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Organometallic Nitrosyl Chemistry. 15.[1,2] New Cyclopentadienylnitrosyl Complexes of Manganese

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The thermally unstable (η^5-RC_5H_4)Mn(CO)(NO)I (R = H or CH_3) complexes undergo Wurtz-type coupling reactions when treated with Zn/Hg to form the known dimers [(η^5-RC_5H_4)Mn(CO)(NO)]$_2$. They react with soft Lewis bases, L, to produce in good yields the compounds (η^5-RC_5H_4)Mn(NO)(L)I [L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, or $P(C_6H_{11})_3$] which possess chiral metal centers. In the presence of hard Lewis bases (i.e., C_5H_5N, C_4H_9N, $HN(C_6H_{11})_2$, C_4H_8O, $(CH_3)_2SO$, or $(CH_3)_2CO$), the carbonyl nitrosyl iodides decompose, the bimetallic complexes (η^5-RC_5H_4)$_2$Mn$_2$(NO)$_3$I being the only nitrosyl-containing products formed. Other members of the series of compounds having the general formula (η^5-RC_5H_4)$_2$Mn$_2$(NO)$_3$X (X = a halide, a pseudohalide, or an organic group) can be efficiently synthesized either by nucleophilic attack of X^- on the [(η^5-RC_5H_4)Mn(CO)$_2$(NO)]$^+$ cations or by metatheses reactions involving the bimetallic complexes having X = I, Br, or NO_2 and organoalkalis. In contrast to its manganese congener, (η^5-C_5H_5)Re(CO)(NO)I (preparable by the treatment of (η^5-C_5H_5)Re(CO)(NO)CH_3 with a stoichiometric amount of I_2) is thermally stable and does not undergo substitution reactions with Lewis bases even under somewhat forcing conditions. All new complexes isolated have been characterized by conventional spectroscopic methods.

Introduction

The chemistry of monomeric cyclopentadienylnitrosyl complexes of manganese has developed rapidly since a reinvestigation of the preparation and chemical properties of the [(η^5-C_5H_5)Mn(CO)$_2$(NO)]$^+$ cation was published in 1964.[3,4] For instance, it has been demonstrated since that time that treatment of this cation and its methylcyclopentadienyl analogue with various nucleophiles leads to the formation of several classes of neutral[3,5] and cationic[6] nitrosyl derivatives. In particular, we have previously reported briefly that nucleophilic attack by I^- on the cations [(η^5-RC_5H_4)Mn(CO)$_2$(NO)]$^+$ (R = H or CH_3) affords as the principal products the thermally unstable complexes (η^5-RC_5H_4)Mn(CO)(NO)I, minor nitrosyl-containing products being the novel bimetallic compounds (η^5-RC_5H_4)$_2$Mn$_2$(NO)$_3$I.[7] These findings were subsequently corroborated by other investigators.[8] In this paper we present full details of our studies concerning the characteristic chemistry of the (η^5-RC_5H_4)Mn(CO)(NO)I complexes. In addition, we describe the synthesis and characterization of the compounds (η^5-RC_5H_4)$_2$Mn$_2$(NO)$_3$X [R = H,CH_3; X = Cl, Br, I, NO_2 and R = H; X = CH_3, C_5H_5, C_9H_7], some of which result from the attack of appropriate nucleophiles on the dicarbonylnitrosyl cations.

Experimental Section

All experimental procedures were performed under anhydrous conditions in an atmosphere of prepurified nitrogen. All solvents were dried, distilled, and thoroughly purged with nitrogen prior to use. All chemicals were of reagent grade purity and were either purchased from commercial suppliers or prepared according to published procedures. Melting points were taken in capillaries under N_2 and are uncorrected.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer and were calibrated with the 1601-cm^{-1} band of polystyrene film. Ambient-temperature proton magnetic resonance spectra were obtained on a Varian Associates T60 spectrometer or a departmental 270-MHz FT spectrometer consisting of an Oxford Instruments superconducting magnet and Nicolet Instrument Corp. hardware. Low-temperature ^1H NMR spectra were obtained on a Bruker WP-80 spectrometer equipped with a Bruker B-VT-1000 probe with the aid of Dr. S. O. Chan. Tetramethylsilane was employed as an internal standard for all ^1H spectra. Carbon-13 NMR spectra were recorded on a Varian Associates CFT20 spectrometer with reference to the solvent used, but all ^{13}C chemical shifts are reported in ppm downfield from Me_4Si. Mass spectra were recorded at 70 eV on an Atlas CH4B spectrometer using the direct probe insertion method with the assistance of Mr. J. W. Nip. The temperature of the ionization chamber was held ~5 °C below the respective decomposition points of the complexes studied. Elemental analyses were performed by Mr. P. Borda of this department.

Reaction of (η^5-$CH_3C_5H_4$)Mn(CO)(NO)I with Zn/Hg. To a stirred zinc amalgam (2% Zn) at room temperature was added a tetrahydrofuran solution (30 mL) containing green-brown (η^5-$CH_3C_5H_4$)Mn(CO)(NO)I[7] (~1 mmol). A gray solid slowly deposited, and the supernatant solution became red-brown in color as the mixture was stirred for 3 h to ensure completion of the reaction. The supernatant solution was removed from the final reaction mixture by syringe and filtered; the resulting filtrate was taken to dryness in vacuo. The red-brown residue was redissolved in benzene (10 mL), and the solution was transferred by syringe to the top of a 2 × 5 cm column of alumina (Woelm neutral grade 1). Elution of the column with benzene produced a single red-violet band which was collected. Removal of solvent from the eluate under reduced pressure afforded 0.13 g (~65% yield) of [(η^5-$CH_3C_5H_4$)Mn(CO)(NO)]$_2$[6] which was identified by its characteristic IR, NMR, and mass spectra.

(η^5-C_5H_5)Mn(CO)(NO)I was converted to [(η^5-C_5H_5)Mn(CO)(NO)]$_2$[3] in a completely analogous manner.

Reactions of (η^5-RC_5H_4)Mn(CO)(NO)I (R = H or CH_3) with $P(OC_6H_5)_3$ or $P(C_6H_{11})_3$. These reactions were performed in a manner identical with that described previously for the analogous conversions involving $P(C_6H_5)_3$.[7] The physical properties of the isolated products (~60% yields) are summarized in Table I.

Preparation of (η^5-$CH_3C_5H_4$)Fe(CO)[$P(C_6H_5)_3$]I. A benzene solution (100 mL) containing 2.82 g (8.88 mmol) of (η^5-$CH_3C_5H_4$)Fe(CO)$_2$I (prepared by the reaction of I_2 with [(η^5-$CH_3C_5H_4$)Fe(CO)$_2$]$_2$)[4] and 2.36 g (9.00 mmol) of $P(C_6H_5)_3$ was stirred at reflux for 18 h. The final reaction mixture was filtered while hot, and the filtrate was taken to dryness in vacuo. The residue was recrystallized from CH_2Cl_2/hexanes to obtain a nearly quantitative yield of (η^5-$CH_3C_5H_4$)Fe(CO)[$P(C_6H_5)_3$]I as green crystals.

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Table I. Physical Properties of the Complexes $(RC_5H_4)Mn(L)(NO)I$ [$R = H$, $L = P(OC_6H_5)_3$; $R = CH_3$, $L = P(OC_6H_5)_3$ or $P(C_6H_{11})_3$]

complex	mp, °C	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	IR ν_{NO},[a] cm^{-1}	^1H NMR (RC_5H_4)[b]
$(C_5H_5)MnP(OC_6H_5)_3(NO)I$	126 dec	47.04	46.90	3.43	3.26	2.39	2.36	1748	4.48 (5 H, s)
$(C_6H_7)MnP(OC_6H_5)_3(NO)I$	84–85	47.94	47.86	3.69	3.51	2.33	2.41	1740	4.70 (2 H, b), 4.33 (1 H, b), 3.66 (1 H, b), 1.60 (3 H, s)
$(C_6H_7)MnP(C_6H_{11})_3(NO)I$	121-122	50.54	50.36	7.06	7.09	2.45	2.45	1707	5.47 (1 H, b), 5.17 (1 H, b), 4.92 (1 H, b), 3.85 (1 H, b), [c]

[a] In CH_2Cl_2 solution. [b] δ, in $CDCl_3$ solution. [c] CH_3 signal obscured by resonances due to L.

Table II. Physical Properties of the Complexes $(\eta^5\text{-}RC_5H_4)_2Mn_2(NO)_3X$

X	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	color	mp,[a] °C	ν_{NO},[b] cm^{-1}
					$R = H$				
I	26.29	26.46	2.21	2.47	9.19	9.23	red-black	182 dec	1748, 1526
Br	29.30	29.53	2.46	2.72	10.25	10.02	red-black	150 dec	1745, 1527
Cl			[c]				red-black	145 dec[d]	1746, 1529
NO_2	31.94	31.75	2.68	2.60	14.90	14.79	red-brown	134 dec	1757, 1544
C_5H_5	45.59	45.37	3.83	3.79	10.63	10.71	red-violet	153 dec	1730, 1510
CH_3	38.28	38.39	3.80	3.83	12.18	12.18	dark red	163 dec	1723, 1501
C_9H_7	51.26	51.27	3.85	3.92	9.44	9.20	red-violet	132 dec	1726, 1505
					$R = CH_3$				
I	29.72	30.31	2.91	3.33	8.66	8.44	red-black	146 dec	1734, 1520
Br	32.90	33.20	3.22	3.24	9.59	9.41	red-black	144 dec	1734, 1522
Cl			[c]				red-black	141 dec[d]	1737, 1522
NO_2	35.56	35.30	3.49	3.49	13.86	13.54	red-brown	135 dec	1745, 1539

[a] All complexes explode violently on decomposition. [b] CH_2Cl_2 solution. [c] Analytically pure samples could not be obtained. [d] Value obtained with use of a slightly impure sample.

Anal. Calcd for $C_{25}H_{22}OFeIP$: C, 54.38; H, 4.02. Found: C, 54.15; H, 4.01. IR (CH_2Cl_2): ν_{CO} 1945 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.33 (15 H, m), 4.78 (1 H, b), 4.33 (1 H, b), 3.80 (1 H, b), 3.63 (1 H, b), 2.12 (3 H, s). Mp 146 °C.

Reactions of $(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I$ (R = H or CH_3) with Other Lewis Bases. Treatment of dichloromethane solutions of $(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I$[7] at ambient temperature with a slight stoichiometric excess of such Lewis bases as C_5H_5N, $(CH_3)_2SO$, $HN(C_6H_{11})_2$, $(CH_3)_2NC(O)H$, or C_4H_9N slowly (~6 h) produced variable yields (10–25%) of the complexes $(\eta^5\text{-}RC_5H_4)_2Mn_2(NO)_3I$ (R = H or CH_3). The products were purified by removal of the solvent in vacuo and recrystallization of the residue from dichloromethane/hexanes. The physical properties of the products are presented in Table II.

Reaction of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]PF_6$ with NaBr. To a stirred acetone solution (100 mL) containing $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]PF_6$[9] (2.5 g, 7.1 mmol) at room temperature was added solid NaBr (0.80 g, 7.8 mmol). The orange solution gradually darkened, and gas evolution was observed. The mixture was stirred for 1 h, and then the solvent was removed under reduced pressure. The gray residue was thoroughly[10] extracted with 3 × 30 mL portions of CH_2Cl_2 and then washed a final time with 40 mL of this solvent. The combined CH_2Cl_2 extracts were concentrated to 40 mL, and hexanes (40 mL) were added. Slow removal of the solvent under reduced pressure induced the crystallization of 0.43 g (44% yield on the basis of the NO ligand) of analytically pure $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3Br$.

The other reactions of the complexes $[(\eta^5\text{-}RC_5H_4)Mn(CO)_2(NO)]PF_6$ (R = H or CH_3) with NaBr, NaCl, and $NaNO_2$ were effected in a similar manner. The elemental analyses and physical properties of the bimetallic products isolated in comparable yields are recorded in Table II.

Reactions of $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3Br$ with NaC_5H_5, CH_3Li, and NaC_9H_7. All three of these reactions were carried out similarly except that the transformation involving CH_3Li was performed at −78 °C. The experimental procedure, using the reaction with NaC_5H_5 as an example, was as follows. To a stirred solution of $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3Br$ (0.41 g, 1.0 mmol) in tetrahydrofuran (40 mL) at room temperature was added dropwise a 0.15 M solution of NaC_5H_5 in the same solvent. A reaction occurred immediately as evidenced by a color change to dark red and the formation of a fine precipitate. The progress of the reaction was monitored by IR spectroscopy, and the addition of the NaC_5H_5 was stopped when the nitrosyl absorptions due to the starting material had disappeared. The solvent was then removed in vacuo, and the remaining gray residue was extracted with dichloromethane (4 × 20 mL). The combined extracts were concentrated under reduced pressure to 30 mL, and hexanes (35 mL) were added. The total volume of this mixture was reduced to 15 mL in vacuo during which time essentially complete crystallization occurred. The red-violet crystals were collected, washed with hexanes, and dried in vacuo to obtain 0.30 g (76% yield) of $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_5H_5)$.

The new complexes $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3R$ (R = CH_3 or C_9H_7) were isolated in similar yields from the reactions involving CH_3Li or NaC_9H_7. The physical properties and analytical data for all three bimetallic complexes are included in Table II.

The related species $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3X$ (X = I or NO_2) could be used instead of the bromo reactant in these transformations with no detrimental effects.

Reaction of $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_5H_5)$ with Nitric Oxide. A tetrahydrofuran solution (20 mL) containing 0.26 g (0.66 mmol) of $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_5H_5)$ was stirred at room temperature under an atmosphere of prepurified nitric oxide.[11] After 15 min, a precipitate began to form, and the reaction mixture began to warm slowly. After 45 min, an IR spectrum of the supernatant solution indicated that all of the organometallic reactant had been consumed. The final reaction mixture was taken to dryness in vacuo, and the remaining brown residue was purified by recrystallization from CH_2Cl_2/hexanes to obtain 0.09 g (36% yield) of $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(NO_2)$.

Preparation of $(\eta^5\text{-}C_5H_5)Re(CO)(NO)I$. An acetonitrile solution of $(\eta^5\text{-}C_5H_5)Re(CO)_3$ at ambient temperature was treated with a slight stoichiometric excess of solid $NOPF_6$ to produce $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NO)]PF_6$ in a manner completely analogous to that reported for the preparation of the manganese congener.[9] The rhenium cation was then reduced with $NaBH_4$ in tetrahydrofuran according to the published procedure.[12] The product of this reaction, $(\eta^5\text{-}C_5H_5)Re$-

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[9] Connelly, N. G. *Inorg. Synth.* **1976**, *15*, 91–92.

[10] The presence of the $NaPF_6$ byproduct makes it very difficult to extract the desired bimetallic products into any solvent.

[11] Nitric oxide (Matheson C.P. grade) was further purified by passing it through a column of activated silica gel maintained at −78 °C. The purity of the effluent gas (>99.5%) was confirmed by mass spectral analysis.

(CO)(NO)CH_3 (0.22 g, 0.68 mmol), was dissolved in dichloromethane (25 mL), and the resulting solution was stirred at room temperature while being treated dropwise with a CH_2Cl_2 solution of I_2 (0.19 g, 0.75 mmol). The reaction mixture gradually darkened, and no gas evolution was observed. The mixture was stirred for 1 h and was then taken to dryness in vacuo. The residue was redissolved in benzene (10 mL), and the solution was transferred by syringe onto a 3 × 8 cm column of alumina. Elution of the column with benzene developed two bands. The first band (orange-red) required 250 mL of benzene for complete elution. The second band (black) could not be eluted with benzene, dichloromethane, or tetrahydrofuran. Solvent was removed from the orange-red eluate under reduced pressure, and the remaining residue was recrystallized from CH_2Cl_2/hexanes to obtain 0.23 g (75% yield) of (η^5-C_5H_5)Re(CO)(NO)I as red crystals.

Anal. Calcd for $C_6H_5ReNO_2I$: C, 16.52; H, 1.16; N, 3.21. Found: C, 16.61; H, 1.07; N, 3.40. IR (CH_2Cl_2): ν_{CO} 1992 cm^{-1}; ν_{NO} 1733 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.78 (5 H, s).

Results and Discussion

It has previously been established[7,8] that (η^5-C_5H_5)Mn(CO)(NO)I and its methylcyclopentadienyl analogue can be easily prepared by either reaction 1 or 2, both of which proceed

$$[(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)]_2 + I_2 \xrightarrow[\text{or } C_6H_6]{CH_2Cl_2} 2(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I \quad (1)$$

$$[(\eta^5\text{-}RC_5H_4)Mn(CO)_2(NO)]PF_6 + I^- \xrightarrow[\text{or acetone}]{THF} (\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I + CO + PF_6^- \quad (2)$$

$$R = H \text{ or } CH_3$$

rapidly to completion at room temperature. The product complexes are air-sensitive, green-brown solids which decompose slowly both in solution and in the solid state at ambient temperature even when maintained under an atmosphere of prepurified nitrogen. Nevertheless, they are sufficiently thermally stable to permit an investigation of their characteristic chemistry.

We have found that treatment of the carbonyl nitrosyl iodides with zinc amalgam results in a Wurtz-type coupling reaction, i.e., eq 3, and formation of the well-known dimers

$$2(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I \xrightarrow[THF]{Zn/Hg} [(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)]_2 \quad (3)$$

[(η^5-RC_5H_4)Mn(CO)(NO)$]_2$ in good yields. This conversion resembles the analogous preparation of the isoelectronic complex [(η^5-C_5H_5)Cr$(NO)_2]_2$ from (η^5-C_5H_5)Cr$(NO)_2$Cl.[13] Furthermore, regardless of the method by which solutions of (η^5-RC_5H_4)Mn(CO)(NO)I are generated, they readily evolve carbon monoxide when treated with stoichiometric amounts of soft Lewis bases, L, i.e., eq 4, and the new crystalline

$$(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I + L \rightarrow (\eta^5\text{-}RC_5H_4)Mn(NO)(L)I + CO \quad (4)$$

$$R = H \text{ or } CH_3;\ L = P(C_6H_5)_3,\ P(OC_6H_5)_3, \text{ or } P(C_6H_{11})_3$$

complexes (η^5-RC_5H_4)Mn(NO)(L)I can be isolated in yields of ~60% (on the basis of the original reactants in eq 1 or 2).[14] This lability of the carbonyl group and the thermal instability of the (η^5-RC_5H_4)Mn(CO)(NO)I complexes contrast directly with the behavior exhibited by their isoelectronic analogues.[15]

Table III. Mass Spectral Data for (η^5-RC_5H_4)Mn(NO)(L)I[a] (L = $P(OC_6H_5)_3$, R = H or CH_3; L = $P(C_6H_{11})_3$, R = CH_3)

R = H			R = CH_3	
m/z	rel abund	assignt	rel abund	*m/z*
310	100	$P(OC_6H_5)_3^+$	100	310
277	8	$(RC_5H_4)Mn(NO)I^+$	3	291
247	13	$(RC_5H_4)MnI^+$	6	261
185	0	$(RC_5H_4)_2Mn^+$	5	213
182	5	MnI^+	6	182
120	17	$(RC_5H_4)Mn^+$	11	134
65	34	$RC_5H_4^+$	26	79
55	7	Mn^+	7	55

data for $(C_6H_7)Mn(NO)[P(C_6H_{11})_3]I$ [m/z (rel abund)]:[a] $(C_6H_7)Mn(NO)I^+$, 291 (18); $P(C_6H_{11})_3^+$, 280 (80); $(C_6H_7)MnI^+$, 261 (42); $(C_6H_7)_2Mn^+$, 213 (21); MnI^+, 182 (37); $(C_6H_7)Mn^+$, 134 (26); $C_6H_7^+$, 79 (88); Mn^+, 55 (100)

[a] The data presented include only L^+ and fragments containing the metal. All spectra also display peaks due to ions resulting from the characteristic fragmentation of L.

Table IV. Mass Spectral Data for (η^5-$CH_3C_5H_4$)Fe(CO)[$P(C_6H_5)_3$]I[a]

m/z	rel abund	assignt[b]
552	1	$(C_6H_7)Fe[P(C_6H_5)_3](CO)I^+$
524	8	$(C_6H_7)Fe[P(C_6H_5)_3]I^+$
445	1	$Fe[P(C_6H_5)_3]I^+$
397	2	$(C_6H_7)Fe[P(C_6H_5)_3]^+$
290	2	$(C_6H_7)Fe(CO)I^+$
262	100	$P(C_6H_5)_3^+$
214	40	$(C_6H_7)_2Fe^+$
183	36	FeI^+
79	11	$C_6H_7^+$
56	10	Fe^+

[a] See footnote *a* to Table III. [b] The assignments involve the most abundant naturally occurring isotopes, i.e., ^{56}Fe, in each fragment.

Thus, (η^5-C_5H_5)Fe$(CO)_2$I and (η^5-C_5H_5)Cr$(NO)_2$I are quite stable at room temperature in a nitrogen atmosphere and require somewhat forcing conditions (e.g., an excess of L in refluxing benzene for 18 h) to undergo substitution of the CO or NO ligands. In a similar vein, although (η^5-C_5H_5)Fe$(CO)_2$R′[16] and (η^5-C_5H_5)Cr$(NO)_2$R′[13] (R′ = alkyl or aryl) complexes are well-known, our attempts to synthesize related (η^5-C_5H_5)Mn(CO)(NO)R′ species from the iodo precursor by metatheses have so far met with failure.

The compounds (η^5-RC_5H_4)Mn(NO)(L)I [R = H or CH_3; L = $P(C_6H_5)_3$, $P(OC_6H_5)_3$, or $P(C_6H_{11})_3$] are green-to-brown air-stable solids which are soluble in dichloromethane and chloroform but less soluble in benzene, tetrahydrofuran, and acetone. The tricyclohexylphosphine derivatives tend to decompose slowly in a solution not containing an excess of $P(C_6H_{11})_3$, and this proclivity of (η^5-C_5H_5)Mn(NO)[$P(C_6H_{11})_3$]I to liberate free phosphine and form an associated species such as [(η^5-C_5H_5)Mn(NO)I$]_x$ has prevented us from isolating a pure sample of the complex. The solution IR spectra of all the complexes (Table I and ref 7) display single nitrosyl-stretching absorptions in the range 1707–1748 cm^{-1} which are some 30–70 cm^{-1} lower than those exhibited by the (η^5-RC_5H_4)Mn(CO)(NO)I compounds.[7] The decrease in ν(NO) as L varies in the order CO > $P(OC_6H_5)_3$ > $P(C_6H_5)_3$ > $P(C_6H_{11})_3$ has been observed previously in another system[17] and is consistent with the documented electron-donating and

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(14) The reactions between the complexes (η^5-RC_5H_4)Mn(CO)(NO)I and $P(C_6H_5)_3$ have been presented earlier[7,8] as evidence for the existence of the organometallic reactants.

(15) The thermal instability of transition-metal carbonyl nitrosyl halides has been previously discussed: Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Chem.* **1977**, *16*, 3173–3178.

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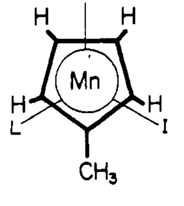
Table V. ^{13}C NMR Spectral Data of Some (η^5-$CH_3C_5H_4$)Mn Compounds[a]

	δ			
compd	CO	$P(C_6H_5)_3$	$C(C_5H_4)$	$C(CH_3)$
(η^5-$CH_3C_5H_4$)$Mn(CO)_3$	225.10		102.42 82.21 81.72	13.30
(η^5-$CH_3C_5H_4$)$Mn(CO)_2[P(C_6H_5)_3]$	232.82 (J_{P-C} = 24.4 Hz)	C_1 138.21 (J_{P-C} = 40.0 Hz) C_2 132.77 (J_{P-C} = 13.2 Hz) C_3 127.90 (J_{P-C} = 8.6 Hz) C_4 129.22	98.76 82.91 81.72	13.60
[(η^5-$CH_3C_5H_4$)$Mn(CO)(NO)[P(C_6H_5)_3]]PF_6$	213.91 (J_{P-C} = 24.0 Hz)	C_1 131.38 (J_{P-C} = 59.2 Hz) C_2 133.12 (J_{P-C} = 10.4 Hz) C_3 129.91 (J_{P-C} = 11.4 Hz) C_4 132.36	115.23 98.11 95.49 93.87, 93.36	11.99
(η^5-$CH_3C_5H_4$)$Mn(NO)[P(C_6H_5)_3]I$		C_1 [b] C_2 133.29 (J_{P-C} = 9.8 Hz) C_3 127.96 (J_{P-C} = 9.4 Hz) C_4 129.89	106.51 97.02 95.61 91.43 86.47	12.82

[a] The indicated assignments are based on previously reported results.[20] [b] Obscured by resonances due to C_2.

-accepting properties of these ligands.[18] The mass spectra of the complexes contain peaks due to ions attributable to the fragmentation of $(RC_5H_4)Mn(NO)I^+$ and L^+ ions (see Table III and ref 7), and parent ion peaks are not detectable even at excitation potentials as low as 20 eV. In contrast, the 70-eV mass spectrum of the iron analogue (η^5-$CH_3C_5H_4$)$Fe[P(C_6H_5)_3](CO)I$ (Table IV) exhibits several peaks due to ions (including the parent ion) in which the metal–phosphine linkage has been maintained. This difference in behavior of the isoelectronic complexes is surprising since it would reasonably be expected that the NO group (generally acknowledged to be a much stronger π acceptor than a CO group)[19] would better stabilize the bond between the soft Lewis base and the metal. It thus appears that in these complexes the σ-donor properties of the nitrosyl ligands are more important than their electron-accepting abilities.

The ^1H NMR spectrum of (η^5-C_5H_5)$Mn(NO)[P(C_6H_5)_3]I$ in $CDCl_3$ consists of a multiplet centered at δ 7.38 and a singlet at δ 4.72 of relative intensity 3:1, and hence these resonances can be assigned to the phenyl and cyclopentadienyl protons, respectively.[7] The spectrum of the analogous triphenyl phosphite complex is similar (Table I) and can be assigned likewise. The ^1H NMR spectra of the methylcyclopentadienyl derivatives also display signals attributable to the protons of the phosphorus-containing ligands as well as a singlet at δ ~2 assignable to the methyl protons of the η^5-$CH_3C_5H_4$ ring. However, in contrast to the parent carbonyl, (η^5-$CH_3C_5H_4$)$Mn(CO)_3$, the four protons on the η^5-ring do not exhibit chemical shift equivalence in these complexes. They constitute an α, β, γ, δ spin system which gives rise to three resonances (four in the case of the $P(C_6H_{11})_3$ derivative) as summarized in Table I. These observations are consistent with the molecules possessing a "piano stool" molecular structure about an asymmetric metal center, i.e.



the protons on the diastereotopic sides of the methylcyclopentadienyl ring producing the multiple signals described above. However, the exact assignment of these resonances is not possible at the present time.

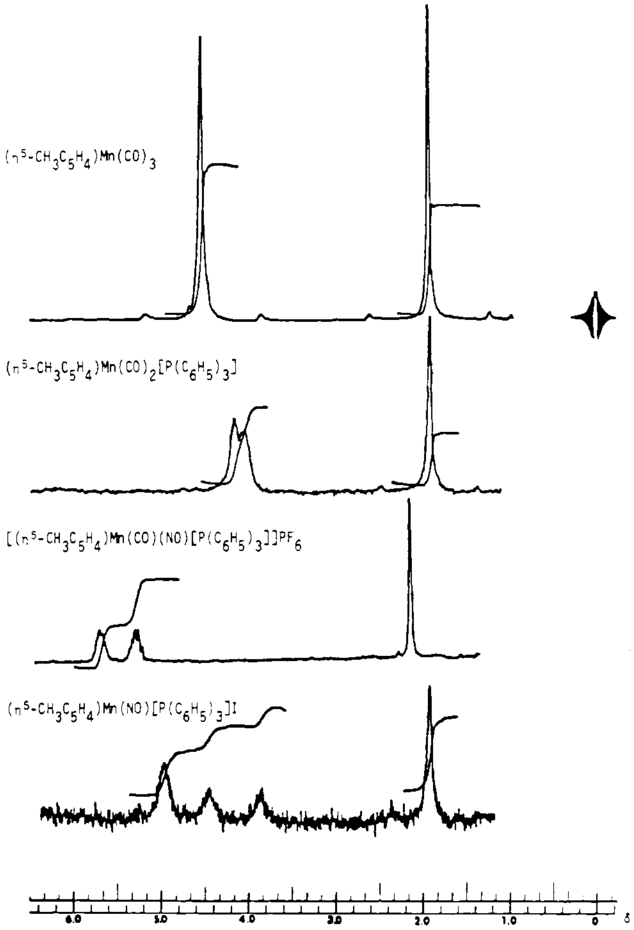


Figure 1. ^1H NMR Spectra of Selected (η^5-$CH_3C_5H_4$)Mn Complexes in $CDCl_3$.

The induction of magnetic inequivalence between the α and β sites of the $CH_3C_5H_4$ ring is greatest for those complexes possessing a chiral metal center as evidenced by the partial ^1H NMR spectra displayed in Figure 1. Furthermore, we have also found that ^{13}C NMR spectroscopy is a more sensitive probe of this phenomenon. For comparison, the ^{13}C data for the complexes considered in Figure 1 are summarized in Table V. Not surprisingly, the chemical shift differences of the ^{13}C signals are greatest for (η^5-$CH_3C_5H_4$)$Mn(NO)[P(C_6H_5)_3]I$ since the four ligands attached to the metal differ to a larger

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(18) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953–2956.
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extent in size and electronic properties.

In the course of studying the chemical reactivity of the original (η^5-RC$_5$H$_4$)Mn(CO)(NO)I (R = H or CH$_3$) complexes, we attempted to prepare derivatives containing N- and O-donor ligands by reactions analogous to those summarized in eq 4. We thus discovered that hard Lewis bases do not simply substitute for the labile CO ligands in the organometallic reactants but rather cause the transformation in eq 5 to occur. The bimetallic products indicated are the only nitrosyl-containing complexes present in the final reaction mixture and can be isolated in yields of 10–25%. Although no mechanism for this conversion is readily evident, two experimental observations are worthy of note. First, the reactions encompassed by eq 5 are relatively slow (~6 h), and careful monitoring of their progress by IR spectroscopy fails to provide any evidence for the existence of intermediate (η^5-RC$_5$H$_4$)Mn(NO)(L′)I species. Second, a small amount of gaseous nitric oxide is present in the atmosphere above the reaction mixtures, and its presence may indicate that transfer of the nitrosyl ligand occurs via free NO. In any event, the mode of reactivity depicted in eq 5 does explain why small amounts of (η^5-RC$_5$H$_4$)$_2$Mn$_2$(NO)$_3$I accompany the preparation of the (η^5-RC$_5$H$_4$)Mn(CO)(NO)I complexes in tetrahydrofuran or acetone.[7,8]

$$(\eta^5\text{-RC}_5\text{H}_4)\text{Mn(CO)(NO)I} \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{Lewis base, L}'} (\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2\text{(NO)}_3\text{I} \quad (5)$$

$$\text{R} = \text{H or CH}_3;\ \text{L}' = \text{C}_5\text{H}_5\text{N, C}_4\text{H}_9\text{N, HN(C}_6\text{H}_{11})_2,\ \text{C}_4\text{H}_8\text{O, (CH}_3)_2\text{SO, or (CH}_3)_2\text{CO}$$

Other members of the series of compounds having the general formula (η^5-RC$_5$H$_4$)$_2$Mn$_2$(NO)$_3$X (X = a halide, pseudohalide, or an organic group, R′) can be readily synthesized by reactions 6 and 7, the products being isolable in moderate yields (~45%) from reaction 6 and in good yields (~75%) from reaction 7. Of the complexes that we have prepared in this fashion, three have been previously reported. The two compounds with R = H and X = C$_5$H$_5$ or NO$_2$ are well-known, having been obtained originally by the treatment of manganocene with NO[21,22] and subsequently characterized fully by X-ray crystallography.[22,23] The third, having R = CH$_3$ and X = Br, has been prepared in a manner analogous to eq 6 and described briefly by others[8] after the completion of our work. Interestingly, we find that the cyclopentadienyl complex (R = H, X = C$_5$H$_5$) can be converted to the nitrito species (R = H, X = NO$_2$) in 36% yield by the action of nitric oxide in tetrahydrofuran at room temperature. It has previously been shown to react with (C$_6$H$_5$)Li in THF to afford (η^5-C$_5$H$_5$)$_2$Mn$_2$(NO)$_3$(C$_6$H$_5$),[24] another member of this class of compounds.

$$[(\eta^5\text{-RC}_5\text{H}_4)\text{Mn(CO)}_2\text{(NO)}]^+ + \text{X}^- \xrightarrow{\text{acetone}} (\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2\text{(NO)}_3\text{X} \quad (6)$$

$$\text{R} = \text{H or CH}_3;\ \text{X} = \text{Cl, Br, or NO}_2$$

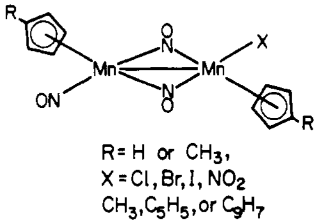
$$(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2\text{(NO)}_3\text{X} + \text{R}'^- \xrightarrow{\text{THF}} (\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2\text{(NO)}_3\text{R}' + \text{X}^- \quad (7)$$

$$\text{R} = \text{H};\ \text{X} = \text{I, Br, or NO}_2;\ \text{R}' = \text{C}_5\text{H}_5\text{, CH}_3\text{, or C}_9\text{H}_7$$

Table VI. Mass Spectral Data for (η^5-RC$_5$H$_4$)$_2$Mn$_2$(NO)$_3$I (R = H or CH$_3$)

R = H			R = CH$_3$	
m/z	rel abund	assignt	rel abund	*m/z*
457	6	(RC$_5$H$_4$)$_2$Mn$_2$(NO)$_3$I$^+$	17	485
427	17	(RC$_5$H$_4$)$_2$Mn$_2$(NO)$_2$I$^+$	43	455
397	8	(RC$_5$H$_4$)$_2$Mn$_2$(NO)I$^+$	14	425
367	29	(RC$_5$H$_4$)$_2$Mn$_2$I$^+$	71	395
247	4	(RC$_5$H$_4$)MnI$^+$	7	261
237	3	Mn$_2$I$^+$	9	237
191	3	(RC$_5$H$_4$)Mn$_2$O$^+$	0	205
185	22	(RC$_5$H$_4$)$_2$Mn$^+$	25	213
180	40	(RC$_5$H$_4$)Mn(NO)$_2$$^+$	69	194
182	6	MnI$^+$	12	182
150	15	(RC$_5$H$_4$)Mn(NO)$^+$	22	164
120	100	(RC$_5$H$_4$)Mn$^+$	100	134
65	34	RC$_5$H$_4$$^+$	57	79
55	40	Mn$^+$	50	55

All of the bimetallic complexes (Table II) are red-tinged, relatively air-stable solids which are soluble in polar organic solvents, sparingly soluble in benzene, and insoluble in hexanes. Their physical properties are consistent with their having the molecular structures (either cis or trans)



the asymmetrically bridging NO groups having been confirmed for the solid-state structures of the members having R = H and X = NO$_2$[22] or C$_5$H$_5$.[23] Thus, their CH$_2$Cl$_2$ solutions display IR absorptions at ~1745 and ~1525 cm^{-1} attributable to the terminal and bridging nitrosyl ligands, respectively. As expected, the nitrosyl-stretching frequencies diminish as the electron density at the metal centers increases; for example, the η^5-CH$_3$C$_5$H$_4$ complexes consistently display lower ν(NO)'s than their η^5-C$_5$H$_5$ analogues. The mass spectra of the iodo derivatives (Table VI) exhibit peaks due to the parent ion, P$^+$, and the ions [P − NO]$^+$, [P − 2NO]$^+$, and [P − 3NO]$^+$, as well as those arising from cleavage of the bimetallic species, e.g., [(RC$_5$H$_4$)Mn(NO)$_2$]$^+$ and [(RC$_5$H$_4$)MnI]$^+$. Similar features can be observed in the obtainable mass spectra of the other bimetallic complexes (Tables VII–X).[25] These spectra also indicate that the parent ions of the complexes possessing the greater electron density at the manganese atoms (i.e., those displaying the lower ν(NO) values in their IR spectra) are most prone to lose preferentially the NO ligands upon fragmentation. This feature is evidenced, for instance, by the relative abundances of the [(RC$_5$H$_4$)$_2$Mn$_2$X]$^+$ ions for various X ligands when R = H or CH$_3$. Such a preferential loss of the nitrosyl groups apparently contradicts the conventional inference that the complexes with the lower nitrosyl-stretching absorptions possess the stronger Mn–NO linkages.

The ^{1}H NMR spectral data of the bimetallic complexes are compiled in Table XI. The spectra of the (η^5-C$_5$H$_5$)$_2$Mn$_2$(NO)$_3$X (X = Cl, Br, NO$_2$, CH$_3$, or C$_9$H$_7$) derivatives exhibit two sharp resonances in the η^5-cyclopentadienyl region, thereby indicating that these complexes exist in solution principally, if not exclusively, as one geometrical isomer, probably the cis form (vide infra). In contrast, the spectra of the compounds having X = I or C$_5$H$_5$ display two pairs of sharp resonances

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(21) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 38–45.

(22) Calderon, J. L.; Cotton, F. A.; DeBoer, B. G.; Martinez, N. *J. Chem. Soc., Chem. Commun.* **1971**, 1476–1477.

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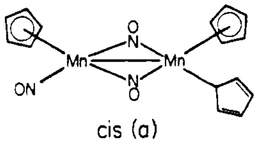
(25) Supplementary material.

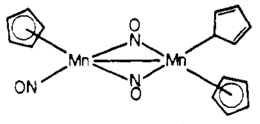
Table XI. ^1H NMR Spectral Data for $(\eta^5\text{-}RC_5H_4)_2Mn_2(NO)_3X$ Complexes (R = H; X = Cl, Br, I, NO_2, CH_3, C_5H_5, or C_9H_7 and R = Me; X = Cl, Br, I, or NO_2)

X	solvent	δ	intensity ratio (*a*:*b*)
		R = H	
Cl	$CDCl_3$	5.50 (5 H, s), 5.30 (5 H, s)	
Br	$CDCl_3$	5.53 (5 H, s), 5.33 (5 H, s)	
I	$CDCl_3$	(a) 5.53 (5 H, s), 5.34 (5 H, s) (b) 5.30 (5 H, s), 5.20 (5 H, s)	~2.4
NO_2	$CDCl_3$	5.43 (5 H, s), 5.32 (5 H, s)	
CH_3	$CDCl_3$	5.17 (5 H, s), 5.10 (5 H, s), −0.60 (3 H, s)	
C_5H_5	$CDCl_3$	(a) 5.33 (5 H, s), 5.27 (5 H, s), 4.43 (5 H, s) (b) 5.47 (5 H, s), 5.40 (5 H, s), 4.50 (5 H, s)	~2.4
	$(CD_3)_2CO$	(a) 5.39 (5 H, s), 5.17 (5 H, b), 4.45 (5 H, s) (b) 5.49 (5 H, s), 5.17 (5 H, b), 4.42 (5 H, s)	~26
C_9H_7	$(CD_3)_2CO$	7.49–6.84 (5 H, m), 6.42 (2 H, s), 5.41 (5 H, s), 4.34 (5 H, s)	
		R = CH_3	
Cl	$CDCl_3$	5.07 (6 H, b), 4.77 (2 H, b), 1.77 (3 H, s), 1.53 (3 H, s)	
Br	$CDCl_3$	5.23 (6 H, b), 4.83 (2 H, b), 1.98 (3 H, s), 1.77 (3 H, s)	
I	$CDCl_3$	5.47 (2 H, b), 5.33 (4 H, b), 4.90 (2 H, b), 2.10 (3 H, s), 1.87 (3 H, s)	
NO_2	$CDCl_3$	5.30 (2 H, b), 5.10 (4 H, b), 4.90 (2 H, b), 2.03 (3 H, s), 1.77 (3 H, s)	

in this region which can be assigned[24] to the cis and trans isomers, i.e., for X = C_5H_5

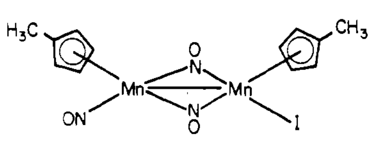


cis (a)



trans (b)

The ratio of isomers in solution is cis:trans ≃ 2.4 in both cases. The related $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_6H_5)$ is known to exist in similar isomeric forms.[24] The spectra of the methylcyclopentadienyl derivatives are slightly more complicated, but they appear to indicate that solely one isomeric form of the compounds exists in $CDCl_3$ solutions. For the species with X = I, the protons on one $\eta^5\text{-}CH_3C_5H_4$ ligand give rise to two resonances of relative intensity 4:3 (identical with the case of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ in Figure 1), whereas the protons on the other $\eta^5\text{-}CH_3C_5H_4$ ring give rise to three signals having an intensity ratio of 2:2:3 (as in the case of $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2[P(C_6H_5)_3]$). It thus seems likely that the first methylcyclopentadienyl ligand is attached to the manganese atom bonded to the terminal nitrosyl ligand while the second is attached to the metal bearing the iodine atom, i.e.



Similar features are evident in the spectrum of the complex having R = CH_3 and X = NO_2 (Table XI) but are not as clearly resolved in the spectra displayed by the X = Cl or Br species.

Table XII. Mass Spectral Data for $(\eta^5\text{-}C_5H_5)Re(CO)(NO)I$

m/*z*	rel abund	assignt[a]
437	79	$(C_5H_5)Re(CO)(NO)I^+$
409	86	$(C_5H_5)Re(NO)I^+$
379	100	$(C_5H_5)ReI^+$
353	29	$(C_3H_3)ReI^+$
314	6	ReI^+
218.5	6	$(C_5H_5)Re(CO)(NO)I^{2+}$
204.5	8	$(C_5H_5)Re(NO)I^{2+}$
189.5	10	$(C_5H_5)ReI^{2+}$
187	6	Re^+

[a] Assignments are based on the ^{187}Re isotope.

We have also carried out a variable-temperature ^1H NMR study of $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_5H_5)$ in acetone-d_6. In this solvent the cis:trans isomer ratio increases to ~26. The assignment of the broad resonance at δ 5.17 due to the protons of the σ-bonded C_5H_5 ligand can be made unambiguously (cf. the spectrum of the indenyl analogue in the same solvent). As the temperature is lowered, this signal further broadens and begins to collapse; it coalesces at ~−35 °C and at ~−90 °C is seen as two reasonably sharp resonances at δ 6.05 and 3.56. It thus appears that this C_5H_5 ring is stereochemically nonrigid in a manner that has been well documented for other metal–$(\eta^1\text{-}C_5H_5)$ linkages.[26] Interestingly, the signals due to the $\eta^5\text{-}C_5H_5$ rings appear as closely spaced doublets at −90 °C, but at present we offer no rationale for this observation. Finally we attempted to prepare $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_5D_5)$ by reaction 7 using NaC_5D_5 as the organoalkali reactant. However, the ^1H NMR spectrum of the isolated product was invariant from that presented in Table XI even though mass spectral analysis confirmed that C_5D_5 had indeed been incorporated. These observations indicate that the three cyclopentadienyl rings in $(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_5H_5)$ can exchange.

In view of the derivative chemistry of the $(\eta^5\text{-}RC_5H_4)Mn(CO)(NO)I$ complexes described in this paper, it was naturally of interest to us to synthesize the analogous rhenium precursors for comparative purposes. Our initial attempt to prepare $(\eta^5\text{-}C_5H_5)Re(CO)(NO)I$ in a manner analogous to that depicted for Mn in eq 2 failed; the original $[(\eta^5\text{-}C_5H_5)Re(CO)_2(NO)]PF_6$ reactant could be recovered unaltered after several days in a refluxing acetone solution containing an excess of NaI. We subsequently discovered that the desired complex could be prepared in 75% yield by the stoichiometric reaction (8). The IR, ^1H NMR (vide supra), and mass

$$(\eta^5\text{-}C_5H_5)Re(CO)(NO)CH_3 + I_2 \xrightarrow{CH_2Cl_2} (\eta^5\text{-}C_5H_5)Re(CO)(NO)I + CH_3I \quad (8)$$

spectral data (Table XII) for the product support the monomeric formulation shown in eq 8. The complex is a red solid which is air stable in the solid state and in solution. In contrast to the manganese congener, the CO group in $(\eta^5\text{-}C_5H_5)Re(CO)(NO)I$ is inert to substitution by Lewis bases, no reaction occurring when the compound is treated with an excess of $P(C_6H_5)_3$ in refluxing toluene for prolonged periods of time. To the best of our knowledge, $(\eta^5\text{-}C_5H_5)Re(CO)(NO)I$ is thus the only known example of a transition-metal carbonyl nitrosyl halide having an inert CO ligand.[15]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of a grant to P.L. (Grant A5885) and postgraduate fellowships to B.W.H. and B.W.S.K.

Registry No. $(C_5H_5)MnP(OC_6H_5)_3(NO)I$, 75847-47-1; $(C_6H_7)MnP(OC_6H_5)_3(NO)I$, 75847-48-2; $(C_6H_7)MnP(C_6H_{11})_3(NO)I$, 75847-49-3; *cis*-$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3I$, 69222-30-6; *cis*-$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3Br$, 75847-50-6; *cis*-$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3Cl$, 75847-51-7; *cis*-$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(NO_2)$, 75880-23-8; *cis*-$(\eta^5\text{-}$

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$C_5H_5)_2Mn_2(NO)_3(C_5H_5)$, 59539-19-4; *cis*-$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(CH_3)$, 75847-52-8; *cis*-$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_9H_7)$, 75862-70-3; $(\eta^5\text{-}CH_3C_5H_4)_2Mn_2(NO)_3I$, 69120-60-1; $(\eta^5\text{-}CH_3C_5H_4)_2Mn_2(NO)_3Br$, 70616-48-7; $(\eta^5\text{-}CH_3C_5H_4)_2Mn_2(NO)_3Cl$, 70616-27-2; $(\eta^5\text{-}CH_3C_5H_4)_2Mn_2(NO)_3NO_2$, 75847-53-9; $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)[P(C_6H_5)_3]I$, 32054-66-3; $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$, 12108-13-3; $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2[P(C_6H_5)_3]$, 12100-95-7; $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)[P(C_6H_5)_3]]PF_6$, 32965-23-4; $(\eta^5\text{-}CH_3C_5H_4)Mn(NO)[P(C_6H_5)_3]I$, 69120-58-7; $(\eta^5\text{-}C_5H_5)Re(CO)(NO)I$, 75847-54-0; $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)I$, 69120-56-5; $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)]_2$, 69155-23-3; $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)I$, 69120-55-4; $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2I$, 32628-97-0; $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]PF_6$, 31921-90-1; $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(NO)]PF_6$, 52202-14-9; $(\eta^5\text{-}C_5H_5)Re(CO)_3$, 12079-73-1; $(\eta^5\text{-}C_5H_5)Re(CO)(NO)CH_3$, 38814-45-8; *trans*-$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3I$, 69155-17-5; *trans*-$(\eta^5\text{-}C_5H_5)_2Mn_2(NO)_3(C_5H_5)$, 75880-24-9.

Supplementary Material Available: Tables VII–X, listings of mass spectral data (4 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of Substituted Thorocenes

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Disubstituted bis(cyclooctatetraene)thorium(I) (thorocene) complexes have been prepared. Unlike thorocene itself, these derivatives are soluble in organic solvents. Proton and ^{13}C NMR spectra of these air-sensitive diamagnetic compounds show a significant decrease in electron density in the rings relative to dipotassium cyclooctatetraene salts. The chemistry of thorocenes and uranocenes is compared. Like uranocenes, thorocenes do not undergo facile ligand-exchange reactions with cyclooctatetraenes; both, however, do give rapid exchange with cyclooctatetraene dianions.

Thorocene (bis(η^8-cyclooctatetraene)thorium, $Th(COT)_2$, Ia) was first prepared by Streitwieser and Yoshida[1] shortly after the preparation of uranocene.[2] Reaction of 2 equiv of dipotassium cyclooctatetraene (K_2COT) with $ThCl_4$ in tetrahydrofuran (THF) yielded yellow crystals of $(COT)_2Th$ upon sublimation. Thorocene has also been produced in the direct reaction of finely divided thorium metal (produced from thorium hydride) with COT at 150 °C.[3] The uranium and plutonium analogues have been prepared in a similar manner. These preparations attest to the thermodynamic stability of the bis(cyclooctatetraene)actinide complexes. X-ray crystal structure analysis showed thorocene to be isostructural with uranocene.[4] Both have a π-sandwich structure with D_{8h} molecular symmetry. The carbon–metal bond distance is slightly longer for the thorium compound, which reflects the generally larger bond radius of Th(IV) vs. U(IV).

The sparing solubility of thorocene in common organic solvents limits investigation of solution properties such as NMR spectra and relative reactivity compared to uranocene. Several physical properties have been determined: mass spectrum;[1] infrared and Raman spectra.[5] By analogy to uranocenes,[6] substituted thorocenes were expected to have greater solubility than the parent compound. The synthesis, spectral characterization, and some reaction chemistry of substituted thorocenes are reported in this paper.

Synthesis. A variety of substituted thorocenes was prepared by reaction of the substituted COT[7] dianion with $ThCl_4$ (eq 1). The success of these preparations depends critically on the thorium tetrachloride used. Material from one supplier was essentially insoluble in THF or DME and gave poor yields or no reaction. Thorium tetrachloride from Alfa was more soluble and gave satisfactory results. Initially, dimethoxyethane (DME) was used as solvent because $ThCl_4$ is reported to decompose upon prolonged exposure to tetrahydrofuran (THF).[8] Subsequently, THF was shown to be a suitable solvent since reaction 1 proceeds readily at room temperature.

$$R \xrightarrow{2K} R^{2-}\,2K^+ \xrightarrow[\text{DME or THF}]{ThCl_4} R_2Th \qquad (1)$$

Ia, $R = C_8H_8$ (68%)
Ib, $R = n\text{-}BuC_8H_7$ (77%)
Ic, $R = C_6H_5C_8H_7$ (27%)
Id, $R = t\text{-}BuC_8H_7$ (18%)
Ie, $R = MeC_8H_7$
If, $R = 1,4\text{-}t\text{-}Bu_2C_8H_6$
Ig, $R = 1,3,5,7\text{-}Me_4C_8H_4$

Compounds Ia–Id were prepared in moderate to good yield on a 5–10-mmol scale and were purified by hexane extraction. Smaller amounts of Ie–Ig (0.5–1.0 mmol) were prepared for spectroscopic studies and were purified by sublimation with substantial material loss due to concomitant decomposition. Yields for Ie–Ig were not determined; Id was prepared by both procedures. Substituted thorocenes are bright yellow solids, and some have sharp melting points. They show strong parent ions (often the base peak) in the mass spectra.

Thorocenes react rapidly with oxygen in a fashion similar to uranocenes to give cyclooctatetraenes (eq 2).[2] The inorganic product, by analogy, is undoubtedly ThO_2.

$$(RC_8H_7)_2Th + O_2 \rightarrow 2RC_8H_7 + ThO_2 \qquad (2)$$

This reaction serves as an additional means of characterization of new thorocenes, since the liberated ligand can be identified by NMR. More importantly, it means that all thorocene chemistry must be performed with the scrupulous exclusion of oxygen. This oxygen sensitivity makes it difficult to obtain satisfactory combustion analyses, but with careful work it was possible to get good analyses; this shows that the crystals are stoichiometric and do not contain solvent of crystallization.

As expected, the substituted thorocenes are more soluble in organic solvents than the parent. Because of the availability of *n*-butylcyclooctatetraene and the high yields in the reaction

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