Contribution from the Mellon Institute,
Pittsburgh, Pennsylvania

Organometallic Chemistry of the Transition Metals. XVIII. Some New Cyclopentadienylmetal Nitrosyl Derivatives of Manganese and Molybdenum[1]

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Ultraviolet irradiation of an aqueous solution containing both sodium nitrite and $[C_5H_5Mn(CO)_2NO][PF_6]$ gives black, crystalline $[C_5H_5Mn(NO)_2]_n$ ($n > 1$). Treatment of $C_5H_5Mo(CO)_2NO$ with iodine in dichloromethane solution gives brown-violet $[C_5H_5Mo(NO)I_2]_2$. This compound reacts with the ligands triphenylphosphine, triphenyl phosphite, and pyridine in dichloromethane solution to give red to brown, soluble, monomeric $C_5H_5Mo(NO)I_2L$ ($L = (C_6H_5)_3P$, $(C_6H_5O)_3P$, or C_5H_5N) and with 2,2′-bipyridyl to give orange, insoluble $C_5H_5Mo(NO)I_2N_2C_{10}H_8$.

A. The Compound $[C_5H_5Mn(NO)_2]_n$

Two polynuclear cyclopentadienylmanganese nitrosyls, $(C_5H_5)_3Mn_2(NO)_3$[3,4] and $(C_5H_5)_6Mn_6(NO)_8$,[4] are known. However, the monomeric $C_5H_5Mn(NO)_2$ isoelectronic with the known[5] $C_5H_5Co(CO)_2$ has not yet been reported. In an attempt to prepare $C_5H_5Mn(NO)_2$, the reaction between the $[C_5H_5Mn(CO)_2NO]^+$ cation and the nitrite anion was investigated. This section describes the black, crystalline product $[C_5H_5Mn(NO)_2]_n$ obtained from this reaction.

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer with sodium chloride optics. In addition, the metal nitrosyl stretching frequencies (1800–1500 cm^{-1}) were investigated in greater detail in Halocarbon oil mulls using a Beckman IR-9 spectrometer with grating optics. Ultraviolet spectra were taken in dichloromethane solution and recorded on a Cary Model 14 spectrometer. Proton nmr spectra were taken in acetone solutions and recorded on a Varian A-60 spectrometer. Mass spectra were taken at 70-ev electron energies on an Associated Electrical Industries MS-9 mass spectrometer. Conductivity measurements were carried out at room temperature on a conductivity bridge (Model RC-16B2) manufactured by Industrial Instruments, Inc., Cedar Grove, N. J.

A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions, (b) handling filtered solutions of organometallic compounds, and (c) admitting to evacuated vessels.

The preparation of $[C_5H_5Mn(CO)_2NO][PF_6]$ from $C_5H_5Mn(CO)_3$ (from the Ethyl Corp., New York, N. Y.) followed a procedure published previously.[4]

Preparation of $[C_5H_5Mn(NO)_2]_n$.—A solution of 7.0 g (100 mmoles) of sodium nitrite in 25 ml of water was added dropwise to 17.5 g (50 mmoles) of $[C_5H_5Mn(CO)_2NO][PF_6]$ in 200 ml of water. Vigorous foaming occurred. The mixture was exposed to intense (450-w input) ultraviolet irradiation for ~16 hr in a 1-l. glass flask. A large quantity of black precipitate separated. This precipitate was filtered, washed with two 50-ml portions of water and four 50-ml portions of methanol, and dried.

This black solid was extracted with four 50-ml portions of dichloromethane followed by three 40-ml portions of boiling chloroform. The black extracts were combined and filtered. Hexane (~40 ml) was added to the filtrate and solvent removed at ~25° (30 mm). The black solid which remained was washed with three 15-ml portions of pentane and dried. The black solid thus obtained was recrystallized twice from a mixture of dichloromethane and hexane to give 0.51 g (5.7% yield) of black solid $[C_5H_5Mn(NO)_2]_n$.

Anal. Calcd for $C_5H_5N_2O_2Mn$: C, 33.3; H, 2.8, N, 15.6; O, 17.8; Mn, 30.5. Found: C, 33.3; H, 3.0; N, 15.3; O, 18.1; Mn, 30.2.

Infrared Spectrum.—ν_{CH} at 3070 (w) cm^{-1}; ν_{NO} (terminal) at 1760 (vs) cm^{-1}; ν_{NO} (bridging) at 1525 (vs) cm^{-1}; other bands at 1417 (m), 1387 (s), 1377 (s), 1352 (w), 1305 (s), 1113 (w), 1053 (w), 1010 (m, br), 934 (vw), 825 (s), 810 (s), 722 (s), 706 (s), and 704 (s) cm^{-1}.

Proton Nmr Spectrum.—Broad, barely detectable resonance at τ ~4.6 in acetone solution was due to the equivalent π-cyclopentadienyl protons.

Discussion

Analogy with the chemistry of related metal π-cyclopentadienyl, nitrosyl, and carbonyl derivatives would suggest $C_5H_5Mn(NO)_2$ to be a monomer (I) closely analogous in properties and structure to $C_5H_5Co(CO)_2$. However, the material described above having the composition $[C_5H_5Mn(NO)_2]_n$ clearly cannot be monomeric for the following reasons.

(a) Attempted molecular weight determinations in solution always yield values at least twice that expected for the simple formula $C_5H_5Mn(NO)_2$.

(b) The presence of bridging nitrosyl groups indicated by a very strong infrared band at 1525 cm^{-1} requires at least two manganese atoms.

(c) The solid manganese compound $[C_5H_5Mn(NO)_2]_n$ is insoluble in nonpolar organic solvents such as pentane or hexane and only sparingly soluble in polar organic solvents such as dichloromethane. By contrast, the isoelectronic liquid $C_5H_5Co(CO)_2$ is readily miscible with both nonpolar and polar organic solvents.

(d) The manganese compound $[C_5H_5Mn(NO)_2]_n$ is nonvolatile whereas $C_5H_5Co(CO)_2$ can be distilled at ~50° (2 mm).

The nonvolatility of $[C_5H_5Mn(NO)_2]_n$ prevents observing its mass spectrum. When such an attempt is made, the major ions are $(C_5H_5)_2MnH^+$ and $C_5H_nMn^+$ (n = 3, 4, and 5) indicative of drastic decomposition upon attempted vaporization. Thus establishment of n must rely on determinations of the molecular weight

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(1) For part XVII of this series see R. B. King, *Inorg. Chem.*, **5**, 2231 (1966).

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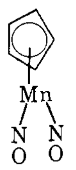
(3) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

(4) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

(5) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955); E. O. Fischer and R. Jira, *Z. Naturforsch.*, **10b**, 355 (1955).

by measurements in solutions. Such determinations using the Mechrolab osmometer have been inconclusive giving values ranging from 350 to 1200. The presence of both terminal and bridging metal nitrosyl groups as indicated by the infrared spectrum and the tendency for manganese atoms to acquire the favored rare gas configuration suggests structure II with two terminal and two bridging nitrosyl groups and no manganese-manganese bond for $[C_5H_5Mn(NO)_2]_2$. Related structures (*e.g.*, III for the trimer $[C_5H_5Mn(NO)_2]_3$) are also possible for $[C_5H_5Mn(NO)_2]_n$ species of higher molecular weight (*i.e.*, $n > 2$).



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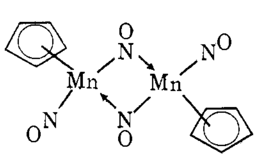

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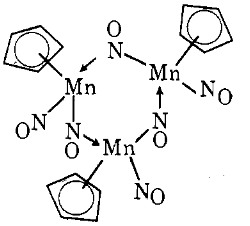

III

The tendency for the species $C_5H_5Mn(NO)_2$ with the favored rare gas configuration to oligomerize and possibly polymerize[6] is entirely novel, since published data on metal nitrosyls do not suggest similar behavior for other systems. However, if one adopts the generally accepted view[7] that the π-C_5H_5 ligand occupies three coordination positions, then the manganese atom in monomeric $C_5H_5Mn(NO)_2$ (I) has a coordination number of five. If two or more molecules of $C_5H_5Mn(NO)_2$ combine to form oligomers such as II and III by conversion of half of the nitrosyl groups to bridging nitrosyl groups, then each manganese atom has the more favored coordination number of six. The tendency for a five-coordinate species to become a more favored six-coordinate species thus may account for the oligomerization and possibly polymerization tendencies of $C_5H_5Mn(NO)_2$.

Another cyclopentadienylmetal nitrosyl derivative isoelectronic with $C_5H_5Co(CO)_2$ is the iron compound $C_5H_5Fe(CO)(NO)$. Attempts to prepare this compound or an oligomer thereof by ultraviolet irradiation of an aqueous solution containing $[C_5H_5Fe(CO)_3][HCl_2]$ and sodium nitrite gave a low yield of a brown material exhibiting metal carbonyl and nitrosyl stretching frequencies at 2040, 1990, 1940, 1765, 1740, and 1710 cm^{-1}. The low yield and difficulties in separating this material from the $[C_5H_5Fe(CO)_2]_2$ also formed in the reaction have prevented a detailed characterization of this material.

B. Preparation and Reactions of $[C_5H_5Mo(NO)I_2]_2$

Recently the monomeric cyclopentadienylmetal dicarbonyls $C_5H_5M(CO)_2$ (M = Co or Rh) have been shown to react with iodine to give $C_5H_5M(CO)I_2$ (M = Co or Rh).[8–10] The reaction of the likewise monomeric cyclopentadienylmetal nitrosyl carbonyl $C_5H_5Mo(CO)_2NO$ with iodine is now described.

Experimental Section

The $C_5H_5Mo(CO)_2NO$ required for this work was obtained by several preparative methods from commercial $Mo(CO)_6$ (Climax Molybdenum Co., New York, N. Y.). None of these methods has yet been developed into a reliable, well-defined, and efficient synthesis.[11] The freshly sublimed bright orange crystals on storage become brown and develop an odor of oxides of nitrogen after several days or weeks.

Procedures for carrying out microanalyses, taking infrared and nmr spectra, and making conductivity mesurements have already been discussed in part A. Microanalyses and yields of all new cyclopentadienylmolybdendum nitrosyl derivatives are given in Table I; their infrared spectra are given in Table II.

Preparation of $[C_5H_5Mo(NO)I_2]_2$.—Filtered solutions of 4.0 g (16.2 mmoles) of $C_5H_5Mo(CO)_2NO$ in 100 ml of dichloromethane and of 4.0 g (15.7 mmoles) of iodine in 250 ml of dichloromethane were mixed under nitrogen. Vigorous gas evolution occurred immediately. After 20 hr the purple crystalline precipitate was filtered, washed with $\sim$100 ml of dichloromethane in several portions, and dried to give 5.68 g (81% yield) of purple $[C_5H_5Mo(NO)I_2]_2$.

Reactions of $[C_5H_5Mo(NO)I_2]_2$ with Lewis Bases.—A mixture of 0.5 g (0.56 mmoles) of $[C_5H_5Mo(NO)I_2]_2$, about 0.4 g (excess in all cases) of the Lewis base ligand (triphenylphosphine, triphenyl phosphite, pyridine, or 2,2′-bipyridyl), and 50 ml of dichloromethane was stirred at room temperature. In all cases the reaction appeared to be complete within about 1 hr, but, to ensure completeness, the reaction mixtures were stirred 16–20 hr.

In the case of the reaction with 2,2′-bipyridyl, the orange product precipitated from the dichloromethane solution as the $[C_5H_5Mo(NO)I_2]_2$ dissolved. The product was filtered, washed with two 20-ml portions of dichloromethane and two 20-ml portions of acetone, and dried. It appeared to be completely insoluble in all of the usual organic solvents.

In the other cases (triphenylphosphine, triphenyl phosphite, and pyridine) the dichloromethane-insoluble $[C_5H_5Mo(NO)I_2]_2$ soon dissolved to form a red (R_3P) or brown (pyridine) solution. After the reaction period was over, the reaction mixture was filtered by gravity and solvent was removed from the filtrate at $\sim$25° (30 mm). The solid residue was washed with diethyl ether. The resulting crystals of the $C_5H_5Mo(NO)I_2L$ compound were recrystallized once or twice from mixtures of dichloromethane and hexane and washed with pentane.

The following Lewis bases failed to give pure crystalline compounds from the above procedure: (a) Tris(dimethylamino)-phosphine: a viscous red-brown liquid was obtained which could not be crystallized. (b) Aniline: a brown liquid was obtained which could not be crystallized. Upon standing in the air for 2 months it solidified, but the crystals were mostly insoluble in dichloromethane. (c) Acetonitrile (used as a solvent instead of dichloromethane): a low yield of purple dichloromethane-insoluble solid was obtained. (d) 1,2-Bis(diphenylphosphino)-ethane: red-brown crystals were observed (ν_{NO} 1663 cm^{-1}) which could not be obtained pure since impurities with similar solubility properties were present.

Conductivity Measurements. A. $C_5H_5Mo(NO)I_2P(C_6H_5)_3$.—

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(6) In the $[C_5H_5Mn(NO)_2]_n$ preparation, much black, dichloromethane-insoluble material was formed which might contain polymers with higher values of n.

(7) For discussions of the bonding in the π-cyclopentadienyl derivatives see G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959), and references cited therein.

(8) R. B. King, *Z. Naturforsch.*, **19b**, 1160 (1964).

(9) R. F. Heck, *Inorg. Chem.*, **4**, 855 (1965).

(10) R. B. King, *ibid.*, **5**, 82 (1966).

(11) Most of the $C_5H_5Mo(CO)_2NO$ used in this work was obtained by reaction in tetrahydrofuran of $NaMo(CO)_3C_5H_5$ with acetic acid and N-nitrosyl-N-methyl-*p*-toluenesulfonamide (yield $\sim$60% based on $Mo(CO)_6$), a modification of the procedure reported by T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956). Other less satisfactory methods include: (a) reaction of $NaMo(CO)_3C_5H_5$ with trifluoroacetyl nitrite in 1,2-dimethoxyethane (yield 10%); (b) reaction of $NaMo(CO)_3C_5H_5$ with acetic acid and potassium nitrite in water (yield 15–25%); and (c) reaction of $NaMo(CO)_3C_5H_5$ with nitric oxide in water (yield 30%), a modification of the preparation reported by E. O. Fischer, O. Beckert, W. Hafner, and H. O. Stahl, *Z. Naturforsch.*, **10b**, 598 (1955).

Table I

$C_5H_5Mo(NO)I_2$ Derivatives

Compound	Preparation	Yield, %	Color (solid) and mp, °C	Analyses, %							Mol wt[a]
					C	H	I	N	P or O	Mo	
$[C_5H_5Mo(NO)I_2]_2$	$C_5H_5Mo(CO)_2NO$	81	Brown-violet	Calcd	13.5	1.1	57.1	3.1	3.6 (O)	21.6	
	+ I_2		>250 dec	Found	13.4	1.1	57.1	3.2	3.5 (O)	21.6	
$C_5H_5Mo(NO)I_2P(C_6H_5)_3$	$[C_5H_5Mo(NO)I_2]_2$	81	Red	Calcd	39.0	2.8	35.9	2.0	4.4 (P)	13.6	707
	+ $(C_6H_5)_3P$		193–194 dec	Found	38.9	2.8	36.4	1.9	4.4 (P)	13.9	572
$C_5H_5Mo(NO)I_2P(OC_6H_5)_3$	$[C_5H_5Mo(NO)I_2]_2$	60	Red	Calcd	36.6	2.6	33.6	1.8	4.1 (P)	12.7	755
	+ $(C_6H_5O)_3P$		138–141 dec	Found	36.5	2.5	34.5	2.2	3.9 (P)	13.2	535
$C_5H_5Mo(NO)I_2NC_5H_5$	$[C_5H_5Mo(NO)I_2]_2$	91	Brown	Calcd	22.9	1.9	48.5	5.3	3.0 (O)	18.3	
	+ pyridine		>160 dec	Found	22.7	1.8	48.6	5.3	3.1 (O)	18.4	
$C_5H_5Mo(NO)I_2N_2C_{10}H_8$	$[C_5H_5Mo(NO)I_2]_2$	88	Orange	Calcd	29.9	2.2	42.3	7.0	2.7 (O)	16.0	
	+ 2,2′-bipyridyl		>250 dec	Found	29.2	1.9	42.3	7.1	3.3 (O)	15.9	

[a] Mechrolab vapor pressure osmometer in benzene solution.

Table II

Infrared Spectra of $C_5H_5Mo(NO)I_2$ Derivatives (cm^{-1})

Compound	ν_{CH}[a]	ν_{NO}[b]	Other bands[a]
$[C_5H_5Mo(NO)I_2]_2$	3060 w	1670 s	1550 vw, 1428 vw, 1410 w, 1362 vw, 1350 vw, 1111 vw, 1058 vw, 1015 vw, 886 w, 816 m, 805 w
$C_5H_5Mo(NO)I_2P(C_6H_5)_3$	3040 vw	1660 s	1574 w, 1473 w, 1430 m, 1303 vw, 1175 w, 1150 m, 1112 m, 1085 m, 1061 w, 1017 w, 994 w, 919 vw, 856 vw, 844 w, 815 m, 745 m, 719 m, 690 m
$C_5H_5Mo(NO)I_2P(OC_6H_5)_3$	3020 w	1679 s	1576 m, 1480 s, 1448 w, 1429 vw, 1409 w, 1280 vw, 1200 m, 1174 s, 1150 s, 1064 w, 1020 m, 1006 w, 1001 w, 915 m, 816 w, br, 766 m, br, 710 w, br, 684 m
$C_5H_5Mo(NO)I_2NC_5H_5$	3050 w	1661 s	1595 m, 1476 w, 1440 s, 1416 m, 1345 w, 1226 w, 1205 w, 1141 vw, 1080 w, 1062 w, 1018 w, 1010 w, 994 vw, 930 vw, 873 w, 853 m, 818 s, 753 m, 684 m
$C_5H_5Mo(NO)I_2N_2C_{10}H_8$	3000 m	1674 s	1590 m, 1547 vw, 1492 w, 1464 m, 1433 m, 1420 m, 1306 m, 1265 w, 1230 w, 1212 w, 1168 w, 1149 w, 1112 w, 1100 w, 1062 w, 1038 w, 1022 w, 1005 m, 998 w, 841 m, 828 m, 800 w, 769 m, 762 m, 719 m

[a] KBr pellet, Perkin-Elmer Model 21 spectrometer, NaCl optics. [b] Halocarbon oil mull, Beckman IR-9 spectrometer, grating optics.

A molar conductance of 19 ± 2 ohm^{-1} cm^2 mole^{-1} was obtained for acetone solutions in the concentration range 0.0004–0.0009 *M*.

B. $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$.—A molar conductance of 28 ± 5 ohm^{-1} cm^2 mole^{-1} was obtained for acetone solutions in the concentration range 0.0003–0.0008 *M*.

C. $C_5H_5Mo(NO)I_2NC_5H_5$.—A molar conductance of 97 ± 13 ohm^{-1} cm^2 mole^{-1} was obtained for acetone solutions in the concentration range 0.0004–0.0016 *M*.

Ultraviolet and Visible Spectra. A. $C_5H_5Mo(NO)I_2P(C_6H_5)_3$.—A maximum was observed at 516 mμ (2200) in a dichloromethane solution (pale red).

B. $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$.—No definite maxima were observed in the region 230–800 mμ in a dichloromethane solution (pale red-brown).

C. $C_5H_5Mo(NO)I_2NC_5H_5$.—Maxima were observed at 241 mμ (29,000) and 296 mμ (10,400) in a dichloromethane solution (yellow-brown).

Proton Nmr Spectra. A. $C_5H_5Mo(NO)I_2P(C_6H_5)_3$.—Resonances at τ 2.41 (apparent single broadened at base) and τ 3.72 (singlet) of approximate relative intensities 3:1 in acetone solution due to the fifteen phenyl protons and the five π-cyclopentadienyl protons, respectively.

B. $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$. Isomer A.—Fifteen phenyl protons at τ 2.69 (singlet) and five cyclopentadienyl protons at τ 3.88 (doublet, J = 3 cps) in acetone solution.

Isomer B.—Fifteen phenyl protons at τ 2.69 (singlet) and five cyclopentadienyl protons at τ 3.69 (singlet) in acetone solution.

C. $C_5H_5Mo(NO)I_2NC_5H_5$.—Barely identifiable resonances at τ ~2.4 (very broad) and τ 3.62 (broad singlet?) of approximate relative intensities 1:1 in acetone solution due to the five pyridine protons and the five π-cyclopentadienyl protons, respectively.

Discussion

If the reaction of iodine with $C_5H_5Mo(CO)_2NO$ were analogous to that of iodine with $C_5H_5Co(CO)_2$, the product would be $C_5H_5Mo(CO)(NO)I_2$ with one carbonyl group and one nitrosyl group. The purple product obtained from the reaction between iodine and $C_5H_5Mo(CO)_2NO$ actually has the composition $C_5H_5Mo(NO)I_2$. The absence of carbonyl groups but the presence of a nitrosyl group indicated by analyses is confirmed by the infrared spectrum which exhibits no metal carbonyl stretching frequencies but a strong metal nitrosyl stretching frequency at 1670 cm^{-1}.

A monomeric product of formula $C_5H_5Mo(NO)I_2$ contains a molybdenum atom with two electrons less than the favored rare gas configuration. However, the compound is diamagnetic ($\chi^{23°} = -68.6 \times 10^{-6}$ cm^3/Mo atom)[12] suggesting that the molybdenum atom attains the rare gas configuration by oligomerization probably by formation of iodine bridges. The complete insolubility of $C_5H_5Mo(NO)I_2$ in noncoordinating organic solvents, even dichloromethane, suggests a formulation with more than one molybdenum atom. Unfortunately, this same insolubility prevents determination of the molecular weight in solution by vapor pressure osmometry or other techniques.

The mass spectrum of $C_5H_5Mo(NO)I_2$ exhibited the ions $(C_5H_5)_2Mo_2(NO)_2I_2^+$, $(C_5H_5)_2Mo_2(NO)I_2^+$, $C_5H_5Mo(NO)I_2^+$, $C_5H_5MoI_2^+$, MoI_2^+, $C_5H_5MoI^+$, MoI^+, $C_5H_5Mo(NO)I_2^{2+}$, and $C_5H_5Mo^+$ listed here in descending *m/e*.[13] The presence in significant quantities of

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[12] This magnetic susceptibility measurement was carried out at 23° on a Faraday balance.

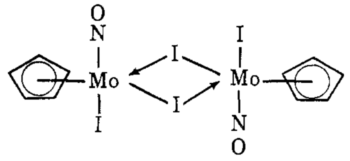
[13] Because of the presence of several stable isotopes in natural molybdenum and iodine in appreciable quantities, each ion actually consists of several lines. Furthermore, the presence of different numbers of molybdenum and iodine atoms in the various observed ions makes even a relative intensity comparison difficult.

the ions $(C_5H_5)_2Mo_2(NO)_2I_2^+$ and $(C_5H_5)_2Mo_2(NO)I_2^+$ with two molybdenum atoms suggests that this cyclopentadienylmolybdenum nitrosyl diiodide is the dimer $[C_5H_5Mo(NO)I_2]_2$. However, the presence of much $C_5H_5Mo(NO)I_2^+$ and no $[C_5H_5Mo(NO)I_2]_2^+$ in the mass spectrum suggests that the binuclear $[C_5H_5Mo(NO)I_2]_2$ is readily converted to the mononuclear $C_5H_5Mo(NO)I_2$ system on vaporization or ionization.

Analogy with known metal carbonyl halide chemistry and the absence of bridging nitrosyl stretching frequencies suggest formulation of $C_5H_5Mo(NO)I_2$ as the dimer IV with iodine bridges. If this is the case, the reaction between $C_5H_5Mo(CO)_2NO$ and iodine can be considered as proceeding by the two steps

$$C_5H_5Mo(CO)_2NO + I_2 \longrightarrow C_5H_5Mo(CO)(NO)I_2 + CO\uparrow \quad (1)$$

$$2C_5H_5Mo(CO)(NO)I_2 \longrightarrow [C_5H_5Mo(NO)I_2]_2 + 2CO\uparrow \quad (2)$$



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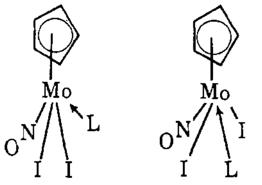

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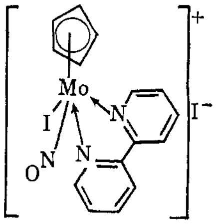

VI

The first step is entirely analogous to the formation of $C_5H_5Co(CO)I_2$ from iodine and $C_5H_5Co(CO)_2$,[8-10] the formation of $Fe(CO)_4I_2$ from iodine and $Fe(CO)_5$,[14] the formation of $[W(CO)_4I_3]^-$ from iodine and $[W(CO)_5I]^-$,[15] and the formation of $C_4H_{10}S_2M(CO)_3I_2$ (M = Mo or W) from iodine and $C_4H_{10}S_2M(CO)_4$ (M = Mo or W).[16] The second step is entirely analogous to the formation of $[Mn(CO)_4X]_2$ from $Mn(CO)_5X$ (X = Cl, Br, or I)[17] or to the formation of $[C_3F_7Fe(CO)_3X]_2$ from $C_3F_7Fe(CO)_4X$.[18]

Halogen bridges in compounds related to $[C_5H_5Mo(NO)I_2]_2$ (*e.g.*, $[Mn(CO)_4X]_2$,[17] $[Ru(CO)_2X_2]_n$,[19] or $[M(NO)_2Cl_2]_n$ (M = Mo or W)[20]) are readily broken by reactions with Lewis base ligands to form monomeric substitution products. Thus the reaction between $[C_5H_5Mo(NO)I_2]_2$ and Lewis bases to give monomeric compounds of the type $C_5H_5Mo(NO)I_2L$ (V, L = $(C_6H_5)_3P$, $(C_6H_5O)_3P$, or C_5H_5N) has ample precedent. In accord with their monomeric, basically nonionic nature, these $C_5H_5Mo(NO)I_2L$ compounds are more soluble than $[C_5H_5Mo(NO)I_2]_2$, dissolving readily in dichloromethane to form red to brown solutions.

The conductivities of the $C_5H_5Mo(NO)I_2L$ (L = $(C_6H_5)_3P$, $(C_6H_5O)_3P$, or C_5H_5N) compounds in acetone solutions are intermediate between those expected for a completely nonionic and a completely ionic compound. This suggests that these basically nonionic compounds may dissociate to a limited extent through the following equilibrium involving 1 mole of the solvent

$$C_5H_5Mo(NO)I_2L + OC(CH_3)_2 \rightleftarrows [C_5H_5Mo(NO)(I)(L)OC(CH_3)_2]^+I^-$$

Varying degrees of ionization by means of this equilibrium may account for the widely different conductivities of the $C_5H_5Mo(NO)I_2L$ derivatives where L is triphenylphosphine, triphenyl phosphite, or pyridine.

Attempted molecular weight determinations in benzene solution on the readily soluble compounds $C_5H_5Mo(NO)I_2L$ (L = $(C_6H_5)_3P$ and $(C_6H_5O)_3P$) gave experimental values 70–80% of the calculated values (Table I). This discrepancy, well outside the experimental error, suggests dissociation in solution according to the general scheme[21]

$$C_5H_5Mo(NO)I_2L \rightleftarrows C_5H_5Mo(NO)I_2 + L$$

Thus the formation of $C_5H_5Mo(NO)I_2L$ compounds from $[C_5H_5Mo(NO)I_2]_2$ and appropriate ligands appears to be a reversible reaction.

Two isomers of $C_5H_5Mo(NO)I_2L$ compounds (Va and Vb) are possible depending upon the relative orientations of the various ligands. The proton nmr spectra of the pyridine and triphenylphosphine complexes failed to suggest the presence of more than one isomer. However, the triphenyl phosphite complex $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$ exhibited two π-cyclopentadienyl resonances—one a doublet at τ 3.88 and the other a singlet at τ 3.69. It thus appears that both isomers Va and Vb (L = $(C_6H_5O)_3P$) are present in $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$. Only one phenyl resonance (at τ 2.69) was observed in $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$. However, the chemical shift difference of the phenyl protons in the isomers Va and Vb is expected to be less than the chemical shift differences between the individual phenyl protons in different positions (*ortho*, *meta*, or *para*) relative to the phosphite oxygen atom. Since in the $C_5H_5Mo(NO)I_2L$ compounds even the different phenyl protons of the ligand are not separated in the nmr spectrum, it is scarcely surprising that the *phenyl* protons of the different isomers Va and Vb are likewise not separated in the nmr spectra.

Geometrical isomerism entirely analogous to that suggested for $C_5H_5Mo(NO)I_2P(OC_6H_5)_3$ has been previously[22] found for the tris(dimethylamino)phosphine complex $C_5H_5Mo(CO)_2IP[N(CH_3)_2]_3$. Both of

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[14] W. Hieber and G. Bader, *Ber.*, **61**, 1717 (1928).

[15] R. B. King, *Inorg. Chem.*, **3**, 1039 (1964).

[16] H. C. E. Mannerskantz and G. Wilkinson, *J. Chem. Soc.*, 4454 (1962).

[17] E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *ibid.*, 3149 (1958); E. W. Abel and G. Wilkinson, *ibid.*, 1501 (1959).

[18] R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3604 (1961).

[19] R. J. Irving, *J. Chem. Soc.*, 2879 (1956).

[20] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).

[21] The alternative possibility of dissociation of these $C_5H_5Mo(NO)I_2L$ compounds by ionization with loss of I^- in benzene solutions (as suggested above for acetone solutions) cannot be completely excluded. However, the low dielectric constant of benzene (2.3) as compared with acetone (21) makes ionization in benzene unlikely.

[22] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

these compounds are similar stereochemically containing, besides the π-cyclopentadienyl ligand, four monodentate ligands of three different types. In both compounds one isomer exhibits a singlet π-cyclopentadienyl resonance and the other isomer a doublet (J = 3 cps) π-cyclopentadienyl resonance. In the latter case the doublet arises by coupling of the ^{31}P nucleus ($I = {}^1/_2$) of the tricovalent phosphorus ligand with the π-cyclopentadienyl protons.

The complex obtained from $[C_5H_5Mo(NO)I_2]_2$ and 2,2′-bipyridyl is different from the other $C_5H_5Mo(NO)I_2L$ complexes in being completely insoluble in organic solvents including acetone and dichloromethane. This insolubility suggests that this dipyridyl compound, although possessing the composition $C_5H_5Mo(NO)I_2L$, has a different structure. The most likely possibility may be an ionic formulation VI analogous to the ionic compound $[C_5H_5CoIN_2C_{10}H_8]I$ obtained from $C_5H_5Co(CO)I_2$ and 2,2′-bipyridyl.[9,10]

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1,1,1,5,5,5-Hexafluoropentane-2,4-dionato Complexes of Manganese(I) Containing Various Monodentate Ligands[1]

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1,1,1,5,5,5-Hexafluoropentane-2,4-dionatotetracarbonylmanganese(I) reacts readily with several phosphites and tertiary phosphines (L) to yield the dicarbonyl derivatives $Mn(CO)_2L_2(CF_3C(O)CHC(O)CF_3)$. It is inferred from the infrared and proton magnetic resonance spectra that the carbonyl groups are *cis* and the phosphorus-containing ligands are *trans* in these complexes. With L being pyridine, 4-methylpyridine, triphenylarsine, and tricyclohexylphosphine, only the tricarbonyls *cis*-$Mn(CO)_3L(CF_3C(O)CHC(O)CF_3)$ are obtained. No substitution is effected by diethyl sulfide, thiourea, and triphenylstibine. These replacement reactions are discussed in terms of π bonding, base strength, and steric requirements of the ligands, both entering and those already present in the complex. Several of the above compounds, plus the unusual pyridine tricarbonyl $Mn(CO)_3(C_5H_5N)_2(CF_3C(O)C{=}C(OH)CF_3)$, can be prepared by the interaction of $Mn(CO)_3L_2Cl$ or $Mn(CO)_4LCl$ with thallium(I) 1,1,1,5,5,5-hexafluoropentane-2,4-dionate. The metal carbonyl stretching frequencies and the chemical shifts of the ring proton in various derivatives are tabulated and discussed. The latter appear to depend, *inter alia*, on the basicity of L and on the presence of phenyl groups attached to the phosphorus-donor atoms.

Introduction

The synthesis of hexafluoroacetylacetonatotetracarbonylmanganese(I), $Mn(CO)_4$(hfac), was reported recently.[2] This complex represents the first example of a neutral manganese(I) tetracarbonyl which contains two "hard"[3] donor atoms coordinated to the metal. All previous attempts at the preparation of such derivatives had been unsuccessful; for example, $Mn(CO)_5Cl$ reacts rapidly with a number of organic amines to yield compounds of the type *cis*-$Mn(CO)_3L_2Cl$ (L = amine), no $Mn(CO)_4LCl$ having been detected.[4]

The presence of two equivalent "hard" oxygens in conjunction with the "soft" carbonyls in $Mn(CO)_4$(hfac) raises an interesting question with regard to the ease of replacement of the CO's by various monodentate ligands as well as to the composition and the stereochemistry of the resultant derivatives.

To elucidate this problem a study was undertaken on reactions of $Mn(CO)_4$(hfac) with several nucleophiles having phosphorus, nitrogen, sulfur, arsenic, or antimony as the donor atom. Reported here are the results of this investigation.

Experimental Section

Materials.—Trimethyl phosphite, tri-*n*-butyl phosphite, triphenyl phosphite, triphenylstibine, thiourea, and diethyl sulfide were purchased from Matheson Coleman and Bell, whereas triphenylarsine and 4-methylpyridine were obtained from Eastman Organic Chemicals. They were not purified further. Triphenylphosphine and tri-*n*-butylphosphine were supplied by Metal and Thermit Co. The former was recrystallized from ethanol. 1,1,1,5,5,5-Hexafluoropentane-2,4-dione was obtained from Columbia Organic Chemicals Co. It was washed with twice its volume of concentrated sulfuric acid and distilled immediately before use. The phosphines $P(C_6H_5)(CH_3)_2$ and $P(C_6H_5)_2(CH_3)$ were prepared as described in the literature.[5] Tricyclohexylphosphine was a gift from Professor F. Basolo of Northwestern University. Other chemicals and solvents used were reagent grade, except low-boiling (30–60°) petroleum ether and hexane. Woelm alumina (neutral), Florisil (60–100 mesh), and cellulose powder (Whatman, 200 mesh) were employed in chromatographic separations and/or purifications.

The complexes $Mn(CO)_4[P(C_6H_5)_3]Cl$ and $Mn(CO)_4$[As-

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(1) Presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug–Sept 1965.

(2) M. Kilner and A. Wojcicki, *Inorg. Chem.*, **4**, 591 (1965). The anion of 1,1,1,5,5,5-hexafluoropentane-2,4-dione will be referred to henceforth as hexafluoroacetylacetonate (hfac).

(3) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

(4) R. J. Angelici and F. Basolo, *ibid.*, **84**, 2495 (1962).

(5) J. Meisenheimer, *et al.*, *Ann.*, **449**, 213 (1926).