2740 *Inorg. Chem.* **1980,** *19,* 2740–2749

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Aryldiazenido (N_2R) Derivatives of (η^5-Methylcyclopentadienyl)tricarbonylmanganese: Synthesis, X-ray Structure Determination, and Reactions with Nucleophiles To Give Dinitrogen Complexes

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Received January 4, 1980

The aryldiazenido complexes $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4R')][BF_4]$ (**1**; R′ = (**a**) CF_3, (**b**) F, (**c**) H) and $[(\eta^5\text{-}C_5H_5)Re(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (**2**) have been synthesized. Compound **1a** crystallizes from acetone–diethyl ether as solvent-free crystals in the space group *Fdd*2 of the orthorhombic system, with $a = 12.866$ (3) Å, $b = 56.605$ (11) Å, $c = 9.964$ (2) Å, and $Z = 16$. The calculated and measured densities are 1.653 and 1.65 (1) g cm^{-3}, respectively. On the basis of 1019 observed, three-dimensional, X-ray counter measured intensities with $I > 2.3\sigma(I)$ in the range $3° < 2\theta \leq 45°$ (Mo Kα), the structure was solved and refined by full-matrix, least-squares methods to $R = 0.055$ and $R_w = 0.053$. The cation has the "piano-stool" geometry in which the aryldiazenido ligand is coordinated to the metal in a typical "singly bent" configuration in agreement with the frequency of the N–N stretching mode ν(NN) in the IR spectrum (ca. 1790 cm^{-1}): Mn–N–N = 171.8 (8)°, N–N–C(aryl) = 125.6 (9)°, Mn–N = 1.693 (7) Å, N–N = 1.211 (8) Å. Both complexes **1** and **2** react with a variety of nucleophiles $X^- = Cl^-, Br^-, I^-, CN^-$, and SCN^- to form the dinitrogen complexes $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2)]$ (**3**) and $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2)]$ (**4**) in the first examples of dinitrogen complex formation from characterizable aryldiazenido complexes. Reactions of some other aryldiazenido complexes with nucleophiles have been investigated to determine whether this is a typical reaction for singly bent aryldiazenido ligands, but no additional examples have been found. Complex **1a** also reacts with PPh_3 to give initially the dinitrogen complex **3**, which is subsequently consumed through displacement of the N_2 by PPh_3 to give $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$.

Introduction

Since King and Bisnette's original synthesis of an isolable (aryldiazenido)metal compound,[1] numerous such compounds have been synthesized and a variety of geometries for the coordination of alkyl- and aryldiazenido ligands have become well established from X-ray structural determinations.[2,3] The 3d transition metals have, thus far, provided relatively few examples of organodiazenido complexes compared with the corresponding 4d and 5d metals, and these have been synthesized for only chromium,[4-6] manganese,[7-11] iron,[12-15] and cobalt.[14] Also it should be noted that there are many instances in which attempts to secure aryldiazenido complexes of 3d metals have failed, especially where metal carbonyl derivatives are involved. For example, King and Bisnette[1] were unable to obtain aryldiazenido derivatives with $[Mn(CO)_5]^-$, $[Co(CO)_4]^-$, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$, or $[V(CO)_6]^-$; $Cr(CO)_6$ is unreactive, whereas $Ni(CO)_4$, $Fe(CO)_5$, and $Co_2(CO)_8$ decompose with CO and N_2 evolution;[16] no stable complexes could be obtained with $[Ph_3SnFe(CO)_4]^-$,[14] $[(\eta^5\text{-}C_5H_4PPh_3)Cr(CO)_3]$,[17] or $[(\eta^5\text{-}C_5H_5)Ni(CO)]^-$;[14] and aryl complexes were among the products from reactions of $[KCo\{P(OMe)_3\}_4]$[18] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$.[19] These unpromising results may well have generated a certain reluctance toward continuing attempts to synthesize aryldiazenido compounds of the 3d row in view of the apparently more encouraging 4d and 5d metals. We believe that this is an incorrect reflection of the potential aryldiazenido chemistry of these elements. In the case of manganese, for example, it turns out that once suitable synthetic routes can be devised to attach the aryldiazenido group to the metal, complexes such as $[Mn(CO)_2(N_2Ph)(PPh_3)_2]$ and $[Mn(CO)_4N_2Ph]_2$ are reasonably stable,[7,8] despite the fact that previous attempts to synthesize them directly from $[Mn(CO)_5]^-$ were unsuccessful.[1,14] In an effort to extend the existing 3d metal chemistry of the aryldiazenido group, we have investigated the reactions of arenediazonium ions with (η^5-methylcyclopentadienyl)tricarbonylmanganese and its derivatives. One feature of particular interest in choosing this manganese compound for study was the existence of the well-characterized and stable dinitrogen complexes $[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2]$,[20,21] $[\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2N_2]$,[22] and $[\{(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2\}_2N_2]$.[22] This provided a good opportunity to examine the possible interconversion of dinitrogen and aryldiazenido ligands bound to manganese, and indeed we were to find that the singly bent aryldiazenido ligand in $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2R)]^+$ (R = aryl) (established by a single-crystal X-ray structure determination) is readily converted into a dinitrogen ligand in $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2)]$ by attack of various nucleophiles such as iodide. Similar chemistry has been subsequently found for the corresponding rhenium ion $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2R)]^+$.

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0020-1669/80/1319-2740$01.00/0

Table I. Infrared Data

compd	solvent[a]	$\nu(CO)$[b]	$\nu(NN)$[b]	$\nu'(NN)$[b]
$[MecpMn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (**1a**)	$CHCl_3$	2090 vs, 2045 vs	1795 vs	1715
	acetone	2083 vs, 2041 vs	*d*	
$[MecpMn(CO)_2(o\text{-}N_2C_6H_4F)][BF_4]$ (**1b**)	$CHCl_3$	2085 vs, 2042 vs	1792 vs	1712
	acetone	2080 vs, 2037 vs	*d*	
$[MecpMn(CO)_2(N_2Ph)][BF_4]$ (1c)	$CHCl_3$	2085 vs, 2038 vs	1790 s	1710
	acetone	2078 vs, 2032 vs	*d*	
$[MecpMn(CO)_2(p\text{-}N_2C_6H_4F)][BF_4]$ (1d)[c]	CH_2Cl_2	2093 vs, 2042 vs	1792 (1767)[e]	1712
$[cpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (2)	CH_2Cl_2	2090 vs, 2030 vs	1760	1730
	acetone	2082 vs, 2023 vs	*d*	

[a] Measured in AgCl cells; solutions react with alkali halide windows (see text). [b] Frequencies in cm^{-1}. Abbreviations: vs, very strong; s, strong; w, weak; br, broad; Mecp, $\eta^5\text{-}CH_3C_5H_4$; cp, $\eta^5\text{-}C_5H_5$; Ph, C_6H_5. ν' values are corrected (see ref 35). [c] Synthesized from $[MecpMn(CO)_2N_2]$ + $[N_2C_6H_4F][BF_4]$. [d] Band partly obscured by solvent absorption. [e] $\nu(^{15}N^{14}N)$.

Experimental Section

Diazonium tetrafluoroborates were synthesized by standard procedures from commercially available substituted anilines and were recrystallized from acetone–diethyl ether. All solvents were dried and purified by standard methods (tetrahydrofuran by contact with sodium and benzophenone) and distilled under nitrogen. Reactions and manipulations were carried out in standard Schlenkware, connected to a switchable inert atmosphere/vacuum supply, and were conducted under nitrogen or argon. (Methylcyclopentadienyl)tricarbonylmanganese (Ventron Alfa Products), triphenylsilane (Matheson Coleman and Bell), and decacarbonyldirhenium (Strem Chemicals) were used directly as purchased. Photochemical reactions were carried out at atmospheric pressure in a 200-mL Pyrex vessel equipped with a water-cooled quartz finger into which was placed a 200-W Hanovia Model 654 A 36 high-pressure mercury UV source. Nitrogen was flushed through the vessel prior to introduction of solvent and reagents, and a slow nitrogen flow was maintained during the reaction. Infrared spectra were recorded on Perkin-Elmer Models 437, 599B, and 237 (with an external recorder), calibrated against carbon monoxide or polystyrene. ^1H NMR spectra were recorded at 100 MHz by using a Varian XL-100 spectrometer and are reported in ppm relative to internal $SiMe_4$. Gas chromatograph–mass spectra were obtained by using a Hewlett-Packard Model 5985 GC-MS system equipped for chemical ionization and operating at 70 eV. Microanalyses were performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (1a). To a solution of $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3]$[23] (135 mg, 0.30 mmol) in 20 mL acetone was slowly added $[o\text{-}CF_3C_6H_4N_2][BF_4]$ (78 mg, 0.30 mmol), and the mixture was stirred for 1 h at room temperature. The color changed from yellow to deep red. The solution was evaporated in vacuo at room temperature to ca. 2 mL, Et_2O added carefully so as to precipitate only unreacted diazonium salt, and the mixture filtered under nitrogen. Cooling the clear red filtrate slowly to −12 °C (refrigerator) gave deep red-violet needle-shaped crystals in 18% yield; mp 114–115 °C. Anal. Calcd $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$: C, 40.03; H, 2.45; N, 6.22. Found: C, 39.70; H, 2.48; N, 6.20.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4F)][BF_4]$ (1b). This was synthesized analogously with **1a** by using $[o\text{-}FC_6H_4N_2][BF_4]$ (63 mg, 0.30 mmol) and stirring for 1.5 h. The solution changed from yellow to deep red-brown. After careful addition of Et_2O to precipitate unreacted diazonium salt, small deep red-brown air-sensitive crystals were obtained in 8% yield from the filtrate after 4 or 5 days at −78 °C; mp 117–118 °C (sealed capillary under vacuum). Anal. Calcd for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4F)][BF_4]$: C, 42.03; H, 2.75; N, 7.01. Found: C, 42.02; H, 2.75; N, 7.00.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2C_6H_5)][BF_4]$ (1c). This compound was synthesized similarly to **1a** by using $[C_6H_5N_2][BF_4]$ and stirring the reaction for 2.5 h. The color changed from yellow to brown. The IR spectrum of the solution showed the presence of (**1c**) (Table I), but no crystals of this compound could be obtained even from solutions kept at −78 °C for several days. Solutions were unstable and very air sensitive.

Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2THF]$ with $[o\text{-}N_2C_6H_4R'][BF_4]$ (R′ = CF_3, F, H). The tetrahydrofuran derivative $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2THF]$ was synthesized, following the published methods.[24] A solution of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ (2 mL, 0.0128 mol) in freshly distilled, pure tetrahydrofuran (150 mL) was irradiated for 1 h to give a deep red solution of the THF derivative [$\nu(CO)$ = 1930 (s), 1850 (s) cm^{-1}]. Addition of solid diazonium salts slowly to this solution at room temperature produced instantaneous vigorous gas evolution and the formation of yellow solutions in which no aryldiazenido complexes were present by IR. At low temperatures (−35 °C) gas evolution was not so vigorous, but again solutions became yellow and no aryldiazenido complexes could be obtained.

Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(C_8H_{14})]$ with $[o\text{-}N_2C_6H_4R'][BF_4]$ (R′ = CF_3, F, H). The cyclooctene derivative was prepared by irradiating the tricarbonyl (2.7 mL, 0.0173 mol) and cyclooctene (25 mL, 0.19 mol) in hexane (80 mL) for 4 h.[24] The deep yellow solution was filtered from the insoluble brown decomposition product and concentrated in vacuo (last traces at 80 °C) to give a dark brown oil containing the cyclooctene derivative [$\nu(CO)$ = 1968 (vs), 1907 (vs) cm^{-1}] and unreacted tricarbonyl [$\nu(CO)$ = 2022 (vs), 1947 (vs) cm^{-1}]. This oil was dissolved in hexane and a solution of the diazonium salt in acetone added at room temperature. A fast reaction occurred to give considerable gas evolution and a brown-red solution. The solution IR spectra showed the presence of the aryldiazenido complexes **1a–c** (as well as absorptions due to the tricarbonyl and unreacted cyclooctene derivative), but no success was achieved in isolating them as solids from these solutions.

Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ with $[o\text{-}N_2C_6H_4CF_3][BF_4]$. A solution of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ (0.1 mL, 0.64 mmol) in acetone (10 mL) was stirred at room temperature with $[o\text{-}N_2C_6H_4CF_3][BF_4]$ (166.4 mg, 0.64 mmol) for 3.5 h. The color of the solution changed from yellow to orange. The solution was concentrated under vacuum at room temperature to ca. 2 mL. Addition of diethyl ether precipitated a great amount of unreacted diazonium salt. The IR spectrum of the clear filtrate showed only the presence of the starting tricarbonyl complex.

Similar reactions were carried out at higher temperatures (up to 40 °C) or by changing the ratio tricarbonyl:diazonium salt to 1:2, but no spectroscopic evidence for the formation of aryldiazenido complexes was obtained.

$[(\eta^5\text{-}C_5H_5)Re(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (2). An excess of $[o\text{-}N_2C_6H_4CF_3][BF_4]$ was added to $[(\eta^5\text{-}C_5H_5)ReH(CO)_2SiPh_3]$[25] (55 mg) in 10 mL of dry acetone, and the mixture was stirred for 3 h at 65 °C. The solution became deep red-brown and was concentrated in vacuo to ca. 2 mL, and Et_2O was added carefully until most of the unreacted diazonium salt precipitated. The filtrate was diluted with toluene and left overnight at −78 °C. The aryldiazenido complex precipitated as an orange, air-stable microcrystalline solid in 30% yield. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$: C, 29.63; H, 1.59; N, 4.94. Found: C, 29.60; H, 1.63; N, 4.89.

Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (1a) with KI. To **1a** (100 mg) dissolved in dry acetone (10 mL) was added a 1:1 stoichiometric amount of finely ground solid KI, and the mixture

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was stirred at room temperature under argon. The progress of the reaction was followed by monitoring the ν(CO) region by IR solution spectroscopy (AgCl cells). When all **1a** was consumed (15 min), hexane (10 mL) was added to precipitate KBF_4 (identified by IR). The remaining clear pink solution was cooled to −78 °C to give two solvent phases; the lower (acetone) layer contained the bulk of the products and was separated.

The GC analysis of this solution showed two major peaks in addition to solvent. The constituents of each peak were examined by GC–mass spectroscopy. The first peak (shorter retention time) showed a parent ion at *m/e* 272 and a fragmentation pattern corresponding to *o*-$IC_6H_4CF_3$ [strongest five peaks (*m/e* (relative intensity)): $IC_6H_4CF_3^+$ (272 (100)), $C_6H_4CF_3^+$ (145 (89)), $C_6H_4F^+$ (95 (25)), CF_2^+ (50 (20)), CF_3^+ (69 (10))]. The second peak showed a parent ion at *m/e* 218 corresponding to the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2)]$ (**3**) and a fragmentation pattern: $[(CH_3C_5H_4)Mn(CO)_2(N_2)]^+$ (218 (24)), $[(CH_3C_5H_4)Mn(CO)_2]^+$ (190 (<1)), $[(CH_3C_5H_4)Mn(CO)]^+$ (162 (23)), $[(CH_3C_5H_4)Mn]^+$ (134 (100)), $CH_3C_5H_4^+$ (79 (28)), MnH^+ (56 (20)), Mn^+ (55 (49)). The IR spectrum of the same solution, or preferably the IR of a KBr disk of **1a** (to avoid solvent bands), showed ν(CO) 1970 (vs) and 1911 (vs) cm^{-1} and ν(NN) 2160 (vs) cm^{-1} due to **3** and absorptions due to $IC_6H_4CF_3$ (or $BrC_6H_4CF_3$). The latter was identified to be ortho by comparison of its IR spectrum with the standard IR spectra[46] of the ortho, meta, and para isomers; essentially the assignment was based on the bands at 1595, 1579, 1313, 1265 cm^{-1} and those in the region 800–600 cm^{-1} in the ortho isomer which are shifted, are absent, or are of different relative intensities in the other two isomers.

Similar reactions were carried out by using KBr, KCl, KCN, and KSCN, and the formation of the dinitrogen complex (**3**) in each case was monitored by using solution IR spectroscopy. In all cases, reactions occurred more quickly when an excess of potassium salt was used.

Synthesis of ^{15}N-Labeled 1d. The dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ (**3**) was prepared by stirring **1a** (50 mg, 0.11 mmol) with an excess of solid KI in acetone, as described before.

Labeled *p*-fluoro diazonium salt $[p\text{-}^{15}N^{14}NC_6H_4F][BF_4]$ was prepared from *p*-fluoroaniline and $Na^{15}NO_2$ (96% ^{15}N) and was allowed to react with the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ in situ. An instantaneous reaction took place, and the color of the solution changed from pink to deep red brownish. The solution was evaporated to dryness in vacuo at room temperature and the residue redissolved in CH_2Cl_2. The IR spectrum showed bands due to the labeled aryldiazenido complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(p\text{-}^{15}N^{14}NC_6H_4F)][BF_4]$ (**1d**-^{15}*N*): ν(CO) 2093, 2042 cm^{-1}; $\nu(^{15}N^{14}N)$ 1767 cm^{-1}. A sample of unlabeled **1d** showed ν(CO) at similar positions and ν(NN) 1792 cm^{-1}.

Reaction of $[(\eta^5\text{-}C_5H_5)Re(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (2) with KI. To **2** (30 mg) in dry acetone (10 mL) was added a 1:1 stoichiometric quantity of finely ground KI, and the mixture was stirred at room temperature. An IR spectrum of the supernatant liquid after 5 min showed almost complete conversion to the dinitrogen complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2)]$ (**4**) [ν(CO) 1960 (vs), 1898 (vs); ν(NN) 2142 (vs) cm^{-1}], which was further identified by MS: M^+ (334/336 (27)), $C_5H_5Re(CO)_2^+$ (306/308 (38)), $C_5H_5Re(CO)^+$ (278/280 (65)), C_5H_5Re (250/252 (100)), Re^+ (185/187 (24)). The solution was pumped to dryness and **4** sublimed in vacuo at room temperature as pale yellow crystals.[26]

Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (1a) with PPh_3. Complex **1a** (102 mg, 0.226 mmol) was dissolved in dry acetone (10 mL), solid triphenylphosphine (59 mg, 0.226 mmol) was added, and the solution was stirred at room temperature for 6 h. The color changed from deep red to yellow. The solution was concentrated in vacuo to ca. 2 mL and hexane added. Yellow crystals of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$ were deposited at −12 °C. Alternatively, the product could be precipitated easily with water. It was identified by comparison with an authentic sample synthesized by published methods.[27] Anal. Calcd for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$ (**5**): C, 69.04; H, 4.87. Found: C, 69.17; H, 4.90. IR (acetone): ν(CO) 1938 (vs), 1875 (vs) cm^{-1}. ^{1}H NMR (acetone-d_6): 1.91 (s, 3 H, CH_3), 4.12 (m, 2 H, C_5H_4), 4.27 (m, 2 H, C_5H_4), 7.41 (m, 15 H, Ph).

Table II. Crystal and X-Ray Data for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (**1a**)

formula: $C_{15}H_{11}BF_7MnN_2O_2$
M_r: 449.7
cryst system: orthorhombic
space group: *Fdd*2, C_{2v}^{19}, No. 43
unit cell dimens: $a = 12.866$ (3) Å; $b = 56.605$ (11) Å; $c = 9.964$ (2) Å; $V = 7256.6$ Å^3; $Z = 16$
cryst dimens: 0.16 mm × 0.11 mm × 0.31 mm
$\rho_o = 1.65$ (1) g cm^{-3} (by flotation)
$\rho_c = 1.653$ g cm^{-3}
$\lambda(\text{Mo K}\alpha_1) = 0.709\,26$ Å
$\mu(\text{Mo K}\alpha) = 5.14$ cm^{-1}
$T = 295 \pm 2$ K
reflctns = 1318 ($h, k, l \geq 0$; $2\theta < 45°$)
obsd reflctns ($I > 2.3\sigma_I$) = 1019
total parameters = 208
$R = 0.055$
$R_w = 0.053$

When the progress of the reaction was monitored by solution IR spectroscopy, the growth and subsequent decay of absorptions at 1970, 1911 [ν(CO)], and 2160 cm^{-1} [ν(NN)] were observed attributable to the dinitrogen complex **3**. This intermediate was separated as follows and identified by IR and GC–MS. The reaction was stopped after 30 min (corresponding to maximum observed concentration of **3**) and the solution chromatographed under nitrogen on a cellulose column prepared in benzene. An orange-yellow fraction was eluted with benzene, which contained the dinitrogen complex **3** and the triphenylphosphine derivative **4** (IR). This fraction was rechromatographed on silica gel prepared and eluted with benzene. The eluate contained only **4**, while the dinitrogen complex **3** remained at the top of the column as a red-orange band. This was subsequently removed by elution with acetone.

X-ray Structure Determination of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (1a). From a sample recrystallized from acetone–diethyl ether, a well-formed single crystal in the form of a parallelepiped of dimensions 0.16 × 0.11 × 0.31 mm was selected for photography and data collection, mounted along the long morphological axis (*c*) on a thin glass fiber. Oscillation, Weissenberg, and precession photographs revealed the following systematic absences: hkl [$h + k$, $k + l$, $(l + h) = 2n + 1$]; $0kl$ [$k + l = 4n + 1$, $4n + 2$, $4n + 3$ (k, $l = 2n + 1$)]; $h0l$ [$h + l = 4n + 1$, $4n + 2$, $4n + 3$ (h, $l = 2n + 1$)]. This allowed the space group to be unambiguously assigned as the orthorhombic group *Fdd*2.

Accurate cell dimensions were obtained by a least-squares analysis of the setting angles of 11 strong reflections with $2\theta > 25°$, which were accurately centered on a computer-controlled Picker FACS-1 four-circle diffractometer equipped with a scintillation detector with pulse-height discrimination, using graphite-monochromatized Mo Kα_1 radiation. Crystal data are given in Table II. The intensities of 1318 unique reflections having $3° < 2\theta \leq 45°$ were measured with the crystal in a general orientation by using a θ–2θ scan operating at 2° min^{-1}. The scan range was from 0.7° below the Kα_1 position to 0.7° above Kα_2. Stationary-crystal, stationary-counter background counts were measured for 20 s at each scan limit. Two standard reflections were measured after every 50 data and showed no evidence of sample decomposition. Intensities were corrected for Lorentz and polarization effects, but not for absorption.

The *x* and *y* parameters for the manganese atom were determined from the three-dimensional Patterson synthesis, the *z* coordinate being set arbitrarily at 0.25. A Fourier synthesis phased by this model revealed the location of most of the nonhydrogen atoms ($R = 0.29$). An electron density difference Fourier map at this stage showed density in the vicinity of the CF_3 group which was interpreted as an alternative rotational orientation of the fluorine atoms. In further refinement a disordered model was adopted in which the F atoms of the original orientation (F(1)–F(3)) were assigned a population parameter of 0.7 and those in the second orientation (F(4)–F(6)) 0.3. Subsequent refinement supported this assignment by producing similar average temperature factors for the fluorine atoms in each orientation. The manganese atom, the cyclopentadienyl carbon atoms, oxygens O(1) and O(2), the fluorine atoms of the BF_4^- group, and those located in the major CF_3 orientation required anisotropic temperature factors in further refinement. The hydrogen atoms of both arene rings were

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Table III. Final Atomic Coordinates and Thermal Parameters[a]

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
Mn	0.28658 (12)	0.54128 (2)	0.75000 (–)	*b*	C(12)	0.4065 (9)	0.5236 (2)	0.6406 (13)	*b*
C(1)	0.1780 (10)	0.5324 (2)	0.8549 (13)	55 (3)	C(13)	0.4510 (8)	0.5423 (2)	0.7119 (10)	*b*
O(1)	0.1115 (7)	0.5266 (2)	0.9244 (10)	*b*	C(14)	0.4327 (10)	0.5374 (2)	0.8505 (12)	*b*
C(2)	0.2023 (10)	0.5382 (2)	0.6014 (13)	59 (3)	C(15)	0.5128 (12)	0.5629 (3)	0.6557 (16)	75 (4)
O(2)	0.1523 (6)	0.5364 (1)	0.5070 (11)	*b*	F(1)	0.2554 (19)	0.6411 (5)	0.6664 (20)	*b*
N(1)	0.2779 (6)	0.5709 (1)	0.7728 (9)	43 (2)	F(2)	0.3442 (13)	0.6640 (2)	0.7804 (13)	*b*
N(2)	0.2819 (6)	0.5922 (1)	0.7776 (9)	44 (2)	F(3)	0.3943 (11)	0.6312 (2)	0.7020 (14)	*b*
C(3)	0.2637 (7)	0.6059 (2)	0.8912 (10)	36 (3)	F(4)	0.2574 (27)	0.6619 (6)	0.7381 (34)	98 (10)
C(4)	0.2394 (8)	0.5955 (2)	1.0106 (13)	55 (3)	F(5)	0.3998 (29)	0.6444 (7)	0.7501 (43)	106 (12)
C(5)	0.2170 (11)	0.6093 (2)	1.1265 (14)	75 (4)	F(6)	0.2484 (32)	0.6368 (8)	0.6279 (45)	98 (14)
C(6)	0.2226 (11)	0.6337 (2)	1.1115 (15)	77 (4)	B	−0.1463 (13)	0.5422 (3)	0.7489 (27)	78 (4)
C(7)	0.2504 (8)	0.6441 (2)	0.9953 (15)	62 (3)	F(7)	−0.1510 (8)	0.5225 (1)	0.8147 (10)	*b*
C(8)	0.2734 (8)	0.6307 (2)	0.8810 (11)	41 (3)	F(8)	−0.2222 (8)	0.5440 (2)	0.6539 (11)	*b*
C(9)	0.3111 (10)	0.6419 (2)	0.7544 (17)	60 (3)	F(9)	−0.0550 (8)	0.5478 (2)	0.6876 (13)	*b*
C(10)	0.3796 (10)	0.5164 (2)	0.8615 (14)	*b*	F(10)	−0.1564 (13)	0.5598 (2)	0.8371 (14)	*b*
C(11)	0.3602 (8)	0.5083 (2)	0.7321 (17)	*b*					

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	398 (7)	292 (7)	449 (8)	14 (8)	25 (9)	−29 (9)
O(1)	79 (6)	87 (6)	97 (8)	−8 (5)	38 (6)	1 (6)
O(2)	80 (6)	102 (7)	87 (6)	28 (5)	−43 (6)	−37 (7)
C(10)	70 (9)	57 (8)	55 (9)	4 (7)	16 (8)	15 (7)
C(11)	43 (7)	23 (5)	106 (12)	10 (5)	16 (8)	5 (8)
C(12)	51 (8)	43 (7)	52 (8)	9 (6)	0 (7)	−17 (7)
C(13)	30 (6)	39 (6)	45 (8)	10 (5)	0 (5)	−7 (6)
C(14)	60 (9)	74 (10)	38 (8)	23 (7)	−9 (7)	−4 (7)
F(1)	217 (20)	259 (25)	91 (13)	−184 (18)	−117 (14)	110 (16)
F(2)	163 (12)	36 (5)	115 (11)	−66 (7)	16 (10)	−7 (6)
F(3)	116 (10)	73 (7)	95 (11)	21 (8)	57 (8)	26 (8)
F(7)	160 (9)	79 (6)	159 (9)	−31 (6)	−39 (7)	59 (6)
F(8)	141 (9)	142 (9)	137 (8)	2 (7)	−44 (8)	58 (8)
F(9)	141 (9)	136 (9)	176 (12)	−39 (7)	35 (9)	−6 (8)
F(10)	308 (18)	141 (10)	163 (12)	−74 (10)	68 (13)	−23 (9)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
H(1)	0.487 (8)	0.563 (2)	0.568 (10)	75	H(7)	0.456	0.548	0.922	58
H(2)	0.500 (7)	0.576 (2)	0.725 (10)	75	H(8)	0.238	0.578	1.015	55
H(3)	0.596 (9)	0.561 (2)	0.643 (10)	75	H(9)	0.199	0.602	1.209	75
H(4)	0.360	0.510	0.944	58	H(10)	0.207	0.643	1.187	79
H(5)	0.323	0.495	0.712	59	H(11)	0.255	0.661	0.992	63
H(6)	0.408	0.522	0.545	50					

[a] Thermal parameters are ×10^4 for Mn and ×10^3 for others. [b] Anisotropic temperature factors in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$ are given in the second section of this table.

included at calculated positions (C–H = 0.95 Å) in structure factor calculations, and a subsequent difference Fourier map revealed the positions of the methyl group hydrogens. The thermal parameters of the hydrogen atoms were set equal to those of the carbon atoms to which they are attached. The methyl group hydrogen positions were refined.

Though the structure is nonenantiomorphic, the absolute configuration was determined by refining the alternative model in which the sign of all atomic coordinates was inverted. A Hamilton R factor test[28] revealed that the new configuration improved the model at more than the 95% confidence level, so this configuration was adopted in final refinement. The refinement converged to $R = 0.055$ ($R_w = 0.053$) with the final cycle having all shift-to-error ratios less than 0.1. The final electron-difference map was featureless with no peaks or troughs greater than 4σ (σ = 0.12 e Å^{-3}). The quantity minimized in refinement was $\sum w(|F_o| - |F_c|)^2$, where w is a weighting factor of the form $w = 1/\sigma_F^2$. Neutral scattering factors were employed[29] and an anomalous dispersion correction[30] was applied to manganese. The computer programs used have been cited elsewhere.[31] The atom labeling scheme is shown in Figure 1 and the packing of the unit cell in Figure 2. Final atomic coordinates and thermal parameters are given in Table III, interatomic distances and angles in Table IV, and least-squares planes and dihedral angles in Table V. Observed and calculated structure factors are given in Table VI, and a stereoview of the cation is given in Figure 3.

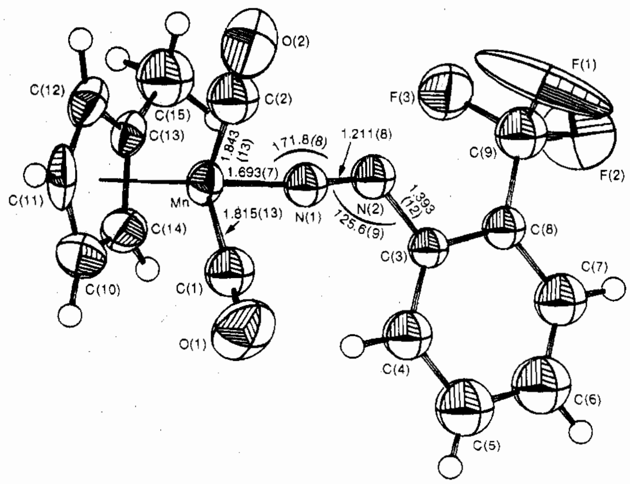

Figure 1. A general view of the cation in [(η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_2$(o-N$_2$C$_6$H$_4$CF$_3$)][BF$_4$] (**1a**) with atom labeling.

Results and Discussion

Synthesis. Direct substitution of a carbonyl group in (η^5-CH$_3$C$_5$H$_4$)Mn(CO)$_3$ is normally quite difficult unless it

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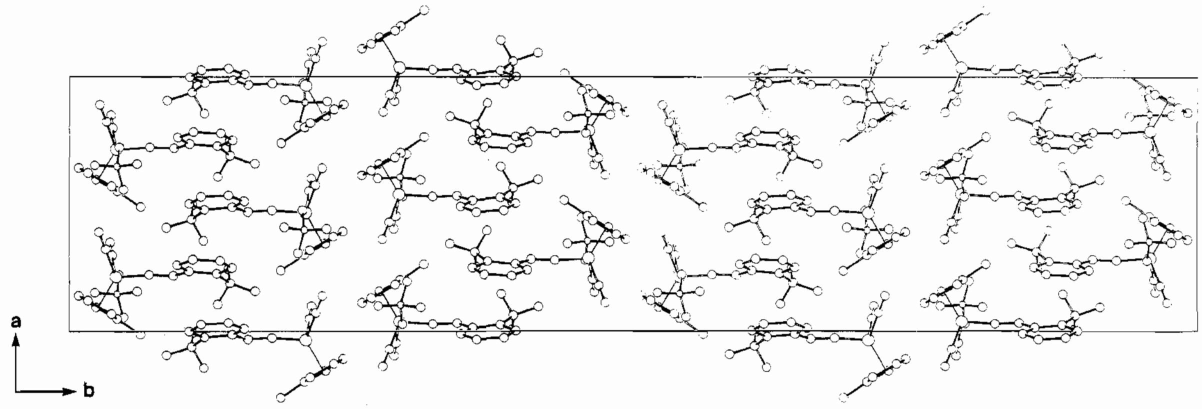


Figure 2. Projection of the unit-cell packing in the structure of $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2(o\text{-N}_2\text{C}_6\text{H}_4\text{CF}_3)][\text{BF}_4]$ (**1a**).

Table IV. Selected Interatomic Distances in Angstroms and Angles in Degrees for $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2(o\text{-N}_2\text{C}_6\text{H}_4\text{CF}_3)][\text{BF}_4]$

(a) Distances

Mn-C(1)	1.815 (13)	C(10)-C(14)	1.374 (17)	
Mn-C(2)	1.843 (13)	C(11)-C(12)	1.391 (16)	
Mn-N(1)	1.693 (7)	C(12)-C(13)	1.401 (14)	
Mn-C(10)	2.155 (13)	C(13)-C(14)	1.428 (16)	
Mn-C(11)	2.104 (9)	C(13)-C(15)	1.516 (17)	
Mn-C(12)	2.139 (11)	C(1)-O(1)	1.150 (12)	1.196 (16)[a]
Mn-C(13)	2.150 (10)	C(2)-O(2)	1.144 (14)	1.191 (17)
Mn-C(14)	2.141 (12)	C(9)-F(1)	1.133 (22)	1.319 (27)
N(1)-N(2)	1.211 (8)	C(9)-F(2)	1.337 (16)	1.413 (16)
N(2)-C(3)	1.393 (12)	C(9)-F(3)	1.345 (14)	1.375 (19)
C(3)-C(4)	1.366 (15)	C(9)-F(4)	1.332 (26)	1.360 (34)
C(3)-C(8)	1.408 (13)	C(9)-F(5)	1.151 (35)	1.191 (39)
C(4)-C(5)	1.425 (16)	C(9)-F(6)	1.525 (44)	1.550 (46)
C(5)-C(6)	1.391 (16)	B-F(7)	1.296 (21)	1.371 (22)
C(6)-C(7)	1.349 (17)	B-F(8)	1.364 (22)	1.428 (24)
C(7)-C(8)	1.404 (15)	B-F(9)	1.361 (19)	1.431 (22)
C(8)-C(9)	1.495 (17)	B-F(10)	1.334 (23)	1.455 (25)
C(10)-C(11)	1.392 (17)			

(b) Angles

Mn-N(1)-N(2)	171.8 (8)	C(5)-C(6)-C(7)	122.8 (13)
Mn-C(1)-O(1)	177.7 (12)	C(6)-C(7)-C(8)	120.9 (10)
Mn-C(2)-O(2)	178.2 (12)	C(7)-C(8)-C(9)	121.4 (10)
N(1)-Mn-C(1)	98.3 (5)	C(3)-C(8)-C(9)	121.0 (10)
N(1)-Mn-C(2)	99.3 (5)	C(10)-C(11)-C(12)	108.8 (10)
N(1)-Mn-C(10)	127.8 (5)	C(10)-C(14)-C(13)	109.1 (11)
N(1)-Mn-C(11)	156.9 (4)	C(11)-C(10)-C(14)	107.6 (11)
N(1)-Mn-C(12)	125.4 (4)	C(11)-C(12)-C(13)	108.4 (11)
N(1)-Mn-C(13)	93.5 (4)	C(12)-C(13)-C(14)	106.0 (11)
N(1)-Mn-C(14)	95.5 (4)	C(12)-C(13)-C(15)	127.5 (10)
N(1)-N(2)-C(3)	125.6 (9)	C(14)-C(13)-C(15)	126.4 (10)
N(2)-C(3)-C(4)	120.3 (8)	C(8)-C(9)-F(1)	115.5 (14)
N(2)-C(3)-C(8)	118.7 (9)	C(8)-C(9)-F(2)	109.7 (12)
C(1)-Mn-C(2)	89.1 (6)	C(8)-C(9)-F(3)	113.3 (11)
C(1)-Mn-C(10)	87.2 (5)	F(1)-C(9)-F(2)	112.7 (16)
C(1)-Mn-C(11)	98.7 (5)	F(1)-C(9)-F(3)	100.7 (20)
C(1)-Mn-C(12)	136.0 (5)	F(2)-C(9)-F(3)	104.1 (12)
C(1)-Mn-C(13)	150.1 (5)	F(7)-B-F(8)	112.4 (16)
C(1)-Mn-C(14)	112.3 (5)	F(7)-B-F(9)	117.8 (15)
C(2)-Mn-C(10)	132.8 (6)	F(7)-B-F(10)	107.8 (20)
C(2)-Mn-C(11)	96.5 (6)	F(8)-B-F(9)	106.8 (19)
C(2)-Mn-C(12)	88.3 (5)	F(8)-B-F(10)	109.4 (15)
C(2)-Mn-C(13)	116.1 (5)	F(9)-B-F(10)	101.9 (15)
C(2)-Mn-C(14)	151.9 (5)	C(4)-C(3)-C(8)	121.0 (10)
C(3)-C(4)-C(5)	121.0 (9)	C(3)-C(8)-C(7)	117.6 (10)
C(4)-C(5)-C(6)	116.6 (12)		

[a] Values in this column are corrected for riding motion.

Table V. Deviations from Least-Squares Planes Calculated and Dihedral Angles for $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2(o\text{-N}_2\text{C}_6\text{H}_4\text{CF}_3)][\text{BF}_4]$[a]

(a) Planes

1. Plane through C(10), C(11), C(12), C(13), and C(14)

$-0.8590x + 0.5089y - 0.0425z - 10.3269 = 0\ (\chi^2 = 6.73)$

C(10)	−0.015	C(11)	0.018	C(12)	−0.014
C(13)	0.005	C(14)	0.007	C(15)	−0.064
Mn	1.777				

2. Plane through C(3), C(4), C(5), C(6), C(7), and C(8)

$-0.9640x + 0.0381y - 0.2633z + 4.3257 = 0\ (\chi^2 = 12.44)$

C(3)	0.024	C(4)	−0.012	C(5)	−0.008
C(6)	0.015	C(7)	−0.003	C(8)	−0.017
N(1)	0.082	N(2)	0.066		

(b) Angles between Planes

no.	planes	dihedral angle, deg
1	Mn-N(1)-N(2) N(1)-N(2)-C(3)	145 (5)
2	N(1)-N(2)-C(3) N(2)-C(3)-C(4)	0 (2)
2	N(1)-N(2)-C(3) N(2)-C(3)-C(8)	−179 (1)

[a] Deviations of atoms from the planes are given in angstroms.

is UV irradiated, and in agreement we found no direct reaction between the tricarbonyl and diazonium salts. Irradiation of the tricarbonyl in the presence of diazonium salts cannot be used because it causes decomposition of the diazonium ion itself, with N_2 evolution. Instead, three derivatives of the tricarbonyl were synthesized by UV irradiation in the presence of the appropriate ligand, and each was subsequently reacted with the diazonium ion either in situ or after separation and purification; these were $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2\text{L}]$ (L = tetrahydrofuran (THF) or cyclooctene)[24] and $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{MnH(CO)}_2\text{SiPh}_3]$.[23] Reaction of the THF derivative in situ proceeded with copious gas evolution, and no aryldiazenido complex could be isolated. It is possible that decomposition of the product, or of the diazonium salt itself, is being catalyzed by secondary photochemical products in solution since the aryldiazenido complex **1** is quite stable in THF. Difficulty was experienced in isolating and purifying the liquid cyclooctene derivative, but the crude material containing tricarbonyl as the main impurity reacted rapidly with diazonium ion again with gas evolution, and this time the aryldiazenido complex was observed by IR spectroscopy to be clearly present in solution. However, it could not be isolated. Finally, reaction of $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{MnH(CO)}_2\text{SiPh}_3]$ with diazonium salts was successful in producing the aryldiazenido complexes **1a–c** according to eq 1. Similarly, $(\eta^5\text{-C}_5\text{H}_5)\text{Re(CO)}_3$ did not react with diazonium salts, but the aryldiazenido

$$[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{MnH(CO)}_2\text{SiPh}_3] + [o\text{-N}_2\text{C}_6\text{H}_4\text{R}'][\text{BF}_4] \rightarrow \underset{\mathbf{1}}{[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(CO)}_2(o\text{-N}_2\text{C}_6\text{H}_4\text{R}')][\text{BF}_4]} + \text{HSiPh}_3$$

$$\text{R}' = \textbf{(a)}\ \text{CF}_3,\ \textbf{(b)}\ \text{F},\ \textbf{(c)}\ \text{H} \qquad (1)$$

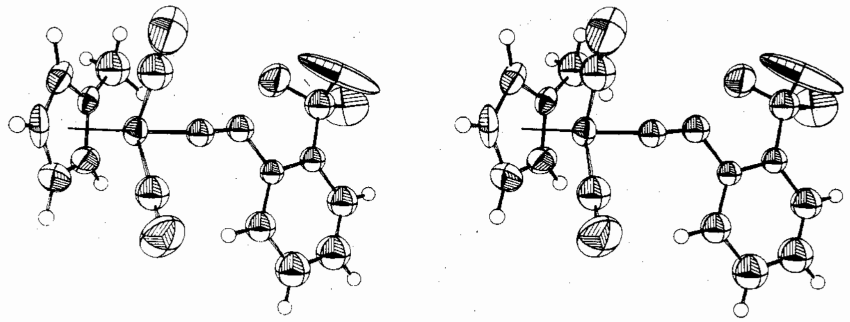


Figure 3. Stereoview of the cation in $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (**1a**).

complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2(o\text{-}N_2C_6H_5CF_3)][BF_4]$ (**2**) was readily synthesized from $[(\eta^5\text{-}C_5H_5)ReH(CO)_2SiPh_3]$.[25] The reaction and the stability of the product **1** is very dependent upon the nature of the substituent R′. With R′ = CF_3 (**1a**), the reaction is moderately rapid and clean, and the product is easily obtained as an air-stable, red-violet crystalline solid, solutions of which can be handled in air for brief periods. With R′ = F (**1b**), the product is an air-sensitive, red-brown solid, less stable and difficult to crystallize. With R′ = H (**1c**) it is very air sensitive and unstable; solutions become rapidly darker and ν(CO) IR bands disappear, with the result that it could not be isolated from solution without decomposition, even at low temperature. With $[p\text{-}CH_3OC_6H_4N_2][BF_4]$ there was obvious reaction, but monitoring the solution by IR showed the absence of any new ν(CO) bands. If an aryldiazenido complex is formed initially, this must decompose quickly with loss of CO and N_2.

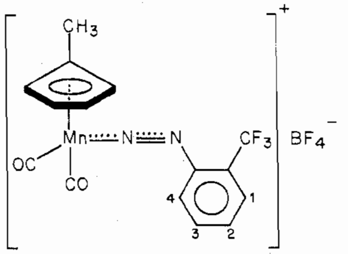
In their study of the substitution of $HSiPh_3$ by PPh_3 in $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3]$, Graham and co-workers concluded that the 16-electron intermediate $[(\eta^5\text{-}CH_3C_5H_4)\text{-}Mn(CO)_2]$ is formed by loss of $HSiPh_3$ and subsequently binds PPh_3.[32] This is probably true also for the $[N_2R]^+$ substitution (eq 2). However, another possibility which has to be considered is "insertion" of the diazonium ion into the Mn–H bond to give a coordinated diazene moiety Mn–N(H)=NR, followed by elimination of $HSiPh_3$ across the Mn–N bond. The insertion step is a frequently[33,34] observed reaction of hydrido complexes with diazonium ions, and indeed Haymore[8] observed $[Mn(NHNPh)(CO)_3(PPh_3)_2]^+$ production in reacting $[PhN_2]^+$ with $[MnH(CO)_3(PPh_3)_2]$. The fact that we observed **1a** to be formed starting with the cyclooctene derivative implies that a hydride insertion route is not a *requisite* for formation of **1**, but of course we cannot on this evidence rule it out as a possible mechanism when the reaction was started with the hydridotriphenylsilyl derivative instead.

$$[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3] \underset{+HSiPh_3}{\overset{-HSiPh_3}{\rightleftharpoons}} [(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2] \xrightarrow{[N_2R]^+} [(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2R)]^+ \quad (2)$$

The infrared spectra of **1a–c** exhibit two ν(CO) and one ν(NN) absorptions near 2085, 2040, and 1790 cm^{-1}, respectively (Table I). The ν(CO) absorptions are at a higher value than those of the hydridotriphenylsilyl complex (ν(CO): 1983, 1926 cm^{-1}), attributable to the charge on the complex (see below) and the replacement of $HSiPh_3$ by the strongly π-accepting aryldiazenido ligand; they, and ν(NN), are also somewhat higher than corresponding bands in the 3d metal complex cation in $[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)][BF_4]$.[12] The yield of aryldiazenido complex was considered too low to warrant synthesis of the ^{15}N isotopically substituted derivative by this route, to confirm the ν(NN) assignment. It was instead prepared by displacement of dinitrogen from $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ (**3**; vide infra) by $[p\text{-}FC_6H_4{}^{14}N^{15}N][BF_4]$ whereupon $\nu(^{14}N^{15}N)$ occurred at 1767 cm^{-1} compared with 1792 cm^{-1} for $\nu(^{14}N^{14}N)$. This value for the ν(NN) stretching frequency is indicative of a singly bent aryldiazenido ligand, whether or not adjusted according to the empirical rules suggested by Haymore and Ibers[35] (Table I). This assertion has been shown to be correct by a determination of the crystal structure of the (α,α,α-trifluorotolyl)diazenido complex **1a**, as discussed below.

The ν(CO) and ν(NN) positions appear not to be very sensitive to the substituent R′ in the few examples we have studied (Table I). The high values of both may be partly accounted for by the positive charge on the complexes, resulting in decreased back-bonding from the metal to the CO and N_2R groups compared with that of similar neutral compounds. This is well substantiated by the pair of complexes $[Fe(CO)_2(N_2Ph)(PPh_3)_2]^+$ [ν(CO) 2038, 1978; ν(NN) 1724 cm^{-1}] and $[Mn(CO)_2(N_2Ph)(PPh_3)_2]$ [ν(CO) 1925, 1849; ν(NN) 1612, 1543, 1476 cm^{-1}],[8,12] and the present compound may be compared with the neutral analogue $[(\eta^5\text{-}C_5H_5)Cr(CO)_2(N_2Ph)]$ [ν(CO) 1996, 1930; ν(NN) 1570 cm^{-1}].[6] With the assumption of no effect of the different arenes, a comparison of ν(CO) for complexes **1** with values for $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]^+$ [ν(CO) 2096, 2049 cm^{-1}][36,37] shows how closely similar are NO and N_2R ligands in their π-acceptor properties in these compounds, with NO probably just slightly the better.[35]

The ^1H NMR spectrum of **1a** (R′ = CF_3) in $CDCl_3$ shows no unusual features, confirming that this complex is relatively stable in solution; resonances occur at δ 2.05 (s, 3 H, CH_3), 5.74 (2 H, C_5H_4), and 5.76 (2 H, C_5H_4) plus three poorly resolved multiplets tentatively assigned as 7.66 (2 H, $H_{2,3}$), 7.95 (1 H, H_4), and 8.30 (1 H, H_1) in structure I.



I

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Table VII. Some Bond Distances (Å) and Angles (Deg) for Singly Bent Aryldiazenido Complexes[a]

compd	M-N	N-N	N-C	M-N-N	N-N-C
$[Mo(S_2CNMe_2)_3(m\text{-}N_2C_6H_4NO_2)]$[b]	1.770 (6)	1.262 (9)	1.410 (10)	170.6 (6)	117.9 (7)
$[OsH(CO)(PPh_3)_2(N_2C_6H_5)]$[c]	1.867 (6)	1.211 (8)	1.460 (10)	171.1 (6)	118.5 (7)
$[ReCl_2(PPhMe_2)_3(N_2C_6H_5)]$[d]	1.77 (2)	1.23 (2)	1.43 (2)	173 (2)	119 (2)
$[Mo(S_2CNMe_2)_3(N_2C_6H_5)]$[b]	1.781 (4)	1.233 (6)	1.417 (7)	171.5 (4)	120.5 (5)
$[Mo(HB(pz)_3)(CO)_2(N_2C_6H_5)]$[e]	1.825 (4)	1.211 (6)	1.43 (2)	174.2 (1)	121.2 (2)
$[Fe(CO)_2(PPh_3)_2(N_2C_6H_5)][BF_4]$[f]	1.702 (6)	1.201 (7)	1.404 (8)	179.2 (5)	124.2 (6)
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$[g]	1.693 (7)	1.211 (8)	1.393 (12)	171.8 (8)	125.6 (9)
$[RuCl_3(PPh_3)_2(p\text{-}N_2C_6H_4CH_3)]\cdot S$[h]	1.784 (5)	1.158 (6)	1.376 (6)	171.9 (5)	137.1 (5)
$[RuCl_3(PPh_3)_2(p\text{-}N_2C_6H_4CH_3)]\cdot S$[i]	1.796 (9)	1.144 (10)	1.40 (1)	171.2 (9)	135.9 (11)

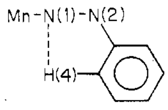
[a] Abbreviations: Ph, C_6H_5; Me, CH_3; pz, $C_3H_3N_2$; M, metal; S, solvent. [b] Reference 43a. [c] Reference 38. [d] Reference 44. [e] Reference 43b. [f] Reference 13. [g] This work. [h] S = CH_2Cl_2; reference 35. [i] S = Me_2CO; reference 42.

Description of the Crystal Structure of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (1a). The structure consists of discrete complete cations and tetrafluoroborate anions, with the geometry of the cation being of the "piano-stool" type. A perspective view of the cation, with the more relevant bond distances and angles, is shown in Figure 1. The carbonyl ligands are essentially linear, as expected, with Mn-C-O angles averaging 178 (1)°. The cyclopentadienyl ring deviates little from statistical planarity and the average Mn-C(cyclopentadienyl) distance is 2.138 (16) Å; the methyl group is displaced somewhat out of the mean plane in a direction away from the metal atom and the other ligands. The $[BF_4]^-$ anion is reasonably well-behaved, and this anion appears to be more or less isolated in the crystal lattice and not engaged in unusually significant interactions with the surrounding atoms. The shortest of these contacts are between the fluorine atoms and phenyl or cyclopentadienyl hydrogen atoms and are in the range 2.42–2.81 Å.

The main feature of interest in the cation is the aryldiazenido ligand, and this clearly adopts the "singly bent" geometry in agreement with the observed N-N stretching frequency described above. The Mn-N(1)-N(2) angle is 171.8 (8)°, and the angle N(1)-N(2)-C(3) is 125.6 (9)°, suggesting a hybrid orbital description approximating to sp at N(1) and sp^2 at N(2). The angle at N(1) is small for a singly bent aryldiazenido ligand and may be compared with the value 171.1 (6)° observed for $[OsH(CO)(N_2Ph)(PPh_3)_2]$.[38] However, the simpler associated ligands present in our complex (especially the absence of bulky triphenylphosphine ligands) appear to cause little crowding, so it does not seem that the deviation of this angle from 180° is a result of steric effects but more likely reflects competition among the different ligands for manganese d electrons and the lack of any molecular symmetry requirement that this angle should necessarily conform to the 180° sp value. The short Mn-N(1) distance (1.693 (7) Å), comparable to that observed in the nitrosyl complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)(PPh_3)]$[39] (1.674 (5) Å), indicates substantial multiple-bond character arising from d_π–p_π bonding between the manganese d orbitals and the π system of the aryldiazenido group. A typical Mn-N single bond length would be about 2.1 Å (ref 40). This is, in fact, the shortest metal-nitrogen distance yet observed for a singly bent aryldiazenido ligand (Table VII) and is comparable with the distance in $[Fe(CO)_2(N_2Ph)(PPh_3)_2][BF_4]$ (1.702 (6) Å).[13] This also reflects the small effective covalent radius of 3d transition metals (ca. 1.17 Å for Mn and Fe single-bond radii)[41] and the positive charge on these complex ions.

Considering now the geometry of the aryldiazenido group itself, the dihedral angles between the planes formed by N(1)-N(2)-C(3) and N(2)-C(3)-C(4) (0°) and by N(1)-N(2)-C(3) and N(2)-C(3)-C(8) (179°) show that the benzene ring and the diazo function are almost coplanar which allows maximum π conjugation throughout the Mn-N-N-aryl network. The dihedral angle is also small in $[OsH(CO)(N_2Ph)(PPh_3)_2]\cdot CH_2Cl_2$ (6°),[38] $[Fe(CO)_2(N_2Ph)(PPh_3)_2]^+$ (6°),[13] $[RuCl_3(p\text{-}N_2C_6H_4CH_3)(PPh_3)_2]$ (3°),[35,42] $[Mo(N_2Ph)(S_2CNMe_2)_3]$ (6°),[43a] and $[Mo(m\text{-}N_2C_6H_4NO_2)(S_2CNMe_2)_3]$ (4°, 6°),[43a] but it is ca. 20° in $[Mo(HB(pz)_3)(CO)_2(N_2Ph)]$.[43b]

Although the number of structurally determined singly bent aryldiazenido compounds is still not large, Table VII shows that most have angle N(1)-N(2)-C(aryl) close to the sp^2 value of 120° but that the iron and manganese compounds exhibit a small opening of this angle (to ca. 125°) which is increased further in the ruthenium complex (ca. 136°). We wondered whether the 125° angles are adopted to prevent an abnormally short N(1)···H(4) contact (structure II), which might result from the planarity of the aryldiazenido group. The observed contact in **1a** is 2.51 Å, but if the angle at N(2) were reduced to 120°, we calculate that it would become 2.40 Å. Whether this is unreasonably short we cannot say for sure, but the N(1)···H(4) contacts are much larger than this in those structures with N(2) angles of ca. 120° (ca. 2.66–2.95 Å), and in the iron and ruthenium complexes (2.63 and 2.78 Å, respectively). Clearly, the N(1)···H(4) contact is extremely sensitive to changes in individual N-N, N-C, and C-C bond lengths. The number of examples is small, but when these bond distances are short and would otherwise cause a rather close N(1)···H(4) contact, there appears to be a tendency for the angle at N(2) to open (rather than a twist about the C-N bond) which presumably best maintains the π conjugation in the Mn-N-N-aryl system. In the ruthenium compound, however, there appears to be an additional, electronic effect since we calculate that reducing the angle from 136 to 120° would produce a contact of ca. 2.5 Å, which is probably not prohibitively short.



II

Chemical Reactions of the Aryldiazenido Ligand. The complexes **1** and **2** are remarkable, and so far unique among aryldiazenido complexes, in being extremely susceptible to

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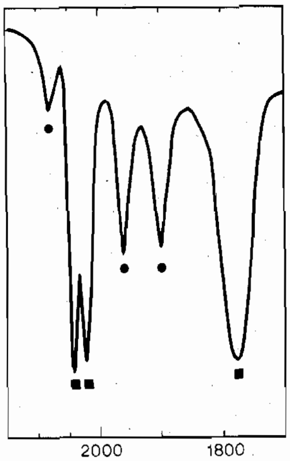


Figure 4. IR spectrum (■) of the aryldiazenido complex (**1a**) taken in a KBr disk, showing absorptions (●) due to the dinitrogen complex (**3**).

attack at the aryldiazenido ligand by nucleophiles such as iodide to give stable dinitrogen complexes[45] (eq 3).

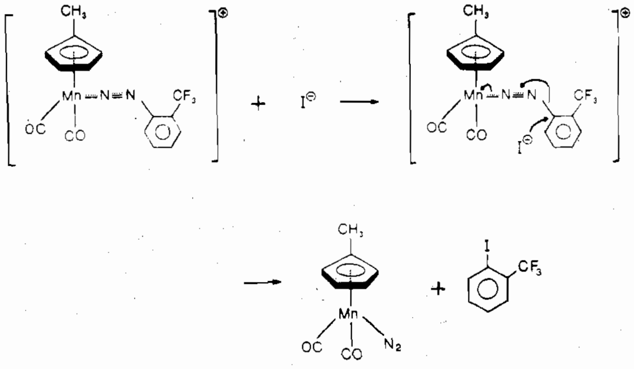
$$[(\eta^5\text{-}ZC_5H_4)M(CO)_2(N_2C_6H_4R')]^+ + X^- \rightarrow [(\eta^5\text{-}ZC_5H_4)M(CO)_2N_2] + XC_6H_4R' \quad (3)$$

$$M = Mn, Re;\ Z = H, Me$$

Correspondingly, these reactions represent the first synthesis of a dinitrogen complex from an organodiazenido complex. They are accomplished simply by stirring an acetone solution of **1** or **2** with solid potassium halide at room temperature. The reaction even occurs in the solid state since in the time taken to run a sample prepared as a KBr disk in the usual way, the IR spectrum shows quite intense absorptions due to the dinitrogen complex (Figure 4). Although the original reactions were carried out under nitrogen, identical results were obtained by using an argon atmosphere, showing that the aryldiazenido ligand is the source of the nitrogen. By comparison with the previous syntheses of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2)]$[20,21] and $[(\eta^5\text{-}C_5H_5)Re(CO)_2(N_2)]$,[26] which require high nitrogen pressure or oxidation of a hydrazine derivative at low temperature, this reaction is particularly easy and convenient. The rhenium compound reacts faster than the manganese, and the rate of reaction with nucleophiles follows the order $I^- > Br^- > CN^- > SCN^- > Cl^-$. It should be noted that this is the first synthesis of the mononuclear methylcyclopentadienyl complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2)]$ (**3**). Previously, despite the existence of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2)]$ the methylcyclopentadienyl analogue was only known as the binuclear complex $[(\eta^5\text{-}CH_3C_5H_4)(CO)_2Mn(\mu\text{-}N_2)Mn(CO)_2(\eta^5\text{-}CH_3C_5H_4)]$.[22]

The products of the KI reaction were unambiguously characterized by GC–mass spectroscopy of the solution. The GC spectrum showed only two major components other than solvent, one (with a shorter retention time) having a mass spectrum with a parent ion at $m/e = 272$ corresponding to $o\text{-}IC_6H_4CF_3$ and the other a parent ion at $m/e = 218$ corresponding to the dinitrogen complex (**3**). The possibility that this species might be the tricarbonyl, which also has $m/e = 218$, can be ruled out since the fragmentation pattern of **3** differed in detail from that of the authentic tricarbonyl and of course the infrared spectrum is quite different. The substituents in the iodo(trifluoromethyl)benzene were shown to be ortho by comparing the IR spectrum with published spectra for the ortho, meta, and para isomers.[46] The products are exactly those that would be expected to occur as a result of direct nucleophilic displacement at carbon as shown in Scheme I. It is interesting to compare this with the reaction of the corresponding nitrosyl complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(NO)][PF_6]$ with KI in acetone, where it is observed that attack occurs at the metal atom, with evolution of CO, to produce $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(NO)I]$.[47] In our case, we could not detect any gas evolution visually and found no GC–MS or IR evidence for the formation of the corresponding unknown species $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(N_2R)I]$. Our result is also quite different from previous instances in which iodide and other anionic nucleophiles have reacted with 18-electron carbonylaryldiazenido complexes. The result in some of these has been to coordinate the nucleophile to the metal as a 2-electron donor, which can be accomplished by a rearrangement of the singly bent (3-electron) N_2R ligand to the doubly bent (1-electron) geometry, e.g., $[Ru(CO)_2(PPh_3)_2(N_2R)]^+$ to $[Ru(CO)_2(PPh_3)_2(N_2R)(I)]$.[48] Depending upon the stability of this six-coordinate species, this may be followed by displacement of one CO group to give the five-coordinate 18-electron complex in which diazo ligand has again assumed the singly bent (3-electron) structure, as in $[Ru(CO)(PPh_3)_2(N_2R)(I)]$ (but not the corresponding osmium complex).[48] In related instances in which CO loss occurs immediately such as the reaction of $[Fe(CO)_2(PPh_3)_2(N_2R)][BF_4]$ with $[Ph_3P{=}N{=}PPh_3][I]$ to give $[Fe(CO)(PPh_3)_2(N_2R)I]$,[49] the six-coordinate dicarbonyl intermediate is probably formed but is too short-lived to be detected. We have reinvestigated the reaction of iodide with these and some other complexes in the hope of finding evidence for the alternative nucleophilic attack at the aryldiazenido group. So that the situations would be comparable, we used the $o\text{-}N_2C_6H_4CF_3$ group throughout, but the results are all negative: $[Ru(CO)_2(PPh_3)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ did not react with KI in acetone or CH_2Cl_2 but did so with LiI in methanol only to give the same complexes as observed by Haymore and Ibers;[48] $[Fe(CO)_2(PPh_3)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ and KI in acetone gave only the iodide salt metathesis product observed before;[12,49] and $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(o\text{-}N_2C_6H_4CF_3)]$ showed no reaction with KI in acetone. At the present time, the factors responsible for the prevalence of nucleophilic displacement at carbon in the manganese and rhenium complexes, and the features to be looked for in seeking other examples, are not very clear. It seems that requirements may be a positive charge on the complex and a relatively high $\nu(NN)$ value (ca. 1750 cm^{-1} or greater) and also that arene ligands are preferable to PPh_3. Thus, the aryldiazenido groups in $[Fe(CO)_2(PPh_3)_2(N_2R)]^+$

Scheme I



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and $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2R)]^+$ really are spectroscopically and dimensionally quite similar but ν(NN) in the manganese case is noticeably higher (1790 vs. 1720 cm^{-1}), as are ν(CO) values (ca. 2090, 2040 vs. 2030, 1980 cm^{-1}), suggesting that the $CH_3C_5H_4$ ligand causes the metal to be poorer at back-bonding to the CO and N_2R groups, thereby raising the electrophilicity of the N_2R group. The phenyls of the PPh_3 ligand may also hinder reaction by partially shielding the N_2R group. On the other hand, the molybdenum compound is neutral and has the lowest ν(NN) and ν(CO) values among these compounds so the N_2R group is not expected to be so electrophilic. We know of only two reports of halide reactions with other aryldiazenido complexes which have ν(NN) greater than ca. 1750 cm^{-1}. $[IrCl(PPh_3)_2(N_2Ph)][PF_6]$ (ν(NN) 1868 cm^{-1}) reacted with LiCl to give $[IrCl_2(PPh_3)_2(N_2Ph)]$; this is to be expected for a 16-electron complex and evidently occurs in preference to the nucleophilic displacement which would have given the known dinitrogen complex $[IrCl(N_2)(PPh_3)_2]$.[50,51] More interestingly, the dipositive ruthenium complex $[RuCl(bpy)_2(p\text{-}N_2C_6H_4OCH_3)][PF_6]_2$ (ν(NN) 2095 cm^{-1})[52] has been reported to evolve N_2 with excess KI at 60 °C to give $[Ru(bpy)_2I_2]$ and $p\text{-}IC_6H_4OCH_3$. This is explained if nucleophilic displacement is occurring, but also substitution of iodide for the N_2 ligand in the resulting dinitrogen complex occurs under these conditions.[53]

Triphenylphosphine reacts with **1a** to give the known[27] triphenylphosphine complex **5** almost quantitatively (eq 4).

$$\underset{\mathbf{1a}}{[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)]^+} + PPh_3 \rightarrow \underset{\mathbf{5}}{[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2PPh_3]} + \text{organic products} \quad (4)$$

But this reaction is not a simple substitution of the N_2R^+ group by PPh_3. Following the reaction by monitoring the ν(CO) region using solution IR spectroscopy (AgCl cells) showed that the dinitrogen complex **3** was formed, first, and reached maximum concentration after about 30 min, after which it was slowly consumed while new peaks at 1938 and 1875 cm^{-1} due to the triphenylphosphine complex **5** systematically increased in intensity, as illustrated in Figure 5. There was no evidence of any peak in the spectra near 2280 cm^{-1} which would be the position of ν(NN) in the free diazonium ion if it was formed in detectable concentration. The presence of the dinitrogen complex **3** as an intermediate was further confirmed by separating it from the PPh_3 complex **5** by column chromatography and characterizing it by GC–MS and IR spectroscopy. When the reaction was allowed to proceed until all of **1a** and **3** had been consumed and then examined by GC–MS, it was evident that several products were present, some of which appeared to be decomposing on the GC column. The only products positively identified were **5**, $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$ (a decomposition product of the dinitrogen complex **3**), and $C_6H_5CF_3$. By comparison with the reactions of X^- discussed above, it might be suggested that PPh_3 reacts with **1a** by attacking carbon to produce the phosphonium ion $[o\text{-}CF_3C_6H_4PPh_3]^+$ and the dinitrogen complex **3**, which then reacts with further PPh_3 to give **5**. However, this is not supported by several observations. First, the triphenylphosphine complex is formed almost quantitatively from equimolar amounts of **1a** and PPh_3, while in 1:2 stoichiometric reactions 1 equiv of triphenylphosphine remains in excess. Second, we have not been able to isolate the hypothetical phosphonium salt but have shown separately that no reaction occurs between a phosphonium salt such as $[Ph_4P]Br$ and the dinitrogen complex **3** so that it is unlikely that the hypothetical $[o\text{-}CF_3C_6H_4PPh_3]^+$ itself is capable of contributing to the yield of **5** by reaction with **3** (and if this did occur one would expect $[\eta^5\text{-}CH_3C_5H_4Mn(CO)_2\{PPh_2(o\text{-}C_6H_4CF_3)\}]$ to be another product). Third, the formation of $C_6H_5CF_3$ and the observation that acrylamide is polymerized when added to the reaction suggest a radical mechanism.

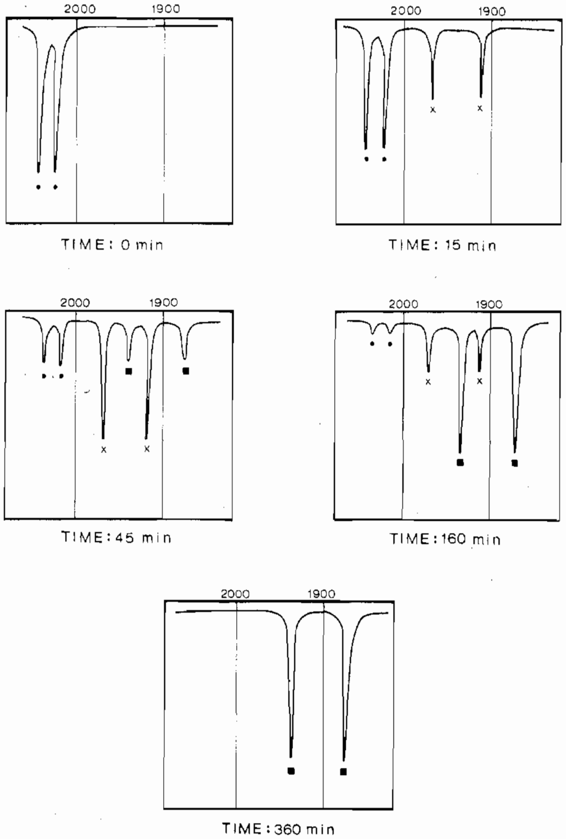

Figure 5. IR spectra, at different intervals of time, of the reaction between $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (**1a**) and PPh_3 (only the carbonyl region is shown): (●) ν(CO), corresponding to the starting material $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)]^+$ (**1a**); (×) ν(CO), corresponding to the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2N_2]$ (**3**); (■) ν(CO) corresponding to the triphenylphosphine derivative $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(PPh_3)]$ (**5**).

It is evident to us that these manganese and rhenium complexes exhibit interesting and unusual reactivity of their aryldiazenido ligands, and we are currently investigating the mechanisms in more detail, examining the reactions with a wider variety of nucleophiles, and seeking further examples of aryldiazenido complexes possessing this type of behavior.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada through operating grants. We are grateful to Drs. W. A. G. Graham and J. K. Hoyano for kindly communicating their synthesis of triphenylsilane derivatives of rhenium prior to publication, to the University of Concepcion, Concepcion, Chile, for a leave of absence (C.F.B.-P.), and to Dr. L. Prizant for preliminary synthetic work.

Registry No. **1a**, 73838-50-3; **1b**, 73838-52-5; **1c**, 73838-54-7; **1d**-^{15}N, 73838-56-9; **2**, 73838-58-1; **3**, 73838-59-2; **4**, 36543-62-1; **5**, 12100-95-7; $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3]$, 32628-49-2; $[(\eta^5\text{-}$

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(53) An alternative interpretation pointed out to us by Professor Meyer is the 1-electron reduction $M\text{–}N_2Ar^+ + I^- \rightarrow M\text{–}N_2Ar\cdot + {}^1/_2I_2$ followed by $M\text{–}N_2Ar\cdot \rightarrow M\text{–}N_2 + Ar\cdot$ or $M\text{–}N_2Ar\cdot \rightarrow M + N_2 + Ar\cdot$. The reaction of **1** with I^- does not appear to involve this route since when it is conducted in the presence of ferrocene or acrylamide, no ferricinium ion or polyacrylamide is formed. However, these are formed in the case of **1** + PPh_3.

$CH_3C_5H_4)Mn(CO)_2(C_8H_{14})]$, 12184-53-1; $[(\eta^5\text{-}C_5H_5)ReH(CO)_2SiPh_3]$, 62598-40-7; *o*-$IC_6H_4CF_3$, 444-29-1; $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3]$, 12108-13-3; $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2THF]$, 51922-84-0; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; CN^-, 57-12-5; SCN^-, 302-04-5; **1d**, 73838-61-6; [*o*-$CF_3C_6H_4N_2$][BF_4], 447-59-6; [*o*-$FC_6H_4N_2$][BF_4], 446-46-8; [$C_6H_5N_2$][BF_4], 369-57-3; [$N_2C_6H_4$-F][BF_4], 459-45-0; [*p*-$^{15}N^{14}NC_6H_4F$][BF_4], 73838-07-0.

Supplementary Material Available: Table VI, observed and calculated structure factors for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (**1a**) (10 pages). Ordering information is given on any current masthead page.

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Molecular Distortions in Sterically Congested Organometals. Crystal Structure of Bis(2,4,6-tri-*tert*-butylphenyl)mercury

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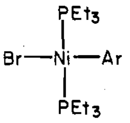
Received December 18, 1979

(2,4,6-Tri-*tert*-butylphenyl)mercury chloride has been prepared and symmetrized to the title compound by treatment with metallic copper in pyridine. The structure of this sterically congested bis(aryl)mercury compound III, including the location of all of the hydrogen atoms, has been determined by an X-ray diffraction study at −155 °C. In contrast to those of coplanar diphenylmercury, the two aromatic rings in the present study lie perpendicular to one another, and moreover the molecule shows considerable distortion from idealized D_{2d} symmetry. A description of the distortions present in the molecule was developed from idealized molecular parameters. The observed distortions are attributed to nonbonded H···H and H···Hg interactions. The extent of such contacts was assessed by means of idealized methyl groups generated with d_{C-H} = 1.08 Å.

Introduction

Ortho substituents are known to exert a profound influence on the chemistry of arylmetal compounds. An early demonstration of such an effect was provided by Chatt and Shaw,[2] who showed that the *o*-tolylnickel complex, Ia, is completely air stable. In contrast, the phenyl analogue Ib rapidly decomposes in air. More recently, an extensive series of mesityl transition-metal derivatives which exhibit remarkable stability have been prepared by Stolze and by Seidel and co-workers.[3]



$$Br{-}\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Ni}}{-}Ar$$

Ia, Ar = *o*-tolyl
b, Ar = phenyl

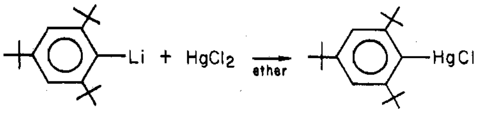
In light of these effects and because of our continuing interest in steric effects on chemical reactivity,[4] we decided to examine the chemistry of arylmetal derivatives with larger ortho substituents. The 2,4,6-tri-*tert*-butylphenyl ligand was chosen for this study since the preparation of the corresponding bromide[5] and its conversion to an aryllithium derivative[6] had previously been reported. We found that both monoaryl- and diarylmercury compounds could be prepared, containing the tri-*tert*-butylphenyl substituent. However, structural characterization of the diaryl derivative shows it to be a severely distorted molecule as a result of intramolecular steric strain. The nature of the strain and the resultant distortion is presented in this study.

Table I. Bonded Distances in Angstroms for the Nonhydrogen Atoms in Bis(tri-*tert*-butylphenyl)mercury (III)

Hg(1)	C(1)	2.077 (6)	C(12)	C(121)	1.566 (9)
Hg(1)	C(7)	2.083 (6)	C(21)	C(22)	1.518 (9)
C(1)	C(2)	1.450 (9)	C(21)	C(23)	1.535 (10)
C(1)	C(6)	1.420 (8)	C(21)	C(24)	1.540 (10)
C(2)	C(3)	1.398 (10)	C(41)	C(42)	1.515 (10)
C(2)	C(21)	1.560 (9)	C(41)	C(43)	1.524 (11)
C(3)	C(4)	1.402 (9)	C(41)	C(44)	1.550 (10)
C(4)	C(5)	1.399 (9)	C(61)	C(62)	1.537 (10)
C(4)	C(41)	1.508 (9)	C(61)	C(63)	1.538 (9)
C(5)	C(6)	1.401 (9)	C(61)	C(64)	1.537 (10)
C(6)	C(61)	1.539 (9)	C(81)	C(82)	1.528 (10)
C(7)	C(8)	1.474 (9)	C(81)	C(83)	1.516 (10)
C(7)	C(12)	1.395 (9)	C(81)	C(84)	1.554 (9)
C(8)	C(9)	1.399 (9)	C(101)	C(102)	1.527 (10)
C(8)	C(81)	1.533 (9)	C(101)	C(103)	1.540 (11)
C(9)	C(10)	1.392 (9)	C(101)	C(104)	1.536 (11)
C(10)	C(11)	1.388 (9)	C(121)	C(122)	1.537 (9)
C(10)	C(101)	1.533 (9)	C(121)	C(123)	1.520 (10)
C(11)	C(12)	1.414 (9)	C(121)	C(124)	1.550 (10)

Results

(2,4,6-Tri-*tert*-butylphenyl)mercury chloride, II, was prepared by reaction of the corresponding lithium reagent[6] with mercuric chloride (eq 1). II is a white solid which was insoluble in hexane and CCl_4 and had only limited solubility in chloroform and benzene. Conversion of II to bis(2,4,6-tri-



(1)

II

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