bonyls, the metal–carbon monoxide bonds are broken resulting in decomposition of the arylazo–metal carbonyls. We feel that this effect presents a severe impediment to the preparation of extensive series of arylazo–metal carbonyls.

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Notes

CONTRIBUTION FROM THE MELLON INSTITUTE,
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Organonitrogen Derivatives of Metal Carbonyls. III. Reactions between Metal Carbonyl Anions and Chloromethyl Isocyanate[1]

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Recently we reported reactions of metal carbonyl anions with haloalkyl sulfides[2] and haloalkyl amines.[3] We have now extended our studies of haloalkyl derivatives containing potentially reactive functional groups to chloromethyl isocyanate. This note describes the reactions of chloromethyl isocyanate with the sodium salts $NaFe(CO)_2C_5H_5$ and $NaMo(CO)_3C_5H_5$.

Experimental Section

The general techniques used for infrared spectra, proton n.m.r. spectra, elemental microanalyses, and molecular weight determinations were similar to those used for work described in previous papers.[1,2] As before tetrahydrofuran was freshly distilled over lithium aluminum hydride. 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 chloromethyl isocyanate, b.p. 81° (740 mm.), was prepared in 49% yield[4] by reaction between chloroacetyl chloride and sodium azide in triethylene glycol dimethyl ether[5] at ~25°. The preparations of the sodium salts $NaFe(CO)_2C_5H_5$ and $NaMo(CO)_3C_5H_5$ have been adequately described.[6,7]

Reaction between $NaMo(CO)_3C_5H_5$ and Chloromethyl Isocyanate.—A solution of 10 mmoles of $NaMo(CO)_3C_5H_5$ in 100 ml. of tetrahydrofuran was prepared from $[C_5H_5Mo(CO)_3]_2$ and dilute sodium amalgam. This solution was stirred ~16 hr. with 1.0 g. (10.9 mmoles) of chloromethyl isocyanate. Solvent was removed from the brownish reaction mixture at 25° (30 mm.). The residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at ~25° (30 mm.). The brown residue was extracted with 100 ml. of pentane in six portions and the filtered pentane extracts were cooled 16 hr. at −78°. Yellow crystals of $C_5H_5Mo(CO)_3CH_2NCO$ separated. These crystals were removed by filtration and recrystallized similarly from pentane to give 0.542 g. (18% yield) of yellow crystalline $C_5H_5Mo(CO)_3CH_2NCO$, m.p. 53–56°.

For the preparation of larger quantities of $C_5H_5Mo(CO)_3CH_2NCO$ a solution of 100 mmoles of $NaMo(CO)_3C_5H_5$ in 500 ml. of tetrahydrofuran prepared from hexacarbonylmolybdenum and a 20% excess of sodium cyclopentadienide was similarly allowed to react with 11.0 g. (121 mmoles) of chloromethyl isocyanate. The product was isolated by a procedure similar to that used for the smaller scale preparation cited above except that a mixture of pentane and diethyl ether rather then pure pentane was used for crystallizations in order to diminish the required amount of solvent. This larger scale preparation gave a total of 12.6 g. (42% yield) of $C_5H_5Mo(CO)_3CH_2NCO$ isolated in two crops.

When freshly recrystallized, $C_5H_5Mo(CO)_3CH_2NCO$ forms yellow crystals, which soon darken on standing. It can be sublimed at 100° (0.2 mm.). A 15% recovery of yellow-orange sublimate, m.p. 54–56°, is obtained, shown by its infrared and n.m.r. spectra to be unchanged $C_5H_5Mo(CO)_3CH_2NCO$.[8]

Anal. Calcd. for $C_{10}H_7MoNO_4$: C, 39.9; H, 2.3; N, 4.7; Mo, 31.9; O, 21.3. Found: C, 39.9; H, 2.2; N, 4.5; Mo, 32.7; O, 20.8.

Infrared Spectrum.[9]—ν_{CH} at 3050 (vw), 2870 (vvw), and 2820 (vvw) cm.$^{-1}$; ν_{CN} (isocyanate) at 2270 (s) cm.$^{-1}$; ν_{CO} (metal) at 2033 (m), 1959 (s), and 1950 (s) cm.$^{-1}$; other bands at 1460 (w), 1415 (w), 1225 (vw), 1142 (w), 1054 (w), 1005 (w), 1001 (w), 848 (w), 836 (m), 819 (m), and 812 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum (CS_2 Solution).—Singlet resonances at τ 4.57 and 6.31 of approximate relative intensities 5:2 due to the five π-cyclopentadienyl protons and the two methylene protons, respectively.

Reaction between $NaFe(CO)_2C_5H_5$ and Chloromethyl Isocyanate.—A solution of 50 mmoles of $NaFe(CO)_2C_5H_5$ in 150 ml. of tetrahydrofuran was treated dropwise with 4.5 g. (50 mmoles) of chloromethyl isocyanate. An exothermic reaction occurred with gas evolution. After stirring for ~16 hr. at room temperature solvent was removed at ~25° (30 mm.). The residue was extracted with five 75-ml. portions of dichloromethane, and solvent was removed from the filtered dichloromethane extracts leaving a brown residue. This residue was extracted with ~100 ml. of diethyl ether in four portions and the filtered diethyl ether solution chromatographed on a 2 × 50 cm. alumina column. Four bands were observed in the indicated order: yellow-orange (I), purple-brown (II), brown (III), and green-black (IV). The green-black band (IV) was so weak that it was not further investigated. The other three bands were eluted with diethyl

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[1] For Part II of this series see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966).

[2] R. B. King and M. B. Bisnette, *ibid.*, **4**, 486 (1965).

[3] R. B. King and M. B. Bisnette, Abstracts of Papers presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 43M; *Inorg. Chem.*, **5**, 293 (1966).

[4] G. Schroeter, *Ber.*, **42**, 3356 (1909).

[5] Triethylene glycol dimethyl ether, b.p. 216°, was used instead of the di-*n*-amyl ether, b.p. 188°, specified by Schroeter.[4]

[6] R. B. King, "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, and references cited therein.

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

[8] Other molybdenum complexes such as $C_3F_7COMo(CO)_3C_5H_5$ and $CH_3SCH_2Mo(CO)_3C_5H_5$ are decarbonylated under these conditions.[2,7]

[9] The metal carbonyl region of this infrared spectrum was taken in a cyclohexane solution and recorded on a Beckman IR-9 spectrometer with the scale expanded by a factor of 2.5. The remaining portion of this infrared spectrum was taken in a potassium bromide pellet and recorded on a Perkin-Elmer Model 21 spectrometer.

ether, and solvent was removed from the individual filtered eluates at 25° (30 mm.). The residue from the yellow-orange band (I) yielded 0.038 g. of yellow-orange crystals, m.p. 41–43°, after one low-temperature crystallization from pentane. The infrared spectrum and complete elemental analyses conclusively demonstrated this material *not* to be $C_5H_5Fe(CO)_2CH_2NCO$.[10] The residue from the purple-brown band (II) gave 0.864 g. (9.8% yield) of $[C_5H_5Fe(CO)_2]_2$[11] after washing with pentane. The residue from the brown band (III) gave 0.330 g. (3.8% yield) of brown $(C_5H_5)_3Fe_3(CO)_4CH_2NCO$, m.p. 159–162°, after washing four times with pentane.

Anal. Calcd. for $C_{21}H_{17}Fe_3NO_5$: C, 47.5; H, 3.2; N, 2.6; O, 15.1; Fe, 31.6; mol. wt., 531. Found: C, 47.8, 48.4; H, 3.1, 3.2; N, 2.4, 2.6; O, 16.1, 15.2; Fe, 30.9, 30.0; mol. wt., 524 (osmometer in benzene).

Infrared Spectrum.[9]—ν_{CH} at 3060 (vvw) cm.$^{-1}$; ν_{CN} (isocyanate) at 2120 (s) cm.$^{-1}$; ν_{CO} at 2023 (m), 1973 (m), and 1764 (m) cm.$^{-1}$; other bands at 1425 (m), 1415 (m), 1145 (sh), 1125 (w), 1053 (vw), 1005 (w), 860 (vw), 842–835 (w, br), and 820 (m) cm.$^{-1}$.

Proton N.m.r. Spectrum (CS_2 Solution).—Resonances at τ 5.15, 5.52, and 6.93 of approximate relative intensities 5:10:2 corresponding to the five protons of one π-cyclopentadienyl ring, the ten protons of the two remaining π-cyclopentadienyl rings, and the two methylene protons, respectively.

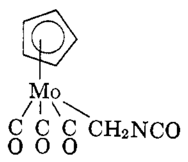
Conductivity.—The conductivity of a 3.7×10^{-4} *M* acetone solution of $(C_5H_5)_3Fe_3(CO)_4CH_2NCO$ was no higher than that of pure acetone.

Discussion

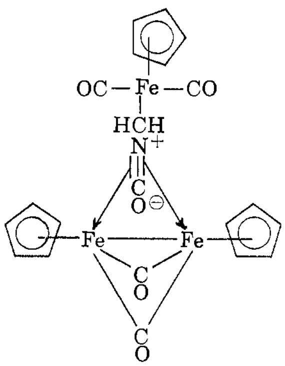
The properties of the complex $C_5H_5Mo(CO)_3CH_2NCO$ obtained from $NaMo(CO)_3C_5H_5$ and chloromethyl isocyanate are those expected for a material with the straightforward structure I completely analogous to numerous other known $RMo(CO)_3C_5H_5$ compounds. Like other such compounds it is yellow, volatile, rather low-melting, and soluble in nonpolar organic solvents. The metal carbonyl region of the infrared spectrum resembles that of other $RMo(CO)_3C_5H_5$ compounds; the n.m.r. chemical shift of the π-cyclopentadienyl protons and the n.m.r. equivalence of the methylene protons further support structure I. The strong band at 2270 cm.$^{-1}$ in the infrared spectrum of $C_5H_5Mo(CO)_3CH_2NCO$ may be assigned to the uncomplexed isocyanate group of structure I.[12]

Reactions which we carried out using $C_5H_5Mo(CO)_3CH_2NCO$ failed to yield any new well-defined organomolybdenum compounds. Upon sublimation at 100° (0.2 mm.) or ultraviolet irradiation in hexane solution $C_5H_5Mo(CO)_3CH_2NCO$ gave mixtures from which only $[C_5H_5Mo(CO)_3]_2$ and unchanged $C_5H_5Mo(CO)_3CH_2NCO$ could be isolated; no decarbonylated product such as the dicarbonyl $C_5H_5Mo(CO)_2CH_2NCO$ was observed. Boiling methanol reacted rapidly with $C_5H_5Mo(CO)_3CH_2NCO$ to give $[C_5H_5Mo(CO)_3]_2$.

The reaction between $NaFe(CO)_2C_5H_5$ and chloromethyl isocyanate failed to give a compound $C_5H_5Fe(CO)_2CH_2NCO$ analogous to $C_5H_5Mo(CO)_3CH_2NCO$ (I). The only observed product containing isocyanate groups was the unusual brown trinuclear complex $(C_5H_5)_3Fe_3(CO)_4(CH_2NCO)$ obtained in only ~3.8% yield.



I



II

The proton n.m.r. spectrum (Figure 1) of this unusual trinuclear iron complex exhibits three singlet resonances at τ 5.15, 5.52, and 6.93 of relative intensities 5:10:2. The first of these resonances may be assigned to the five equivalent protons of one of the three π-cyclopentadienyl rings, the second of these resonances may be assigned to the ten equivalent protons of the other two of the three π-cyclopentadienyl rings, and the third resonance to the two equivalent protons of the CH_2NCO group. It thus appears that two of the three cyclopentadienyl rings are equivalent but that the third ring is "unique."

The infrared spectrum of $(C_5H_5)_3Fe_3(CO)_4(CH_2NCO)$ in cyclohexane solution or in a potassium bromide pellet (Figure 1) exhibits bands at 2023 and 1973 cm.$^{-1}$ due to terminal metal carbonyl groups and at 1764 cm.$^{-1}$ due to bridging metal carbonyl groups. In addition, a strong band at 2120 cm.$^{-1}$ (halocarbon oil mull) is observed which may be assigned to the carbon–nitrogen multiple bond of the CH_2NCO group.[13] This

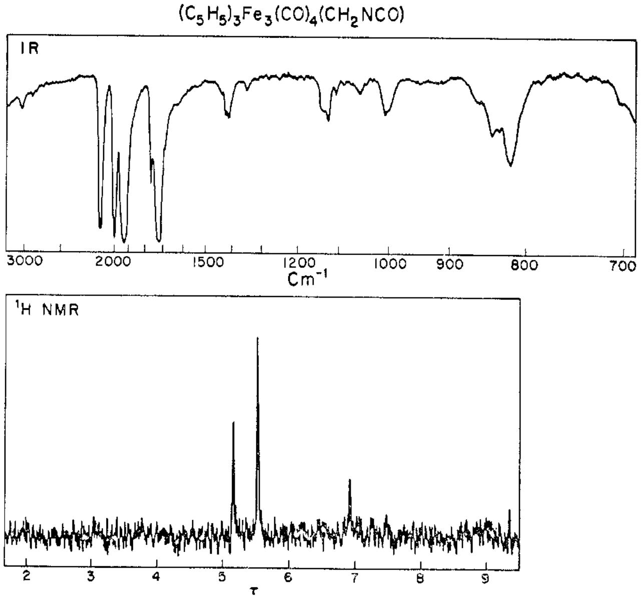


Figure 1.

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(10) Since this material represented less than 0.3% of the iron introduced into the reaction mixture, it was not investigated in detail.

(11) Additional $[C_5H_5Fe(CO)_2]_2$ appeared to be present in the residue from the diethyl ether extraction prior to chromatography.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 267, reports organic isocyanates to exhibit a very strong band at 2269 ± 6 cm.$^{-1}$.

(13) Some ν_{CO} bands in metal carbonyls may occur around 2120 cm.$^{-1}$. However, the presence of π-cyclopentadienyl rings lowers metal carbonyl frequencies to the extent that a band at 2120 cm.$^{-1}$ in a neutral *π-cyclopentadienyl* metal compound is unlikely to arise from a metal carbonyl group.

shift to lower frequencies of about 150 cm.$^{-1}$ in the position of ν_{CN} in $(C_5H_5)_3Fe_3(CO)_4(CH_2NCO)$ relative to $C_5H_5Mo(CO)_3CH_2NCO$ suggests that the isocyanate group in the iron complex is π-bonded to the iron atom.

A possible structure for $(C_5H_5)_3Fe_3(CO)_4(CH_2NCO)$ in agreement with these proton n.m.r. and infrared spectral data (Figure 1) and its negligible conductance is II. A key feature of this proposed structure II is an isocyanate group bridging between two metal atoms. In the indicated dipolar resonance structure the carbon–nitrogen triple bond is isoelectronic with the carbon–carbon triple bond in acetylenes which is known to act as a similar bridging group in compounds such as $(RC_2R)Co_2(CO)_6$[14] and $(RC_2R)[NiC_5H_5]_2$[15] obtained from acetylenes and $Co_2(CO)_8$ or $[C_5H_5NiCO]_2$, respectively.

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant No. AF-AFOSR-580-64. We are also indebted to Mr. A. Fronzaglia for taking many of the infrared spectra.

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Enneafluoro-2-(fluorosulfato)butane and Trifluoroacetyl Fluorosulfate

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The reactive compounds fluorine fluorosulfate (FSO_3F) and peroxodisulfuryl difluoride ($S_2O_6F_2$) have been used to prepare a variety of fluorosulfate-containing compounds.[1–6] Fluorine fluorosulfate has been shown to react with haloolefins by cleaving the oxygen–fluorine bond. In this manner, FSO_3F was added across the carbon–carbon double bonds of tetrafluoroethylene, tetrachloroethylene, and perfluorocyclopentene to form the corresponding perhalofluorosulfates.[2] Also, peroxodisulfuryl difluoride has been added across the carbon–carbon double bonds of perhaloolefins to yield bis(fluorosulfato)perhaloalkanes.[4–6] Hexafluoro-1,2-bis(fluorosulfato)propane is prepared in such a manner.[5] When this latter compound is heated to 60° in the presence of potassium fluoride, it undergoes a novel defluorosulfurylization reaction to give tetrafluoro-2-(fluorosulfato)propionyl fluoride. When other bis(fluorosulfato) compounds, such as tetrafluorobis(fluorosulfato)ethane, hexafluoro-1,2-bis(fluorosulfato)cyclobutane, and octafluoro-2,3-bis(fluorosulfato)butane are similarly treated, total decomposition to SO_2F_2, CO, CO_2, O_2, and fluorocarbons is observed.[5]

Peroxodisulfuryl difluoride reacts with halomethanes containing fluorine and also a different halogen (*e.g.*, chlorine or bromine) to form perfluoromethyl fluorosulfates.[6] In contrast, carbon tetrachloride and $S_2O_6F_2$ give carbonyl chloride.[4] However, when the halomethane contains three fluorine atoms, there appears to be greater resistance to oxygenation and fluorosulfation occurs (*e.g.*, with CF_3Cl and CF_3Br).[6] It might be expected, then, that trifluoroacetyl bromide, under controlled conditions, would undergo replacement of the relatively labile bromine atom in the presence of $S_2O_6F_2$ to yield the acyl fluorosulfate. This was found to be the case and is thought to be the first example of this type of fluorosulfate.

Experimental Section

Reagents.—Fluorine fluorosulfate and peroxodisulfuryl difluoride were prepared by the catalytic fluorination of sulfur trioxide in the presence of silver(II) fluoride at 225 and 155°, respectively.[7,8] Purity was checked by vapor density measurements and infrared spectra. A mixture of *cis*- and *trans*-perfluoro-2-butene was obtained from the Matheson Company, Inc., and was used without further purification. Trifluoroacetyl bromide was synthesized from trifluoroacetic acid and phosphorus tribromide. Alkali fluorides were anhydrous and of reagent grade quality.

Sulfur was determined as barium sulfate after basic hydrolysis with 0.1 *N* sodium hydroxide at 100° for 2 weeks. Fluorine was determined by a null-point potentiometric method after fusion with sodium metal at 300° for 24 hr.[9,10] Vapor densities were determined by using Regnault's method with a Pyrex glass flask of 254.4-ml. volume, equipped with a 1.25-mm. Teflon stopcock (Fischer and Porter Co.). Reaction products were separated by fractional codistillation,[11] and vapor pressure measurements were obtained through the use of an apparatus similar to that described previously.[12] Infrared spectra were obtained by using a Perkin-Elmer Model 137 Infracord spectrophotometer. Infrared cells were constructed of Pyrex glass with a 5-cm. path length and sodium chloride windows. Mass spectra were obtained with a Consolidated Engineering Corp. Type 21-103 mass spectrometer. Nuclear magnetic resonance spectra were recorded through the use of a Varian Model 4311 B high-resolution spectrometer.

Preparation of Enneafluoro-2-(fluorosulfato)butane.—A 5:1 mixture of *cis*- and *trans*-perfluoro-2-butene and dry nitrogen was placed in a 1-l. Pyrex glass reaction vessel which was equipped with a 1.25-mm. Teflon stopcock and which was surrounded by an ice bath. An equimolar quantity of fluorine fluorosulfate was slowly titrated into the vessel and a colorless liquid gradually collected on the bottom of the vessel. The reaction

$$C_4F_8 + FSO_3F \xrightarrow{3°} CF_3CF_2CF(SO_3F)CF_3$$

was rapid and exothermic. The yield of the reaction was about 91%, with only a small amount of unreacted C_4F_8 and SiF_4 found after separation by fractional codistillation.

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