)_3C_5H_5$ in ~150 ml. of 1,2-dimethoxyethane was stirred 16 hr. at room temperature with 2.54 g. (20 mmoles) of 2-chloromethylpyridine. Solvent was then removed at 25° (30 mm.). The deep red residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at 25° (30 mm.). A mixture of viscous yellow liquid and yellow crystals remained. After an unsuccessful attempt to obtain a pure crystalline product by crystallization from a mixture of dichloromethane and hexane, this semisolid mixture was extracted with 50 ml. of diethyl ether in three portions. Cooling the filtered diethyl ether extracts overnight at −78° precipitated yellow crystals. These were removed by filtration and heated 42 hr. at 60° (0.1 mm.) in a sublimer to remove any white volatile $W(CO)_6$. A small amount (~0.06 g.) of yellow crystals of $NC_5H_4CH_2W(CO)_3C_5H_5$ collected on the probe. The residue from the sublimation was recrystallized twice from a mixture of dichloromethane and hexane to give 0.437 g. (5.1% yield) of yellow crystalline $NC_5H_4CH_2W(CO)_3C_5H_5$, m.p. 113–114°.

Anal. Calcd. for $C_{14}H_{11}NO_3W$: C, 39.6; H, 2.6; N, 3.3; O, 11.3; W, 43.3. Found: C, 40.2; H, 3.0; N, 3.1; O, 11.3; W, 42.1.

Infrared Spectrum.—ν_{CH} at 3075 (vw), 3040 (sh), 2950 (vvw), and 2900 (vvw) cm.$^{-1}$; see Table I for ν_{CO}; other bands at 1583 (m), 1551 (w), 1465 (m), 1416 (m), 1302 (w), 1242 (w), 1227 (w), 1148 (w), 1056 (vw), 1047 (w), 1005 (w), 985 (w), 932 (vw, br), 842 (w), 828 (m), 778 (m), and 745 (m) cm.$^{-1}$.

Ultraviolet Spectrum.—Maximum at 295 mμ (ϵ 12,700) in cyclohexane solution.

Reaction between $NaMo(CO)_3C_5H_5$ and 2-Chloromethylpyridine.—A solution of 30 mmoles of $NaMo(CO)_3C_5H_5$ in 150 ml. of tetrahydrofuran was prepared from $[C_5H_5Mo(CO)_3]_2$ and sodium amalgam and stirred overnight at room temperature with 3.81 g. (30 mmoles) of 2-chloromethylpyridine. Solvent was removed from the resulting reaction mixture at 25° (30 mm.). The residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered yellow dichloromethane extracts at ~25° (30 mm.) leaving a yellow crystalline residue. This yellow crystalline residue was washed with ~100 ml. of pentane in five portions followed by ~60 ml. of diethyl ether[14] in four portions. It was then extracted with ~80 ml. of dichloromethane[14] in four portions, and the filtered extracts were treated with 25 ml. of hexane. Concentration to ~15 ml. at ~25° (30 mm.) deposited yellow crystals of $NC_5H_4CH_2COMo(CO)_2C_5H_5$. These were washed with pentane and then recrystallized from dichloromethane–hexane by a similar procedure to give 5.046 g. (50% yield) of yellow crystalline $NC_5H_4CH_2COMo(CO)_2C_5H_5$, m.p. 146–150° dec.

An additional 0.639 g. (6.3% yield) of $NC_5H_4CH_2COMo(CO)_2C_5H_5$ was isolated from the diethyl ether washings by addition of hexane, evaporating at ~25° (30 mm.), and washing the yellow crystals with several portions of pentane.

Anal. Calcd. for $C_{14}H_{11}MoNO_3$: C, 49.8; H, 3.3; N, 4.2; O, 14.3; Mo, 28.5; mol. wt., 337. Found: C, 49.7; H, 3.5; N, 4.1; O, 14.2; Mo, 28.4; mol. wt., 368.

Infrared Spectrum.—ν_{CH} at 3060 (vvw) and 2830 (vvw) cm.$^{-1}$; see Table I for ν_{CO}; other bands at 1550 (w), 1475 (m), 1439 (w), 1414 (w), 1377 (m), 1264 (w), 1154 (w), 1140 (w), 1104 (w), 1051 (w), 1020 (vw), 1008 (w), 993 (s), 989 (m), 954 (vw), 884 (w), 850 (vw), 834 (w), 825 (w), 821 (w), 804 (s), and 758 (s) cm.$^{-1}$.

Ultraviolet Spectrum.—In dioxane solution the absorbance increased monotonically without any maxima in proceeding from 400 to 200 mμ.

Reaction between $NaMn(CO)_5$ and 2-Chloromethylpyridine.—A solution of 10 mmoles of $NaMn(CO)_5$ in 100 ml. of tetrahydrofuran was stirred ~16 hr. with 1.27 g. (10 mmoles) of 2-chloromethylpyridine. Solvent was then removed at 25° (30 mm.) and the residue extracted with three 50-ml. portions of dichloromethane. Removal of solvent from the filtered dichloromethane extracts at ~25° (30 mm.) left a yellow-brown crystalline residue. After washing this residue with ~100 ml. of pentane in five portions, it was sublimed at 80–100° (0.1 mm.) for 22 hr. to give 1.292 g. (45% yield) of a pale yellow crystalline sublimate of $NC_5H_4CH_2COMn(CO)_4$, m.p. 129–131°. During the sublimation period any minor amounts of $Mn_2(CO)_{10}$ still present after the pentane washings sublimed beyond the water-cooled probe into

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(14) Product did not separate upon cooling these solutions at −78° for 1 day or more.

the vacuum system. Attempted sublimation of $NC_5H_4CH_2CO$-$Mn(CO)_4$ at temperatures above ~120° at ~0.1 mm. led to extensive decomposition producing $Mn_2(CO)_{10}$ and various nonvolatile materials.

Anal. Calcd. for $C_{11}H_6MnNO_5$: C, 46.0; H, 2.1; N, 4.9; O, 27.9; Mn, 19.2; mol. wt., 287. Found: C, 46.8; H, 2.5; N, 4.7; O, 26.9; Mn, 19.6; mol. wt., 285.

Infrared Spectrum.—ν_{CH} at 3060 (vvw, br), 2890 (vvw), and 2850 (vvw) cm.$^{-1}$; see Table I for ν_{CO}; other bands at 1482 (s), 1440 (w), 1379 (vw), 1310 (vw), 1275 (vw), 1237 (vw), 1176 (vw), 1150 (w), 1144 (vw), 1105 (w), 1060 (w), 978 (s), 953 (w), 884 (w), 854 (w), 842 (w, br), and 763 (s) cm.$^{-1}$.

Ultraviolet Spectrum.—In dioxane solution the absorbance increased monotonically without any maxima in proceeding from 400 to 220 mμ.

Discussion

The infrared spectrum of the manganese compound $(CH_3)_2NCH_2CH_2Mn(CO)_5$ clearly indicates that the $(CH_3)_2NCH_2CH_2$ ligand is not bonded to the manganese atom only with a manganese–carbon σ bond. Instead the presence of a strong band at 1620 (KBr pellet) or at 1660 (cyclohexane solution) cm.$^{-1}$ demonstrates the presence of an acyl carbonyl group suggesting the cyclic acyl structure II. The close relationship between $CH_3SCH_2CH_2COMn(CO)_4$[3] and $(CH_3)_2NCH_2CH_2COMn(CO)_4$[15] is emphasized by the very similar infrared spectra obtained for the metal carbonyl region (2100–1900 cm.$^{-1}$) in cyclohexane solutions under high resolution conditions. The metal carbonyl frequencies of $(CH_3)_2NCH_2CH_2COMn(CO)_4$ are 10 to 20 cm.$^{-1}$ lower than the corresponding metal carbonyl frequencies in $CH_3SCH_2CH_2COMn(CO)_4$ in accord with the poorer π-acceptor (*i.e.*, "back bonding") ability of nitrogen relative to sulfur.[16]

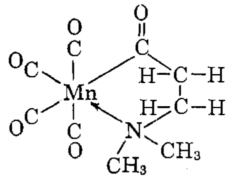
The formation of the cyclic acyl derivative $(CH_3)_2NCH_2CH_2COMn(CO)_4$ (II) in the reaction between $NaMn(CO)_5$ and 2-chloroethyldimethylamine is hardly surprising. Keblys and Filbey[17] have demonstrated alkylmanganese pentacarbonyls, $RMn(CO)_5$, to react with various amines to form acylmanganese tetracarbonyl amines, $RCOMn(CO)_4NR'_3$, according to the equation

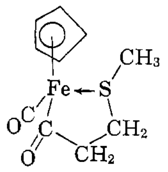
$$RMn(CO)_5 + R'_3N \longrightarrow RCOMn(CO)_4NR'_3$$

Reaction between $NaMn(CO)_5$ and 2-chloroethyldimethylamine would be expected first to give the straightforward substituted alkylmanganese pentacarbonyl $(CH_3)_2NCH_2CH_2Mn(CO)_5$ with elimination of sodium chloride. However, $(CH_3)_2NCH_2CH_2Mn(CO)_5$ can undergo an intramolecular Keblys–Filbey reaction, the lone pair on the nitrogen atom attacking the manganese atom. The resulting product is the observed cyclic acyl derivative $(CH_3)_2NCH_2CH_2COMn(CO)_4$ (II).

Reaction between $NaFe(CO)_2C_5H_5$ and 2-chloroethyl methyl sulfide has been shown to give the yellow-brown liquid compound $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ with an iron–carbon σ bond to the sulfur ligand and with no iron–sulfur bonds.[3] Ultraviolet irradiation of $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ gives a complex mixture including the red crystalline cyclic acyl derivative $CH_3SCH_2CH_2COFeCOC_5H_5$ (III).

In an attempt to prepare nitrogen analogs to these compounds the reaction between $NaFe(CO)_2C_5H_5$ and 2-chloroethyldimethylamine was investigated. However, no compound $(CH_3)_2NCH_2CH_2Fe(CO)_2C_5H_5$ analogous to $CH_3SCH_2CH_2Fe(CO)_2C_5H_5$ could be isolated. A pentane-soluble yellow-brown liquid, possibly $(CH_3)_2NCH_2CH_2Fe(CO)_2C_5H_5$, did appear to be present in this reaction mixture. However, during attempted purification it decomposed. The major decomposition product of this yellow-brown liquid in laboratory light under nitrogen at room temperature appeared to be crystalline $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$. The cyclic acyl structure IV for this new iron complex was clearly indicated by its infrared spectrum, which exhibited a single strong metal carbonyl band at 1890 cm.$^{-1}$ and a single strong acyl carbonyl band at 1590 cm.$^{-1}$.


II


III

This cyclic acyl derivative $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ (IV) was only a minor product (<3% yield) from the reaction between $NaFe(CO)_2C_5H_5$ and 2-chloroethyldimethylamine. The iron complex obtained in greatest quantity from this reaction was a yellow-orange solid insoluble in pentane, diethyl ether, or benzene, but soluble not only in dichloromethane and acetone but also in water. The high molar conductance in acetone solution (125 ± 25 ohm^{-1} cm.^{2} mole^{-1} in the concentration range 3.7×10^{-4} to 9.3 to 10^{-4} M) confirmed the ionic nature of this material suggested by its solubility properties and its nonvolatility. When carefully freed from a persistent impurity of $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ by repeated benzene washings, the infrared spectrum of this yellow-orange salt exhibited several strong bands in the terminal metal carbonyl region but no bands in the regions normally indicative either of bridging metal carbonyl groups or acyl carbonyl groups. Analyses for all six elements on several independent preparations were in best agreement with the composition $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$. The mole of water was suggested to be present by the persistently high direct oxygen analyses and by the inability to accommodate this "extra" oxygen by extra carbonyl groups which would show up in the infrared spectrum as acyl or bridging carbonyl groups. This water could easily have been introduced in many possible ways during the rather lengthy procedure for isolation of this product.

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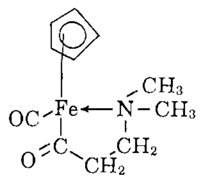
[15] Strictly speaking, an arrow should be drawn from the nitrogen atom to the manganese atom in order to indicate the manganese–nitrogen bond. As was done with the corresponding sulfur compounds[4] this arrow will be omitted in formulas of such nitrogen compounds in the text.

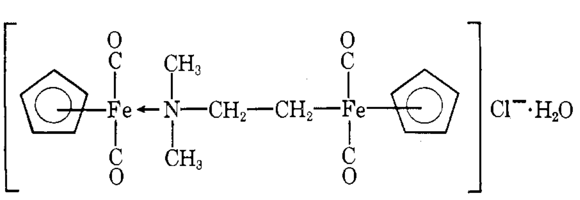
[16] For a general discussion of not only π-acceptor strengths of various ligands but also their effects on the metal carbonyl stretching modes see F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964), and references cited therein, especially E. W. Abel, M. A Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

[17] K. A. Keblys and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

The most likely formulation for $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$ is V which may be regarded as a salt of the $[C_5H_5Fe(CO)_2L]^+$ cation where L represents the amine $(CH_3)_2NCH_2CH_2Fe(CO)_2C_5H_5$ already discussed above as an expected but never observed product from this reaction between $NaFe(CO)_2C_5H_5$ and 2-chloroethyldimethylamine. Salts (mostly hexafluorophosphates) of the cations $[C_5H_5Fe(CO)_2L]^+$ have been isolated for many possible ligands including carbon monoxide,[18] ethylene and higher olefins,[18,19] tertiary phosphines,[18b] $C_5H_5Fe(CO)_2X$,[20,21] amines,[20] and nitriles.[20] The instability of aqueous solutions of V prevented metathesis reactions designed to demonstrate the integrity of the cation proposed to be present.

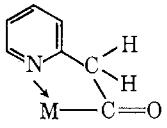

IV

The proton n.m.r. spectra of solutions of $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$ were studied in an attempt to obtain additional evidence for the proposed formulation. In many such spectra the peaks were drastically broadened, apparently due to paramagnetic decomposition products. However, the best spectra exhibited two distinct cyclopentadienyl resonances of approximately equal relative intensities, demonstrating the presence of two nonequivalent π-cyclopentadienyl rings in accord with structure V.


V

Difficulties in the completely unequivocal characterization of this ionic product from the reaction between $NaFe(CO)_2C_5H_5$ and 2-chloroethyldimethylamine led us to investigate reactions between $NaFe(CO)_2C_5H_5$ and related haloalkyl amines. The reaction between $NaFe(CO)_2C_5H_5$ and N-2-chloroethylpiperidine followed an entirely different course, yielding the orange crystalline $C_5H_{10}NCH_2CH_2Fe(CO)_5C_5H_5$ clearly demonstrated by the absence of acyl carbonyl bands in its infrared spectrum to have the $C_5H_{10}NCH_2CH_2$ group bonded to the iron atom only with an iron–carbon σ bond. Neither an ionic derivative similar to yellow-orange V nor a cyclic acyl derivative similar to dark red IV was isolated from the reaction between $NaFe(CO)_2C_5H_5$ and N-2-chloroethylpiperidine. In our hands, ultraviolet irradiation of $C_5H_{10}NCH_2CH_2Fe(CO)_2C_5H_5$ even failed to give a cyclic acyl derivative; instead starting material was recovered unchanged. These observations suggest that the greater steric requirements of a piperidino group relative to a dimethylamino group are sufficient to impede cyclization, producing a cyclic acyl derivative. Even the yellow liquid obtained in a low yield and an impure condition from $NaMn(CO)_5$ and N-2-chloroethylpiperidine appeared from its infrared spectrum and other observed physical properties (including low melting point and high solubility) to be $C_5H_{10}NCH_2CH_2Mn(CO)_5$ with only manganese–carbon bonds rather than the cyclic acyl derivative $C_5H_{10}NCH_2CH_2COMn(CO)_4$, also with a manganese–nitrogen bond.

Reactions between $C_5H_{10}NCH_2CH_2Fe(CO)_2C_5H_5$ and certain iodine derivatives such as I_2, CH_3I, and $C_5H_5Fe(CO)_2I$ in pentane or diethyl ether were carried out hoping to obtain ionic derivatives which would clarify the nature of the product $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl\cdot H_2O$ (V) obtained from $NaFe(CO)_2C_5H_5$ and 2-chloroethyldimethylamine. In all of the three cases cited above yellow to yellow-brown products were obtained in poor to fair yields. The materials obtained in reasonable quantities were indicated by analyses and the presence of two to four π-cyclopentadienyl resonances in the n.m.r. spectra to be complex mixtures. They were not investigated further.


VI

Pyridine and other similar "aromatic" heterocyclic amines have been well-established[22] to form more stable metal carbonyl complexes than saturated aliphatic amines, presumably owing to the π-acceptor capacity of the pyridine ring permitting stabilization of the metal–nitrogen bond by partial double-bond formation. We thus felt that incorporation of the pyridine–metal bond into the cyclic acyl derivative would lead to the formation of cyclic acyl derivatives with the ring system VI which would be more stable than the cyclic acyl derivatives containing nitrogen or sulfur already prepared. This consideration led to an investigation of the reaction between various metal carbonyl anions and 2-chloromethylpyridine. Since the haloalkyl group in this case is attached to a neighboring carbon atom rather than directly to the nitrogen atom, a chloro*methyl* rather than the 2-chloro*ethyl* group previously used is needed in order to obtain the apparently favored five-membered ring for the cyclic acyl derivative. Additionally, 2-chloromethylpyridine possesses the advantages of being derived from a commercially available hydrochloride and of having a more reactive chlorine

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[18] (a) E. O. Fischer and K. Fichtel, *Ber.*, **94**, 1200 (1961); (b) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961); (c) R. B. King, *Inorg. Chem.*, **1**, 964 (1962).

[19] E. O. Fischer and K. Fichtel, *Ber.*, **95**, 2063 (1962).

[20] E. O. Fischer and E. Moser, *J. Organometal. Chem.*, **3**, 16 (1965).

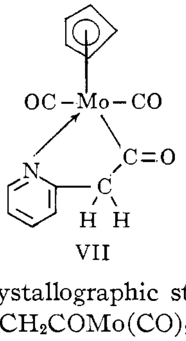
[21] E. O. Fischer and E. Moser, *Z. Naturforsch.*, **20b**, 184 (1965).

[22] The general subject of Lewis base–metal carbonyl complexes is reviewed by T. A. Manuel in "Advances in Organometallic Chemistry (F. G. A. Stone and R. West, Ed.)," Vol. 3, Academic Press, New York, N. Y., 1966. R. B. K. is indebted to Dr. Manuel for sending him a preprint of this article.

atom than the previously used 2-chloroethyl derivatives. The reactivity of the chlorine atom in 2-chloromethylpyridine was sufficient to react not only with the sodium salts $NaMn(CO)_5$ and $NaFe(CO)_2C_5H_5$ which also react with 2-chloroethyl methyl sulfide, 2-chloroethyldimethylamine, and N-2-chloroethylpiperidine, but also with the less reactive sodium salts $NaM(CO)_3C_5H_5$ (M = Mo or W) which do not react with the 2-chloroethyl derivatives.

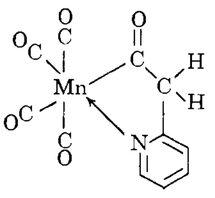
By reaction of 2-chloromethylpyridine with the appropriate sodium salts four substances of compositions $NC_5H_4CH_2Fe(CO)_2C_5H_5$, $NC_5H_4CH_2W(CO)_3C_5H_5$, $NC_5H_4CH_2COMo(CO)_2C_5H_5$, and $NC_5H_4CH_2COMn(CO)_4$ were obtained. The presence of strong acyl carbonyl bands in the 1600–1700 cm.$^{-1}$ region of the infrared spectrum of the molybdenum and manganese complexes indicates them to be the cyclic acyl derivatives VII and VIII, respectively. The absence of such acyl carbonyl bands in the infrared spectra of the iron and tungsten compounds indicates that the $NC_5H_4CH_2$ ligands in them are bonded to the metal atoms only with metal–carbon bonds.

Comparison of the proton n.m.r. spectra of these four compounds obtained from 2-chloromethylpyridine (Table II) is of interest. The chemical shifts of the methylene protons of the iron compound $NC_5H_4CH_2Fe(CO)_2C_5H_5$ and the tungsten compound $NC_5H_4CH_2W(CO)_3C_5H_5$ in which the methylene group is directly bonded to the metal atom are more than 1 p.p.m. upfield from those of the molybdenum and manganese compounds VII and VIII in which the methylene group is bonded to an acyl carbonyl group. The chemical shifts of the pyridine ring protons of the iron and tungsten compounds are similar to one another and very different from those of the pyridine ring protons of the molybdenum and manganese compounds VII and VIII. The chemical shifts of the pyridine ring protons of the latter two compounds VII and VIII are likewise very similar except for the curiously large difference of ~0.8 p.p.m. between the "*para*" protons of the two complexes. This suggests that the proton attached to the carbon atom opposite the nitrogen atom in the pyridine ring in $NC_5H_4CH_2COMo(CO)_2C_5H_5$ (VII) is located near enough to the π-cyclopentadienyl ring due to the relative orientations of the pyridine and cyclopentadienyl rings such that the chemical shift is raised ~0.8 p.p.m. by a "through space" shielding effect. An X-ray crystallographic study of the stereochemistry of $NC_5H_4CH_2COMo(CO)_2C_5H_5$ is required to establish this possibility more conclusively.



VII

The molybdenum derivative $NC_5H_4CH_2COMo(CO)_2C_5H_5$ (VII) and the tungsten derivative $NC_5H_4CH_2W(CO)_3C_5H_5$ are a particularly interesting pair. The two compounds are "isomers" except for the difference in the central metal atom—a minor difference since molybdenum and tungsten have the same number of outer "valence" electrons and generally exhibit similar chemical properties. The molybdenum compound appeared to be much less soluble in organic solvents than the tungsten compound—a fact reflected in the ability of the tungsten compound but the inability of the molybdenum compound to dissolve in cyclohexane sufficiently to obtain an infrared spectrum of the metal carbonyl region. The melting point of the molybdenum compound (146–150°) was significantly higher than that of the tungsten compound (113–114°), a reversal of the usual trends in the melting points of $RMo(CO)_3C_5H_5$ and the corresponding $RW(CO)_3C_5H_5$ derivatives (*e.g.*, $CF_3COMo(CO)_3C_5H_5$, m.p. 64–65°; $CF_3COW(CO)_3C_5H_5$, m.p. 80–82°).[23] Similar comparisons may be made in the melting points and solubilities of $NC_5H_4CH_2Fe(CO)_2C_5H_5$ and $NC_5H_4CH_2COMn(CO)_4$. All of these observations suggest that cyclic acyl derivatives such as VII and VIII are less soluble and higher melting than similar compounds with the organonitrogen ligand bonded to the metal atom only by a metal–carbon σ bond.



VIII

The tendency for metal carbonyl anions to form cyclic acyl derivatives on reaction with 2-chloromethylpyridine is directly related to the tendency for the acyl derivatives formed from the same metal carbonyl anions and acyl halides to undergo decarbonylation on heating or irradiation. Both of these tendencies are directly related to the strength of the metal–carbon monoxide bond in these compounds.[23] Thus $NaMn(CO)_5$ and $NaMo(CO)_3C_5H_5$, which form cyclic acyl derivatives with 2-chloromethylpyridine, react with acyl halides and related compounds such as trifluoroacetic anhydride to form acyl derivatives (*e.g.*, $CF_3COMn(CO)_5$ and $CF_3COMo(CO)_3C_5H_5$, respectively) which readily lose one mole of carbon monoxide on heating to ~80° to form the corresponding alkyl derivatives. Furthermore, $NaFe(CO)_2C_5H_5$, which does not form a cyclic acyl derivative with 2-chloromethylpyridine, reacts with acid halides and related compounds to form acyl derivatives $RCOFe(CO)_2C_5H_5$ which cannot be decarbonylated on mere heating but which can be decarbonylated on ultraviolet irradiation.[23] In this connection, ultraviolet irradiation of $NC_5H_4CH_2Fe(CO)_2C_5H_5$ did not convert it to a cyclic acyl derivative in significant quantities; however, some evidence for the formation of trace amounts of a

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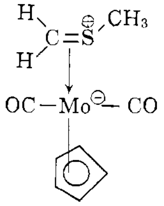
(23) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 15 (1964).

strongly adsorbed orange cyclic acyl derivative was observed during the chromatography of one preparation of $NC_5H_4CH_2Fe(CO)_2C_5H_5$. Finally, $NaW(CO)_3C_5H_5$, which does not form a cyclic acyl derivative with 2-chloromethylpyridine, reacts with acyl halides to form acyl derivatives of the type $RCOW(CO)_3C_5H_5$ which could be decarbonylated neither on heating below the decomposition temperature nor on irradiation at room temperature or slightly above.



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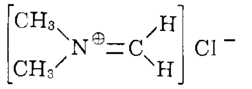

X

In our studies on organosulfur derivatives of metal carbonyls we investigated reactions between chloromethyl methyl sulfide and metal carbonyl anions.[2,3] These studies resulted in the discovery of unusual compounds such as $CH_3SCH_2Mo(CO)_2C_5H_5$ (IX) for which structures with a carbon–sulfur double bond π-bonded to a metal atom were proposed. Somewhat analogous to chloromethyl methyl sulfide is chloromethyldimethylamine. A material of composition $(CH_3)_2NCH_2Cl$ is known.[24] However, this material is an ionic nonvolatile solid in contrast to the volatile liquid CH_3SCH_2Cl and has the structure X containing a cation with a carbon–nitrogen double bond. A sample of this material was prepared and allowed to react with tetrahydrofuran solutions of the sodium salts $NaFe(CO)_2C_5H_5$ and $NaMo(CO)_3C_5H_5$. However, in both cases the corresponding coupling products $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Mo(CO)_3]_2$, respectively, instead of any $(CH_3)_2NCH_2$ metal complexes were the major metal carbonyl products obtained from these reactions. In the case of the reaction between $NaFe(CO)_2C_5H_5$ and $(CH_3)_2NCH_2Cl$ a small quantity of an unstable brown liquid possibly containing some $(CH_3)_2NCH_2Fe(CO)_2C_5H_5$ was observed; this was not studied in detail.

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(24) H. Böhme, W. Lehners, and G. Keitzer, *Ber.*, **91**, 340 (1958).

Contribution from the Mellon Institute,
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Organonitrogen Derivatives of Metal Carbonyls. II. Arylazo Derivatives of Molybdenum[1,2]

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Aryldiazonium tetrafluoroborates or hexafluorophosphates react with $NaMo(CO)_3C_5H_5$ in tetrahydrofuran solution to form the red compounds $RN_2Mo(CO)_2C_5H_5$ ($R = C_6H_5$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$O_2NC_6H_4$, and 1-$C_{14}H_7O_2N_2$). The p-tolyl derivative p-$CH_3C_6H_4N_2Mo(CO)_2C_5H_5$ reacts with triphenylphosphine or dimethyl disulfide with loss of metal carbonyl groups but preservation of the arylazo ligand to give red $(C_6H_5)_3PMoCO(N_2C_7H_7)C_5H_5$ or brown $[CH_3SMo(N_2C_7H_7)C_5H_5]_2$, respectively.

Formally low oxidation states of transition metals were first encountered in the metal carbonyls[3] and metal nitrosyls[4] over 75 years ago. Derivatives of these CO and NO^+ ligands[5] have frequently played an important role in the subsequent development of coordination chemistry. About 15 years ago the analogy between the carbonyl and aryl isocyanide groups was recognized[6] leading to the preparation of numerous RNC complexes analogous to well-established metal carbonyls.[7] Although aryl isocyanides did not stabilize extremely low oxidation states to the large extent of carbon monoxide,[8] stable zerovalent isocyanide derivatives such as $Cr(CNR)_6$ could be readily prepared.

The aryl isocyanide ligand, RNC, may be considered

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(1) For Part I of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 293 (1966).

(2) For a preliminary communication of some of this work see R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 5694 (1964).

(3) The first known metal carbonyl was $Ni(CO)_4$. See L. Mond, C. Langer, and F. Quincke, *J. Chem. Soc.*, **57**, 749 (1890).

(4) Probably the first known metal nitrosyls were the nitroprussides $M_2[Fe(CN)_5NO]$ prepared by Playfair in 1849. See N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford, London, 1950, pp. 1343–1346.

(5) The formal charge on ligands, especially those with strongly partial double bonding tendencies such as CO, NO, and C_nH_n ($n = 4, 5, 6, 7$, etc.), in transition metal complexes is often unclear. In particular, it is convenient to regard formally the nitrosyl ligand as NO^+ for development of the analogy between related transition metal nitrosyl and arylazo derivatives. We realize, of course, that in many metal nitrosyl derivatives the charge on the nitrosyl ligand will more closely approach NO^-; such compounds, however, may be regarded as NO^+ complexes where the nitrosyl group acquires a net negative charge by accepting electron density from the filled d orbitals of the transition metal atoms by means of partial metal–nitrogen double bonding. A similar effect is likely to occur in the arylazo compounds discussed in this paper.

(6) W. Hieber, *Z. Naturforsch.*, **5b**, 129 (1950).

(7) For a review of isocyanide complexes of metals see L. Malatesta, *Progr. Inorg. Chem.*, **1**, 284 (1959).

(8) For example, isocyanide analogs of the metal carbonyl anions with the metal in a negative oxidation state are unknown.