the reaction was allowed to warm to room temperature. Bubbling was observed upon warming, and after 1 day the evolved gases were collected by Toepler pump and identified by GC as hydrogen (0.023 mmol). In the glovebox, the solids were extracted with toluene until the extract was no longer visibly green. The yield of $U(C_8H_8)_2$ was determined spectrophotometrically by using the 615-nm absorption (0.0134 mmol, 3%).

B. C_5H_6. In a reaction conducted as described above, a portion (0.335 g, ca. 0.85 mmol U present) of the solid product of a 4/1 t-C_4H_9Li/UCl_4 reaction was reacted with excess freshly distilled C_5H_6. Vigorous bubbling occurred when the reaction was warmed to room temperature. After overnight stirring, H_2 (0.14 mmol) was collected. The IR spectra of the solids exhibited bands at 1010 and 750 cm^{-1}.

C. Terminal Alkynes. Reactions of the black product of a 4/1 t-C_4H_9Li/UCl_4 reaction with 3,3-dimethyl-1-butyne and with 1-hexyne were also investigated briefly. 3,3-Dimethyl-1-butyne reacted to form a brown THF-soluble oil which exhibited an alkynide stretching absorption at 2030 cm^{-1} in the IR. Gas evolution was qualitatively monitored in a 1-hexyne reaction, and a pressure increase was observed upon reaction. The rather intractable products were not further characterized.

Reaction of the 1-Equiv Product with NaC_5H_5. Synthesis of U-$(C_5H_5)_3$(THF). UCl_4 (1.14 g, 3 mmol) was reacted with t-C_4H_9Li (0.192 g, 3 mmol) in 30 mL of hexane in a Schlenk flask as described above for Schlenk reactions. The black solid product was separated by filtration and extracted with THF to form a deep purple solution. NaC_5H_5 (0.79 g, 9 mmol) was added to the THF solution, causing an immediate color change to deep brown. The mixture was stirred overnight, the THF was removed by rotary evaporation, and the dark

brown residue was extracted with benzene. Removal of solvent from this solution left a brown, free-flowing powder which was characterized by IR and ^1H NMR spectroscopy, complexometric metal analysis, and quantitative deuterolytic decomposition as $U(C_5H_5)_3$(THF) (0.65 g, 42%).

Catalysis. A portion (0.264 g, ca. 0.67 mmol U present) of the solid black product of a 4/1 t-C_4H_9Li/UCl_4 reaction and 3-hexyne (5 mL, 44 mmol) were placed in a calibrated test tube (70.1 mL) fitted with a greaseless high-vacuum stopcock in the glovebox. The vessel was attached to a high-vacuum line, evacuated, and filled with hydrogen (1 atm). The pressure drop was monitored and the hydrogen replenished. A rate of 10^{-3} turnover/min was observed. The reaction was terminated at 15 turnovers, and the liquid products were analyzed by GC. A 3-hexene/hexane ratio of 20 was found with cis-3-hexene, the predominant isomer (90%). Deuterolysis of the residue after the catalysis gave 0.2 equiv of HD and 0.41 equiv of D_2/equiv of uranium.

The catalytic hydrogenation of 1-hexene to 1-hexane was similarly effected by a 4/1 t-C_4H_9Li/UCl_4 reaction product at a rate of 2.5 $\times 10^{-3}$ turnover/min. The reaction was terminated after 20 turnovers.

X-ray Evidence for C–H Bond Activation and C–C Bond Formation in the Cyclopentadienylmanganese Tricarbonyl Series: Peculiar CO Insertion, Formation, and Expansion of Alicyclic Rings in Friedel–Crafts Reactions with *tert*-Butyl Chloride

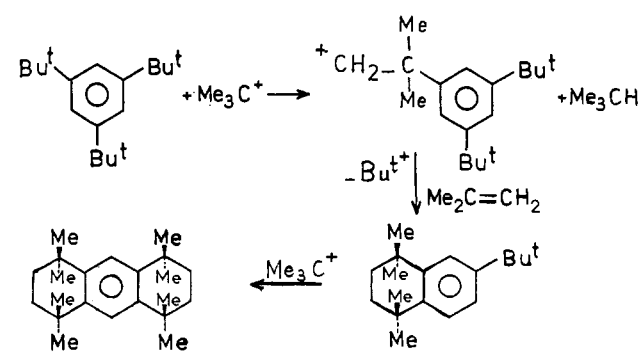M. P. BALEM,[1a] M. LE PLOUZENNEC,*[1a] and M. LOUËR[1b]

The reaction of $CpMn(CO)_3$ (CMT) with t-BuCl and $AlCl_3$ in CH_2Cl_2 gives a series of CMT complexes with one or two t-Bu substituents and/or one or two CO-t-Bu groups on the Cp ring and three complexes in which the Cp is substituted by both alicyclic rings (of various sizes) and CO-t-Bu-groups. The reaction products result from alicyclic ring formation and expansion and "CO insertion" into a Cp–t-Bu bond; but this latter process does not occur starting with t-BuCMT. Friedel–Crafts acylations of $CpMn(CO)_3$ also provide analogous mixtures of complexes, which indicates that the formation of cyclized products only occurs if the Cp ring is substituted by an acyl group. The crystal and molecular structure of one of these reaction products, the methyl ester of (6,7-($\alpha,\alpha,\delta,\delta$-tetramethylcyclohexene)cymantrenoyl)propanoic acid (**12a**, Scheme III), has been resolved. It crystallizes in the space group $P2_1/n$ with cell dimensions $a = 7.996$ (3) Å, $b = 25.00$ (1) Å, $c = 10.486$ (4) Å, $\beta = 96.18$ (2)°, and $Z = 4$. Refinement based on 1237 observed ($I \geq 3\sigma(I)$) diffractometer data converged at $R = 0.059$ and $R_w = 0.068$. Small but significant disparities are observed in Mn–C_{Cp} distances.

Introduction

A peculiar side process[2] in the reaction of t-BuCl with 1,4-di- and 1,3,5-tri-*tert*-butylbenzene (and also presumably with benzene itself) is the formation of a cyclized compound outlined in Scheme I.

Among aromatics complexed to metal carbonyls, few are susceptible to extensive Friedel–Crafts chemistry, the cyclopentadienylmanganese tricarbonyl (cymantrene or CMT) series being one of the most reactive.[3] The above process has not been observed starting with $C_6H_6Cr(CO)_3$[4] or ferrocene.[5]

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Scheme I

No study on such a reactivity of cymantrene has ever been noted; therefore, we intended to study its reaction with *tert*-butyl chloride under the Friedel–Crafts conditions. A very

particular reactivity was then observed which led us to extend our studies to other acylated complexes such as acetyl and benzoyl chlorides and succinic anhydride. In this paper, we describe these reactions together with the X-ray structure of one of the reaction products, the methyl ester of (6,7-($\alpha,\alpha,$-δ,δ-tetramethylcyclohexene)cymantrenoyl)propanoic acid (**12a**, Scheme III) in order to provide unambiguous evidence for alicyclic ring formation.

Experimental Section

General Information. Infrared spectra were recorded on a Pye Unicam LTD spectrometer: cells NaCl (1 mm); solvent CCl$_4$. ^{1}H NMR spectra were run on a Varian A60A spectrometer (60 MHz: temperature 38 °C; solvent CDCl$_3$; internal standard Me$_4$Si; chemical shifts reported as δ downfield from internal standard. Mass spectra were recorded on a Varian MAT 311 double-focusing spectrometer operating at 70 eV. Chromatographic separations were performed on thick-layer (1-mm) plates of silica gel G. Merck with a 1:2 mixture of diethyl ether and hexane as eluent unless otherwise noted. R_f's were ascertained by thin-layer chromatography using silica gel C. Merck plates (0.3 mm) and a 1:2 mixture of diethyl ether and hexane as eluent. All experiments were carried out in the dark under dry oxygen-free nitrogen. Solvents were carefully purified, dried, and stored under nitrogen.

Alkylation of Cymantrene by *tert*-Butyl Chloride. A 4-g (30-mmol) sample of fine powder of aluminum chloride was added to a solution of 2.3 g (25 mmol) of *tert*-butyl chloride in 30 mL of anhydrous dichloromethane. After 20 min of stirring at room temperature, a solution of 2 g (10 mmol) of cymantrene (**1**) in 30 mL of dry dichloromethane was added dropwise; the reaction mixture was refluxed at 45 °C for an additional 4 h and then allowed to cool and be hydrolyzed by 10 mL of 10 N HCl and 100 g of ice. After removal of the solvent in vacuo, the residual oil was dissolved in diethyl ether. This solution was washed with water and dried on magnesium sulfate, and the solvent removed similarly. The residue was chromatographed onto preparative silica plates: a first elution with hexane gave compounds **1** (160 mg), **2**, and **3**; then, with a 1:2 mixture of diethyl ether and hexane, compounds **4-8** were obtained.

{η^5-[4-(*t*-Bu)]Cp}Mn(CO)$_3$ (**2**): 0.65 g (25% yield); oil; R_f (eluent = hexane) 0.59; mass spectrum m/e 260 (M$^+$, C$_{12}$H$_{13}$MnO$_3$); IR (cm^{-1}, CCl$_4$) 2040 (sh, m), 1945 (wd, s) (C≡O); ^{1}H NMR (CDCl$_3$) δ 1.18 (s, 9 *H*, *t*-Bu), 4.62 (t, 2 H, (Cp), 4.87 (t, 2 H, Cp).

{η^5-[4,6-(*t*-Bu)$_2$]Cp}Mn(CO)$_3$ (**3**): 0.63 g (20% yield); yellow crystals; mp 68 °C (recrystallization from hexane); R_f (eluent = hexane) 0.67; mass spectrum m/e 316 (M$^+$, C$_{16}$H$_{21}$MnO$_3$); IR (cm^{-1}, CCl$_4$) 2040 (sh, m), 1945 (wd, s) (C≡O); ^{1}H NMR (CDCl$_3$) δ 1.18 (s, 18 H, *t*-Bu), 4.62 (d, 2 H, Cp), 4.87 (t, 1 H, Cp).

{η^5-[4-(CO-*t*-Bu)]Cp}Mn(CO)$_3$ (**4**): 0.29 g (10% yield); oil; R_f 0.54; mass spectrum m/e 288 (M$^+$, C$_{13}$H$_{13}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2050 (sh, s), 1965 (m), 1950 (m) (C≡O), 1680 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.37 (s, 9 H, *t*-Bu), 4.83 (d, 2 H, Cp), 5.46 (d, 2 H, Cp).

{η^5-[4-(CO-*t*-Bu)]Cp}Mn(CO)$_3$ (**5**): 0.24 g (7% yield); oil; R_f 0.70; mass spectrum m/e 344 (M$^+$, C$_{17}$H$_{21}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2050 (sh, s), 1960 (m), 1945 (m) (C≡O), 1680 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.24 (t, 18 H, *t*-Bu), 4.86 (m, 1 H, Cp), 5.28 (m, 1 H, Cp), 5.43 (m, 1 H, Cp).

{η^5-[4-(CO-*t*-Bu)-6,7-(CMe$_2$(CH$_2$)$_2$CMe$_2$)]Cp}Mn(CO)$_3$ (**6**): 0.20 g (5% yield); oil; R_f 0.73; mass spectrum m/e 398 (M$^+$, C$_{21}$H$_{25}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2045 (sh, s), 1955 (m), 1940 (m) (C≡O), 1680 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.33 (s, 9 H, *t*-Bu), 1.26 (s, 12 H, Me in the alicyclic ring), 1.40 (m, 4 H, CH$_2$ in the alicyclic ring), 5.23 (s, 2 H, Cp).

{η^5-[4-(CO-*t*-Bu)-6,7-(CMe$_2$(CH$_2$)$_3$CMe$_2$)]Cp}Mn(CO)$_3$ (**7**): 0.08 g (2% yield); oil; R_f 0.76; mass spectrum m/e 412 (M$^+$, C$_{22}$H$_{27}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2045 (sh, s), 1955 (m), 1940 (m) (C≡O), 1680 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.35 (s, 9 H, *t*-Bu), 1.23 (s, 12 H, Me in the alicyclic ring), 1.43 (m, 6 H, CH$_2$ in the alicyclic ring) 5.23 (s, 2 H, Cp).

{η^5-[4-(CO-*t*-Bu)-6,7-(CMe$_2$(CH$_2$)$_4$CMe$_2$)]Cp}Mn(CO)$_3$ (**8**): traces; mass spectrum m/e 426 (M$^+$, C$_{23}$H$_{29}$MnO$_4$).

Acylation of *tert*-Butylcymantrenes. 1. Acylation by Succinic Anhydride. Succinoylation performed with 10 mmol (3.16 g) of **3**, 20 mmol (2 g) of succinic anhydride, and 40 mmol (5.3 g) of aluminum chloride followed a procedure close to that of the cymantrene. The mixture of acids isolated from the crude reaction mixture by extraction

with 20% aqueous Na$_2$CO$_3$ followed by acidification of the aqueous layer with 10 N HCl and extraction with diethyl ether was esterified with a diethyl ether solution of diazomethane in excess before chromatography on preparative silica plates.

{η^5-[4-(CO(CH$_2$)$_2$CO$_2$Me)]Cp}Mn(CO)$_3$ (**9a**)[7]: 0.35 g (11% yield).

{η^5-[4-(CO(CH$_2$)$_2$CO$_2$Me)-6-(*t*-Bu)]Cp}Mn(CO)$_3$ (**10a**): 0.93 g (25% yield); oil; R_f 0.55; mass spectrum m/e 374 (M$^+$, C$_{17}$H$_{19}$MnO$_6$); IR (cm^{-1}, CCl$_4$) 2050 (sh, s), 1960 (sh, m), 1950 (sh, s) (C≡O), 1965 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 9 H, *t*-Bu), 2.73 (m, 4 H, CH$_2$), 3.70 (s, 3 H, Me), 5.00 (m, 1 H, Cp), 5.33 (m, 1 H, Cp), 5.50 (m, 1 H, Cp).

{η^5-[4-(CO(CH$_2$)$_2$CO$_2$Me)-5,7-(*t*-Bu)$_2$]Cp}Mn(CO)$_3$ (**11a**): 0.21 g (5% yield); oil; R_f 0.78; mass spectrum m/e 430 (M$^+$, C$_{21}$H$_{27}$MnO$_6$); IR (cm^{-1}, CCl$_4$) 2040 (sh, s), 1945 (wd, s) (C≡O), 1705 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 9 H, *t*-Bu), 1.28 (s, 9 H, *t*-Bu), δ(CH$_2$) 2.76 (m, 4 H, CH$_2$), 3.70 (m, 3 H, Me), 5.03 (m, 1 H, Cp), 5.33 (m, 1 H, Cp).

{η^5-[4-(CO(CH$_2$)$_2$CO$_2$Me)-6,7-(CMe$_2$(CH$_2$)$_2$CMe$_2$)]Cp}Mn(CO)$_3$ (**12a**): 0.64 g (15% yield); yellow crystals; mp 95 °C (recrystallization from hexane); R_f 0.61; mass spectrum m/e 428 (M$^+$, C$_{21}$H$_{25}$MnO$_6$); IR (cm^{-1}, CCl$_4$) 2040 (sh, s), 1955 (wd, s), 1940 (wd, s) (C≡O), 1965 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 12 H, Me in the alicyclic ring), 1.50 (s, 4 H, CH$_2$ in the alicyclic ring), 2.73 (m, 4 H, CH$_2$ in the side chain), 3.70 (s, 3 H, Me in the side chain), 5.30 (s, 2 H, Cp).

{η^5-[4-(CO(CH$_2$)$_2$CO$_2$Me)-6,7-(CMe$_2$(CH$_2$)$_3$CMe$_2$)]Cp}Mn(CO)$_3$ (**13a**): 0.31 g (7% yield); oil; R_f 0.67; mass spectrum m/e 442 (M$^+$, C$_{22}$H$_{27}$MnO$_6$); IR (cm^{-1}, CCl$_4$) 2040 (sh, s), 1955 (sh, s), 1945 (sh, m) (C≡O), 1700 (C=O); ^{1}H NMR (CDCl$_3$), δ 1.23 (s, 12 H, Me in the alicyclic ring), 1.56 (m, 6 H, CH$_2$ in the alicyclic ring), 2.76 (m, 4 H, CH$_2$ in the side chain), 3.70 (s, 3 H, Me in the side chain), 5.33 (s, 2 H, Cp).

{η^5-[4-(CO(CH$_2$)$_2$CO$_2$Me)-6,7-(CMe$_2$(CH$_2$)$_4$CMe$_2$)]Cp}Mn(CO)$_3$ (**14a**): traces; mass spectrum m/e 456 (M$^+$, C$_{23}$H$_{29}$MnO$_6$).

2. Acylation by Acid Chlorides. Acylation of **2** or **3** by acetyl and benzoyl chlorides was carried out according to the process described above for the alkylation of cymantrene, starting with 10 mmol of *tert*-butylcymantrene (**3.16 g of 3**), 20 mmol of acide chloride (1.57 g of acetyl chloride or 2.81 g of benzyl chloride), and 25 mmol (3.4 g) of aluminum chloride. For chromatographic separation of acetyl compounds, the best results were obtained with a 1:3 mixture of diethyl ether and hexane as eluent.

{η^5-[4-(COMe)]Cp}Mn(CO)$_3$ (**9b**):[8] 0.32 g (13% yield).

{η^5-[4-(COC$_6$H$_5$)]Cp}Mn(CO)$_3$ (**9c**):[8] 0.43 g (14% yield).

{η^5-[4-(COMe)-6-(*t*-Bu)]Cp}Mn(CO)$_3$ (**10b**): 1.05 g (35% yield); oil; R_f 0.58; mass spectrum m/e 302 (M$^+$, C$_{14}$H$_{15}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2040 (sh, s), 1960 (sh, s), 1940 (sh, m) (C≡O), 1695 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.22 (s, 9 H, *t*-Bu), 2.33 (s, 3 H, Me), 4.93 (m, 1 H, Cp), 5.26 (m, 1 H, Cp), 5.46 (m, 1 H, Cp).

{η^5-[4-(COC$_6$H$_5$)-6-(*t*-Bu)]Cp}Mn(CO)$_3$ (**10c**): 0.73 g (20% yield); oil; R_f 0.65; mass spectrum m/e 364 (M$^+$, C$_{19}$H$_{17}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2040 (sh, s), 1970 (sh, m), 1955 (sh, m) (C≡O), 1675 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.22 (s, 9 H, *t*-Bu), 5.00 (m, 1 H, Cp), 5.35 (m, 1 H, Cp), 5.53 (m, 1 H, Cp), 7.61 (m, 5 H, C$_6$H$_5$).

{η^5-[4-(COMe)-6,7-(CMe$_2$(CH$_2$)$_2$CMe$_2$)]Cp}Mn(CO)$_3$ (**12b**): 0.60 g (17% yield); yellow crystals; mp 80 °C (recrystallization from hexane); R_f 0.65; mass spectrum m/e 356 (M$^+$, C$_{18}$H$_{21}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2040 (sh, s), 1960 (sh, s), 1940 (sh, m) (C≡O), 1695 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.21 (s, 12 H, Me in the alicyclic ring), 1.60 (s, 4 H, CH$_2$ in the alicyclic ring), 2.30 (s, 3 H, Me in the side chain), 5.30 (s, 2 H, Cp).

{η^5-[4-(COC$_6$H$_5$)-6,7-(CMe$_2$(CH$_2$)$_2$CMe$_2$)]Cp}Mn(CO)$_3$ (**12c**): 0.50g (12% yield); oil; R_f 0.72; mass spectrum m/e 418 (M$^+$, C$_{23}$H$_{23}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2040 (v sh, s), 1960 (v sh, s), 1940 (sh, s) (C≡O), 1665 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.23 (s, 6 H, Me the alicyclic ring), 1.28 (s, 6 H, Me in the alicyclic ring), 1.62 (s, 4 H, CH$_2$ in the alicyclic ring), 5.40 (s, 2 H, Cp), 7.63 (m, 5 H, C$_6$H$_5$).

{η^5-[4-(COMe)-6,7-(CMe$_2$(CH$_2$)$_3$CMe$_2$)]Cp}Mn(CO)$_3$ (**13b**): 0.18 g (5% yield); oil; R_f 0.70; mass spectrum m/e 370 (M$^+$, C$_{19}$H$_{23}$MnO$_4$); IR (cm^{-1}, CCl$_4$) 2040 (v sh, s), 1960 (sh, s), 1940 (sh, s) (C≡O), 1695 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.21 (s, 12 H, Me in the alicyclic ring), 1.60 (m, 6 H, CH$_2$ in the alicyclic ring), 2.30 (s, 3 H, Me in the side chain), 5.30 (s, 2 H, Cp).

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Table I. Fractional Atomic Coordinates and Isotropic Equivalent Thermal Parameters (Å²)

atom	x	y	z	B_{eqv}
Mn	0.6006 (2)	0.33323 (8)	0.6371 (2)	3.43 (4)
O(1)	0.926 (1)	0.2883 (4)	0.7424 (10)	10.8 (3)
O(2)	0.696 (1)	0.3300 (4)	0.3746 (7)	7.5 (3)
O(3)	0.463 (1)	0.2257 (3)	0.6072 (9)	7.9 (3)
O(4)	0.362 (1)	0.4364 (3)	0.3966 (7)	6.2 (2)
O(5)	−0.050 (1)	0.4321 (4)	0.4751 (7)	6.5 (3)
O(6)	−0.138 (1)	0.4501 (3)	0.2702 (7)	5.0 (2)
C(1)	0.796 (2)	0.3071 (5)	0.7018 (11)	5.6 (4)
C(2)	0.666 (1)	0.3314 (6)	0.4804 (10)	5.0 (3)
C(3)	0.518 (2)	0.2680 (5)	0.6183 (11)	4.9 (3)
C(4)	0.412 (1)	0.3917 (4)	0.5924 (10)	3.0 (3)
C(5)	0.367 (1)	0.3597 (4)	0.6956 (10)	3.4 (3)
C(6)	0.493 (1)	0.3671 (4)	0.8012 (10)	3.2 (3)
C(7)	0.619 (1)	0.4042 (4)	0.7655 (10)	2.6 (3)
C(8)	0.565 (1)	0.4182 (4)	0.6353 (10)	3.2 (3)
C(9)	0.490 (1)	0.3451 (5)	0.9391 (10)	4.0 (3)
C(10)	0.623 (1)	0.3758 (5)	1.0307 (10)	4.3 (3)
C(11)	0.785 (1)	0.3882 (5)	0.9726 (9)	3.9 (3)
C(12)	0.761 (1)	0.4255 (4)	0.8549 (9)	3.0 (3)
C(13)	0.320 (2)	0.3539 (6)	0.9856 (12)	7.2 (4)
C(14)	0.528 (2)	0.2848 (5)	0.9468 (12)	6.3 (4)
C(15)	0.923 (1)	0.4311 (5)	0.7937 (11)	5.1 (3)
C(16)	0.704 (2)	0.4818 (5)	0.8964 (11)	5.2 (4)
C(17)	0.325 (1)	0.3992 (4)	0.4617 (10)	4.0 (3)
C(18)	0.193 (1)	0.3587 (4)	0.4171 (11)	4.2 (3)
C(19)	0.068 (1)	0.3841 (5)	0.3105 (10)	3.8 (3)
C(20)	−0.047 (1)	0.4243 (5)	0.3629 (10)	4.3 (3)
C(21)	−0.252 (2)	0.4894 (5)	0.3134 (12)	5.8 (4)

{η⁵-[4-(COC₆H₅)-6,7-(CMe₂(CH₂)₃CMe₂)]Cp}Mn(CO)₃ (**13c**): 0.22 g (5% yield); oil; R_f 0.79; mass spectrum m/e 432 (M⁺, C₂₄H₂₅MnO₄); IR (cm⁻¹, CCl₄) 2040 (v sh, m), 1940 (s) (C≡O), 1685 (C=O); ¹H NMR (CDCl₃) δ 1.23 (s, 12 H, Me in the alicyclic ring), 1.62 (m, 6 H, CH₂ in the alicyclic ring), 5.40 (s, 2 H, Cp), 7.63 (m, 5 H, C₆H₅).

{η⁵-[4-(COMe)-6,7-(CMe₂(CH₂)₄CMe₂)]Cp}Mn(CO)₃ (**14b**): traces; mass spectrum m/e 380 (M⁺, C₂₀H₂₅MnO₄).

{η⁵-[4-(COC₆H₅)-6,7-(CMe₂(CH₂)₄CMe₂)]Cp}Mn(CO)₃ (**14c**): traces; mass spectrum m/e 446 (M⁺, C₂₅H₂₇MnO₄).

X-ray Analysis of {η⁵-[4-(CO(CH₂)₂CO₂Me)-6,7-(CMe₂(CH₂)₂-(CMe₂)]Cp}Mn(CO)₃ (12a). Collection and Reduction of the X-ray Data. Preliminary Weissenberg and precession photographs showed that the molecule crystallizes in the monoclinic space group *P2₁/n*, with systematic absences *h0l, h + l = 2n + 1*, and *0k0, k = 2n + 1*. The unit cell parameters *a* = 7.996 (3) Å, *b* = 25.000 (1) Å, *c* = 10.486 (4) Å, β = 96.18 (2)°, and *V* = 2084 Å³ were obtained by least-squares refinement from 25 accurately centered diffractometer reflections by using Mo Kα (λ = 0.709 26 Å) graphite-monochromated radiation. The calculated density is 1.365, consistent with *Z* = 4. The yellow prism used was mounted on a glass fiber and measured to be 0.08 × 0.08 × 0.15 mm. Data were collected at room temperature on a Nonius CAD4 automatic four-circle diffractometer using the θ–2θ scan technique. The integrated intensities were obtained from scan angles (in degrees) calculated from *S* = 1.00 ± tan θ and increased by 25% at each end of the background count. The counter apperture was calculated by *d* = 2.00 ± 0.3 tan θ (in millimeters). The intensity and estimated standard deviation of 1237 independent reflections with θ < 40° and intensities above the 3σ level were collected. Three standard reflections were monitored every 200 min of exposure, and no significant variation was observed. Values of *I* were corrected for Lorentz and polarization effects. Since the linear absorption coefficient was 9.55 cm⁻¹ and minimum and maximum transmission factors were respectively 0.87 and 0.93, no absorption corrections were applied.

Determination and Refinement of the Structure. The positions of the Mn atom and 16 of the 27 C and O atoms were found with the aid of the MULTAN program.[9] From a three-dimensional electron density difference map, the positions of the remaining nonhydrogen atoms were obtained. Scattering factors for manganese, carbon and oxygen atoms were taken from ref 10 as were the terms Δf′ and Δf″

Scheme II
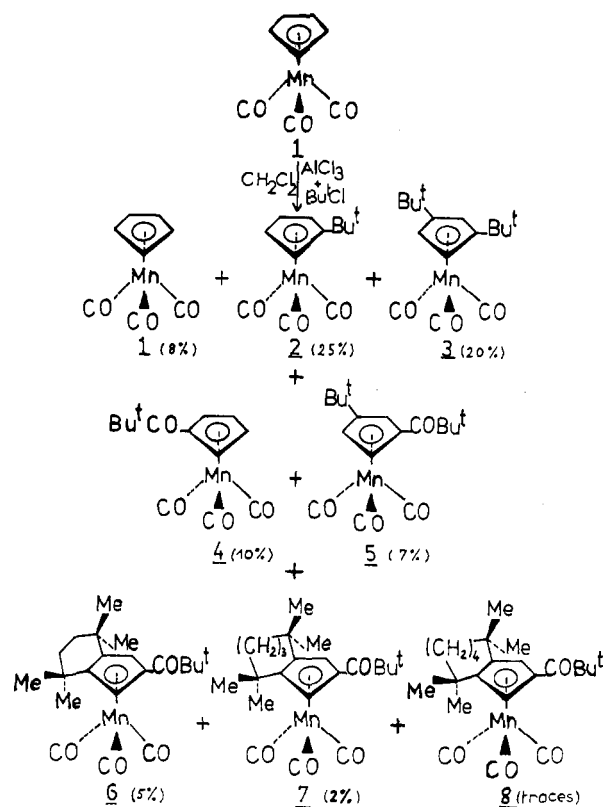
for anomalous dispersion due to manganese. After successive full-matrix least-squares refinement[11] with anisotropic thermal parameters, the positions of all the hydrogen atoms were calculated and verified on a Fourier difference synthesis. They were introduced with a temperature factor of 4 and not refined. Further cycles of refinement yielded $R = \sum|F_o - F_c|/\sum|F_o| = 0.059$ and $R_w = (\sum w|F_o - F_c|^2/\sum w|F_o|^2)^{1/2} = 0.068$. The estimated standard deviation (esd) of an observation of unit weight was 1.24. A final difference Fourier map showed no peaks above the general background. Tables of observed and calculated structure factors are available.[12] Final positional and thermal parameters of nonhydrogen atoms are collected in Table I.

Results

Friedel–Crafts Condensation between *tert*-Butyl Chloride and Cymantrene. In the presence of aluminum chloride, *tert*-butyl chloride reacts with cymantrene giving, besides classical Friedel–Crafts products **2** and **3** (Scheme II), several unexpected products **4–8** in which a CO-*t*-Bu substituent is found on the Cp ring. **6–8** bear alicyclic ring substituents; thus, the cyclization in Scheme I proceeds with the CpMn(CO)₃ series and furthermore involves expansion of the alicyclic ring with more CH₂ units, which provides compounds **7** and **8**. The presence of an acyl substituent on Cp appears to be necessary for this process since the alicyclic ring is never found as the only Cp substituent.

Note that the formation of acylated compounds does not occur starting from *tert*-butylcymantrenes **2** or **3** instead of the parent complex **1**.

Acylation of *tert*-Butylcymantrenes. Reaction of succinic anhydride on *tert*-butylcymantrenes, in the presence of AlCl₃, provides the six esters **9a–14a** (Scheme III) including in particular three cyclized complexes (**12a, 13a,** and **14a**) in

(9) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr.* **1971**, *127*, 368.

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(11) Prewitt, C. K. "SFLS-5, A Fortran IV Full-Matrix Least-Squares Program", Report ORNL-TM-305; Oak-Ridge National Laboratory: Oak Ridge, TN, 1966.

(12) Supplementary material.

Scheme III[a]

$g; R = -(CH_2)_2CO_2Me$. $b; R=Me$. $c; R=Ph$
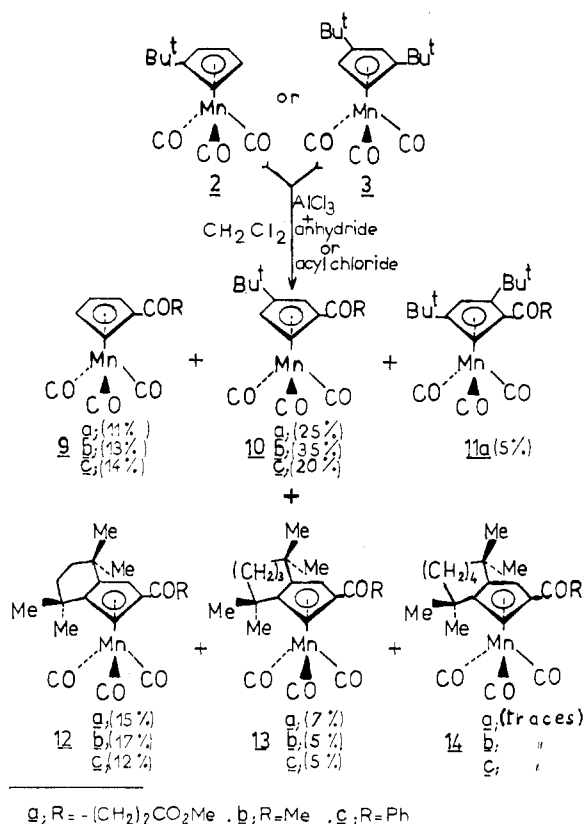
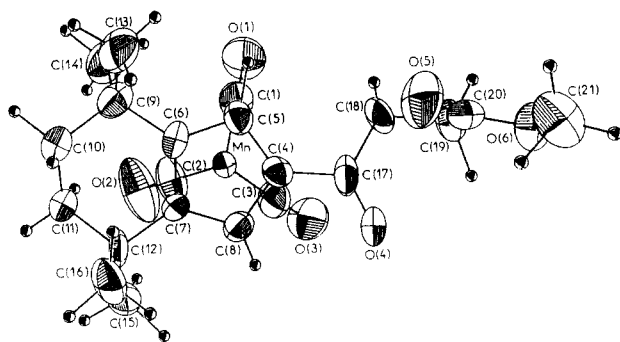[a] Reported yields are relative to the acetylation of **3**.

Figure 1. ORTEP drawing of $MnO_6C_{21}H_{25}$.

which the Cp ring also bears an acyl group. Similar reactions with CH_3COCl and $PhCOCl$ proceed in the same way to give the analogues respectively **12b**, **13b**, and **14b** and **12c**, **13c**, and **14c** (Scheme III).

The molecular structure of **12a** was established by a X-ray diffraction study allowing, in association with the infrared, ^{1}H NMR, and mass spectra, the unambiguous determination of the structures of **6**, **7**, **12**, and **13**. It is noteworthy that the syn and anti methyl groups appear in the same singlet at 60 MHz for **12a** and other analogous complexes bearing an alicyclic ring substituent, except for **12c** (possibly because of the presence of the benzoyl substituent in the latter case). For **7** and **13**, the three methylene units of the alicyclic ring appear in the ^{1}H NMR spectrum as a sharp multiplet near 1.5 ppm. Their intensities are consistent with the mass spectral finding of ring expansion and their chemical shift indicates that they are not located in juxta cyclic position. The structures of **8** and **14** are only shown by the mass spectra since these compounds were isolated in traces quantities.

Structure Description. Intramolecular distances and angles and their estimated standard deviations (esd's) are shown in Table II, together with the closest intermolecular contacts.

Table II

Intramolecular Bond Distances (Å)			
Mn-C(1)	1.763 (13)	Mn-C(4)[a]	2.113 (10)
Mn-C(2)	1.777 (11)	Mn-C(5)[a]	2.136 (10)
Mn-C(3)	1.761 (14)	Mn-C(6)[a]	2.176 (10)
		Mn-C(7)[a]	2.224 (10)
		Mn-C(8)[a]	2.143 (11)
C(1)-O(1)	1.178 (16)	C(3)-O(3)	1.147 (18)
C(2)-O(2)	1.162 (14)		
C(4)-C(5)	1.425 (12)	C(6)-C(7)	1.446 (13)
C(4)-C(8)	1.420 (12)	C(7)-C(8)	1.430 (12)
C(5)-C(6)	1.429 (12)	mean	1.430
C(7)-C(12)	1.492 (12)	C(10)-C(11)	1.525 (13)
C(6)-C(9)	1.550 (13)	C(11)-C(12)	1.542 (12)
C(9)-C(10)	1.555 (14)	mean	1.533
C(9)-C(14)	1.538 (15)	C(9)-C(13)	1.505 (14)
C(12)-C(15)	1.511 (13)	C(12)-C(16)	1.558 (14)
C(4)-C(17)	1.481 (13)		
C(17)-C(18)	1.499 (13)	C(20)-O(5)	1.196 (12)
C(18)-C(19)	1.552 (13)	C(20)-O(6)	1.321 (13)
C(19)-C(20)	1.504 (15)	C(21)-O(6)	1.447 (12)

Intramolecular Bond Angles (Deg)			
C(1)-Mn-C(2)	90.6 (6)	C(4)-Mn-C(5)	39.2 (3)
C(2)-Mn-C(3)	90.9 (6)	C(5)-Mn-C(6)	38.7 (3)
C(1)-Mn-C(3)	90.4 (6)	C(6)-Mn-C(7)	38.4 (3)
		C(7)-Mn-C(8)	38.2 (3)
		C(4)-Mn-C(8)	39.0 (3)
Mn-C(1)-O(1)	177 (1)	Mn-C(3)-O(3)	179 (1)
Mn-C(2)-O(2)	175 (1)		
C(4)-C(5)-C(6)	107.3 (9)	C(7)-C(8)-C(4)	110.4 (9)
C(5)-C(6)-C(7)	109.7 (9)	C(8)-C(4)-C(5)	107.7 (9)
C(6)-C(7)-C(8)	105.0 (9)		
C(9)-C(6)-C(7)	123.4 (9)	C(12)-C(11)-C(10)	113.8 (9)
C(6)-C(7)-C(12)	124.8 (9)	C(11)-C(10)-C(9)	114.1 (9)
C(7)-C(12)-C(11)	108.0 (8)	C(10)-C(9)-C(6)	108.8 (9)
C(14)-C(9)-C(6)	112.0 (9)	C(13)-C(9)-C(6)	110.9 (9)
C(14)-C(9)-C(10)	109.5 (9)	C(13)-C(9)-C(10)	107.9 (9)
C(11)-C(12)-C(15)	111.0 (9)	C(11)-C(12)-C(16)	109.8 (8)
C(7)-C(12)-C(15)	113.4 (8)	C(7)-C(12)-C(16)	105.6 (8)
C(5)-C(4)-C(17)	129.8 (9)	C(8)-C(4)-C(17)	122.5 (1.0)
C(4)-C(17)-C(18)	116.6 (1.0)	O(5)-C(20)-O(6)	125.0 (1.2)
C(17)-C(18)-C(19)	109.1 (8)	O(6)-C(20)-C(19)	111.6 (1.0)
C(18)-C(19)-C(20)	112.4 (9)		

Intermolecular Closest Contacts[b]			
O(5)-C(2)[1]	3.395 (16)	C(4)-C(21)[3]	3.425 (16)
O(5)-C(15)[1]	3.371 (14)	C(8)-C(21)[4]	3.489 (16)
C(2)-C(20)[2]	3.580 (16)	C(15)-C(21)[5]	3.574 (17)

[a] Cp group. [b] Symmetry transformations: (1) $x - 1, y, z$; (2) $1 + x, y, z$; (3) $x, 1 - y, 1 - z$; (4) $\bar{x}, \bar{y}, \bar{z}$; (5) $1 - x, 1 - y, 1 - z$.

Two least-squares planes (and deviations of atoms therefrom) are collected in Table III. Figure 1 is an ORTEP[13] drawing which shows the general appearance of the molecule and the atomic numbering. As in $CpMn(CO)_3$,[14] the orientation of the carbonyl tripod is eclipsed with respect to C(5). There is a small but significant disparity in the Mn-C_{Cp} distances: Mn is farther from C(6) and C(7) (belonging to both rings) than from the other Cp carbons. Note that a similar trend in (naphthalene) chromium tricarbonyl was correlated by Cais et al.[15] to the catalytic activity due to the decoordination of the middle double bond. The six-membered ring, except C(11), is approximately planar (plane 2) and makes an angle of 10.4° with the Cp group (plane 1) (see Table III). C(11)

(13) Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(14) Berndt, A. F.; Marsh, R. E. *Acta Crystallogr.* **1962**, *118*, 123.

(15) Cais, M.; Fraenkel, D.; Weidenbaum, K. *Coord. Chem. Rev.* **1975**, *16*, 27.

Table III

Least-Squares Planes and Atomic Deviations Therefrom, Å[a]

plane no.	A	B	C	D	atom	x	y	z	dist	esd
1	0.5588	−0.7656	−0.3187	−7.9944	C(4)[b]	2.6293	9.7915	6.1757	−0.001	0.010
					C(5)[b]	2.1460	8.9920	7.2522	−0.002	0.011
					C(6)[b]	3.0385	9.1783	8.3521	0.004	0.011
					C(7)[b]	4.0833	10.1060	7.9806	−0.004	0.010
					C(8)[b]	3.8015	10.4554	6.6233	0.003	0.011
					C(9)[c]	2.8578	8.6279	9.7901	−0.134	0.011
					C(10)[c]	3.8159	9.3942	10.7451	−0.490	0.012
					C(11)[c]	5.1806	9.7041	10.1393	0.229	0.011
					C(12)[c]	5.1209	10.6364	8.9125	−0.128	0.010
2	0.6187	−0.7716	−0.1480	−6.4120	C(6)[b]	3.0385	9.1783	8.3521	−0.025	0.011
					C(7)[b]	4.0833	10.1060	7.9806	−0.040	0.010
					C(9)[b]	2.8578	8.6279	9.7901	0.075	0.011
					C(10)[b]	3.8159	9.3942	10.7451	−0.065	0.012
					C(12)[b]	5.1209	10.6364	8.9125	0.055	0.010
					C(11)[c]	5.1806	9.7041	10.1393	0.630	0.011
					C(4)[c]	2.6293	9.7915	6.1757	−0.430	0.010
					C(5)[c]	2.1460	8.9920	7.2522	−0.271	0.011
					C(8)[c]	3.8015	10.4554	6.6233	−0.283	0.011

χ^2 values				dihedral angle	
plane no.	χ^2	plane no.	χ^2	planes	angle, deg
1	0	2	122	1-2	10.4

[a] The equation of the plane is of the form $Ax + By + Cz - D = 0$, where A, B, C, and D are constants and x, y, and z are orthogonalized coordinates. [b] Atoms in the plane. [c] Other atoms.

Scheme IV
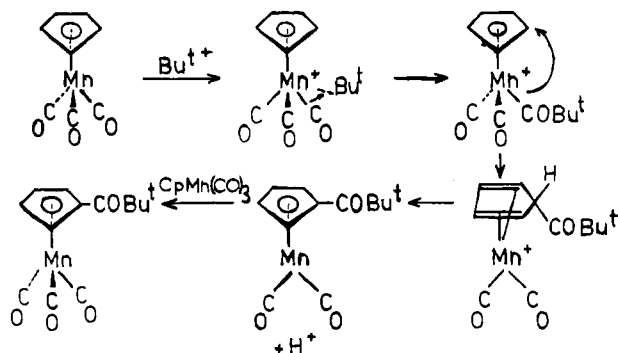
is 0.63 Å below plane 2, on the same side of the carbonyl tripod. All the C–C and C–O distances of the rings and substituents fall in the usual range.

Discussion

A possible mechanism for this unprecedented CO insertion in Cp may consist in the attack of t-Bu$^+$ on Mn, followed by CO insertion into the Mn-t-Bu bond and endo attack of the Cp by the acyl group to form a substituted η^4-cyclopentadiene intermediate (Scheme IV). Labeling experiments would have been undertaken to check this.

However, this hypothesis is supported by the proposed "ricochet" type mechanism for electrophilic substitution in ferrocene.[16a] In the latter, the attack of the metal by an electrophile is followed by endo migration to the Cp ring. Recent results indicate migration of a one-electron ligand from the metal to the Cp ring in $(\eta^5$-Cp)FeH(triphos).[16b] Coordination by AlX$_3$ of a carbonyl oxygen was also found to greatly enhance the CO insertion into a metal–alkyl bond.[16c] A similar path is viable in the present case, but our system

is complicated so that simple experimental evidence for the mechanism is lacking.

The formation of acylated complexes does not occur starting from η^5-t-BuCpMn(CO)$_3$ instead of the parent complex **1**, presumably because the initial attack of **2** by t-Bu$^+$ is unfavorable for steric and conformational reasons (the t-Bu substituent forces the Mn(CO)$_3$ tripod in a staggered conformation; subsequently there is no longer an available site of attack on Mn for which the two bulky t-Bu groups can be transoid with regard to each other). This observation is consistent with the intermediacy of the square-planar-pyramid pentacoordinate species proposed in Scheme IV and excludes a direct insertion into a Cp–t-Bu bond.

So the need for an acyl substituent allowing the cyclization can be explained, a fulvene form must be taken into account. Fulvene forms of this type have been proposed when acyl–Cp complexes were reacted with AlCl$_3$ to account for the racemization of (+)-1,2-(α-oxotetramethylene)ferrocene[17a] and the ligand exchange in acylferrocenes.[17b] If an acyl group is not present, the fulvene form cannot be reached. We propose that the key point is that ring closure of the carbonium ion A is much favored as the carbonium center attacks a fulvenic double bond (rather than Cp; compare Scheme I).
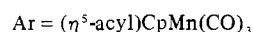
A
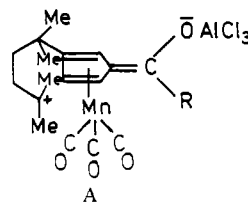
Ring expansion C$_6$ → C$_7$ → C$_8$ is related to carbonium intermediates B and C resulting from combinations of car-

$ArCMe_2(CH_2)_3CMe_2^+$ $ArCMe_2(CH_2)_4CMe_2^+$

B   C

$Ar = (\eta^5$-acyl)CpMn(CO)$_3$

(16) (a) Rosenblum, M. "Chemistry of the Iron Group Metallocenes"; Interscience: New York, 1965; Vol. 1, p 129. (b) Davies, S. G.; Felkin, H.; Watts, O. *J. Chem. Soc., Chem. Commun.* **1980**, 159. (c) Butts, S. B.; Holt, E. M.; Strauss, S. H.; Alcock, N. W.; Stimson, R. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 5864.

(17) (a) Slocum, D. W.; Turcker, S. P.; Engelmann, T. R. *Tetrahedron Lett.* **1970**, 621. (b) Astruc, D. *Ibid.* **1973**, 3437.

bonium ions. However, the formation of B and C is unclear, although the mechanism may be somewhat related to that indicated in Scheme I (many possibilities of recombination of carbocations are feasible[18]).

Although complicated and largely unexplained, these data show how various kinds of C–C bond formation (ring closure, expansion, and functionalization) may be strongly influenced or induced by the metal moiety in cymantrenes.

(Contract No. 77.70774) and Dr. D. Astruc for helpful discussions.

(18) Roberts, R. M.; Fonken, G. J. "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed.; Interscience: New York, 1963; Vol. 1, p 821. Drahowzal, F. A. "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed.; Interscience: New York, 1964; Vol. 2, Part I, p 417.

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Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes: Derivatives of Dicarbonyl(η5-cyclopentadienyl)rhenium and the X-ray Structure of [(η5-C5H5)Re(CO)2[p-NN(CH3)C6H4OMe]]

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The aryldiazenido complexes [(η5-C5H5)Re(CO)2(N2R)][BF4] (**1**: R = C6H4X with X = (**a**) *p*-Me, (**b**) *p*-OMe, (**c**) *o*-OMe, (**d**) *p*-NEt2, and (**e**) *o*-CF3; R = C6H3X2 with X2 = (**f**) 2,6-Me2 and (**g**) 3,5-Me2) have been synthesized from the reaction of the appropriate arenediazonium tetrafluoroborate with (η5-C5H5)Re(CO)2THF. They react with NaBH4 at N(1) to produce the corresponding aryldiazene complexes [(η5-C5H5)Re(CO)2(NHNR)] (**3**), which exhibit δ(NH) near 15 in the ¹H NMR but react with MeLi at N(2) to yield the hydrazido(2–) derivatives [(η5-C5H5)Re(CO)2[NN(Me)R]] (**6**). An X-ray structure determination on **6b** (R = *p*-C6H4OMe) shows it to contain a *bent* metal–hydrazido(2–) skeleton, with selected dimensions Re–N(1) = 1.937 (7) Å, N(1)–N(2) = 1.283 (10) Å, and Re–N(1)–N(2) = 138.1 (6)°. Compound **6b** crystallizes from hexane as dark red solvent-free crystals in the space group $P2_1/c$ of the monoclinic system with a = 5.895 (1) Å, b = 21.096 (4) Å, c = 12.829 (2) Å, β = 112.05 (1)°, and Z = 4. The calculated and measured densities are 2.055 and 2.02 (2) g cm⁻³, respectively. On the basis of 2178 observed, three-dimensional, X-ray-counter measured intensities with $I > 2.3\sigma(I)$ in the range 3° ≤ 2θ ≤ 50° (Mo Kα), the structure was solved and refined by full-matrix, least-squares methods to R = 0.037 and R_w = 0.040. These hydrazido(2–) complexes can be protonated at N(1) with HBF4 to yield the hydrazido(1–) complexes [(η5-C5H5)Re(CO)2[NHN(Me)R]][BF4] (**8**) with δ(NH) near 16. The aryldiazenido complexes also react with MeLi, PhLi, and *n*-BuLi to give monocarbonyl compounds formulated to be acyl or benzoyl derivatives, resulting from nucleophilic attack at one CO group.

Introduction

The chemistry of derivatives of the fragments CpM(CO)2 (Cp = η5-C5H5; M = Mn, Re) is rich and varied.[1] The cationic nitrosyl complex [CpRe(CO)2(NO)]+ and particularly its phosphine derivative [CpRe(CO)(PPh3)(NO)]+ have proven especially interesting in that the carbonyl group is attacked by hydride ion to yield rare examples of stable formyl complexes.[2]

We have been interested in comparing the chemistry of this nitrosyl with that of the structurally and electronically related aryldiazenido complexes of general formula [CpRe(CO)2-(N2R)]+, recently prepared in this laboratory.[3,4] For these and the corresponding (methylcyclopentadienyl)manganese complexes, we previously showed[3,4] that some nucleophiles such as I⁻ appear to attack the aryl ring with formation of the dinitrogen complexes [CpRe(CO)2(N2)]. Therefore, the reaction of H⁻ with these complexes could, in principle, be

visualized to occur at a choice of possible sites, including CO (to give a formyl ligand, HCO), N(1) (to give an aryldiazene ligand, NHNR), N(2) (to give a hydrazide(2–) ligand, NN-(H)R), or the aryl ring (to give the dinitrogen complex). In this paper we report reactions with NaBH4 and alkyl- or phenyllithium. In the rhenium system, we find that borohydride reacts to form the neutral aryldiazene complexes [CpRe(CO)2(NHNR)], whereas methyllithium yields the new neutral hydrazido(2–) complexes [CpRe(CO)2[NN(Me)R]]. In all cases the dinitrogen complex [CpRe(CO)2(N2)] is also formed. We have no evidence for the formation of a formyl complex with borohydride, but the alkyl- and phenyllithium reactions do appear to produce the corresponding acyl and benzoyl complexes also. Similar reactions of the corresponding manganese system are also reported, but these are largely frustrated by the formation of paramagnetic products, together with the dinitrogen complex.

Experimental Section

Diazonium tetrafluoroborates were synthesized by diazotization of commercially available substituted anilines using NaNO2 and were recrystallized from acetone–diethyl ether. The ¹⁵N isotopic label was introduced at N(1) with Na¹⁵NO2 (96% ¹⁵N). All solvents were dried and purified by standard methods (tetrahydrofuran by reflux with sodium and benzophenone) and distilled under nitrogen. Reactions and manipulations were carried out in standard Schlenkware, con-

(1) Caulton, K. G. *Coord. Chem. Rev.* **1981,** *38,* 1.
(2) (a) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980,** *102,* 1927. (b) Tam, W.; Wong, W.-K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979,** *101,* 1589.
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