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.

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Registry No. **1**, 12079-65-1; **2**, 12109-77-2; **3**, 79452-20-3; **4**, 79452-21-4; **5**, 81194-05-0; **6**, 81194-06-1; **7**, 81194-07-2; **8**, 81194-08-3; **9a**, 63851-74-1; **9b**, 12116-28-8; **9c**, 12130-12-0; **10a**, 79595-17-8; **10b**, 33039-53-1; **10c**, 79595-15-6; **11a**, 79595-16-7; **12a**, 79452-25-8; **12b**, 79452-27-0; **12c**, 79452-30-5; **13a**, 79452-26-9; **13b**, 79452-28-1; **13c**, 79452-31-6; **14a**, 79468-06-7; **14b**, 79452-29-2; **14c**, 79452-32-7; *tert*-butyl chloride, 507-20-0; succinic anhydride, 108-30-5; acetyl chloride, 75-36-5; benzoyl chloride, 98-88-4.

Supplementary Material Available: Listings of the structure factor amplitudes, thermal parameters of nonhydrogen atoms, and calculated atomic coordinates for hydrogen atoms (8 pages). Ordering information is given on any current masthead page.

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Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes: Derivatives of Dicarbonyl(η^5-cyclopentadienyl)rhenium and the X-ray Structure of [(η^5-C_5H_5)Re(CO)$_2$[*p*-NN(CH_3)C_6H_4OMe]]

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The aryldiazenido complexes [(η^5-C_5H_5)Re(CO)$_2$(N_2R)][BF_4] (**1**: R = C_6H_4X with X = (**a**) *p*-Me, (**b**) *p*-OMe, (**c**) *o*-OMe, (**d**) *p*-NEt_2, and (**e**) *o*-CF_3; R = $C_6H_3X_2$ with X_2 = (**f**) 2,6-Me_2 and (**g**) 3,5-Me_2) have been synthesized from the reaction of the appropriate arenediazonium tetrafluoroborate with (η^5-C_5H_5)Re(CO)$_2$THF. They react with $NaBH_4$ at N(1) to produce the corresponding aryldiazene complexes [(η^5-C_5H_5)Re(CO)$_2$(NHNR)] (**3**), which exhibit δ(NH) near 15 in the ^{1}H NMR but react with MeLi at N(2) to yield the hydrazido(2−) derivatives [(η^5-C_5H_5)Re(CO)$_2$[NN(Me)R]] (**6**). An X-ray structure determination on **6b** (R = *p*-C_6H_4OMe) 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 $3° \leq 2\theta \leq 50°$ (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 HBF_4 to yield the hydrazido(1−) complexes [(η^5-C_5H_5)Re(CO)$_2$[NHN(Me)R]][BF_4] (**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 = η^5-C_5H_5; M = Mn, Re) is rich and varied.[1] The cationic nitrosyl complex [CpRe(CO)$_2$(NO)]$^+$ and particularly its phosphine derivative [CpRe(CO)(PPh$_3$)(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)$_2$(N_2R)]$^+$, 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)$_2$(N_2)]. 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 $NaBH_4$ 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)$_2$(N_2)] 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 $NaNO_2$ and were recrystallized from acetone–diethyl ether. The ^{15}N isotopic label was introduced at N(1) with Na^{15}NO$_2$ (96% ^{15}N). 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-

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nected to a switchable inert-atmosphere/vacuum supply, and were conducted under nitrogen or argon. (Methylcyclopentadienyl)tricarbonylmanganese (Alfa Ventron), triphenylsilane (Matheson Coleman and Bell), and decacarbonyldirhenium (Strem Chemicals) were used directly as purchased. $(\eta^5\text{-}C_5H_5)Re(CO)_3$ was synthesized by the published method.[5] Photochemical reactions were carried out as described previously.[4] Infrared spectra were recorded on Perkin-Elmer Models 457, 599B, and 237 (with external recorder), calibrated against carbon monoxide or polystyrene. ^1H NMR spectra were recorded at 100 MHz with a Varian XL-100 spectrometer modified for Fourier-transform spectroscopy and are reported in ppm downfield relative to internal $SiMe_4$. Gas chromatograph–mass spectra were obtained with a Hewlett-Packard Model 5985 GC–MS system operating at 70 eV. Microanalyses were performed by Mr. M. K. Yang of the Microanalytical Laboratory of Simon Fraser University. There was occasional difficulty in obtaining carbon analyses acceptably close to theoretical values for some of the aryldiazenido complexes **1** and their derivatives, even though these samples were crystalline and spectroscopically pure (by IR, NMR).

$CpRe(CO)_2THF$. This was synthesized by a modification of the published method.[6] A solution of $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ (1 g, 3 mmol) in freshly distilled, pure tetrahydrofuran (250 mL) was irradiated for 45 min to give a deep brownish yellow solution. Evaporation of the solvent to ca. 20 mL and cooling to −78 °C afforded $CpRe(CO)_2THF$ as a golden yellow solid: yield ~50%; IR (THF) $\nu(CO)$ 1910 vs, 1836 vs cm^{-1}.

$[CpRe(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ (1a). To a solution of $[CpRe(CO)_2THF]$ (200 mg, 0.53 mmol) in 20 mL of acetone was slowly added solid $[p\text{-}CH_3C_6H_4N_2][BF_4]$ (108.7 mg, 0.53 mmol), and the mixture was stirred for 15 min at room temperature. The reaction was instantaneous, and the color changed from yellow to orange. The solution was evaporated in vacuo at room temperature to ca. 2 mL, and excess diethyl ether was carefully added to precipitate the aryldiazenido complex as a microcrystalline orange solid. This was washed by stirring with several portions of ether until the ether solution was clear: yield 97%; mp 130 °C. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$: C, 32.75; H, 2.34; N, 5.46. Found: C, 32.99; H, 2.35; N, 5.55.

$[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1b). A procedure similar to that used for **1a** gave this as a pink-red microcrystalline solid, mp 114 °C, in 95% yield. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$: C, 31.76; H, 2.27; N, 5.29. Found: C, 31.90; H, 2.29; N, 5.40.

$[CpRe(CO)_2(o\text{-}N_2C_6H_4OMe)][BF_4]$ (1c). A procedure similar to that used for **1a** gave this as a red microcrystalline solid, mp 108 °C, in 93% yield. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(o\text{-}N_2C_6H_4OCH_3)][BF_4]$: C, 31.76; H, 2.27; N, 5.29. Found: C, 31.43; H, 2.27; N, 5.01.

$[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ (1d). A procedure similar to that used for **1a** gave this as a dark green microcrystalline solid: mp 141–142 °C; 95% yield. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}N_2C_6H_4N(C_2H_5)_2]][BF_4]$: C, 35.79; H, 3.33; N, 7.37. Found: C, 35.63; H, 3.45; N, 7.49.

$[CpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (1e). A procedure similar to that used for **1a** gave this as a brown-orange microcrystalline solid, mp 132 °C, in 93% 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, 28.98; H, 1.65; N, 4.90.

$[CpRe(CO)_2(2,6\text{-}N_2C_6H_3Me_2)][BF_4]$ (1f). A procedure similar to that used for **1a** gave this as an orange microcrystalline solid, mp 118 °C, in 95% yield. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[2,6\text{-}N_2C_6H_3(CH_3)_2]][BF_4]$: C, 34.16; H, 2.66; N, 5.31. Found: C, 34.15; H, 2.56; N, 5.19.

$[CpRe(CO)_2(3,5\text{-}N_2C_6H_3Me_2)][BF_4]$ (1g). A procedure similar to that used for **1a** gave this as a reddish brown microcrystalline solid, mp 133–134 °C, in 93% yield. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[3,5\text{-}N_2C_6H_3(CH_3)_2]][BF_4]$: C, 34.16; H, 2.66; N, 5.31. Found: C, 32.75; H, 2.54; N, 5.03.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(p\text{-}N_2C_6H_4CF_3)][BF_4]$ (2a). This was synthesized as described previously.[4]

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ (2b). To a solution of $[(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3]$[7] (300 mg, 0.67 mmol) in acetone (15 mL) was slowly added solid $[p\text{-}CH_3C_6H_4N_2][BF_4]$ (137.3 mg, 0.68 mmol), and the mixture was stirred for 3 h at room temperature. The color changed from yellow to brownish 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. An excess of Et_2O was added now to precipitate the aryldiazenido complex; a reddish brown oil was obtained, which was stirred with several portions of Et_2O until the ether solution was clear. Addition of hexane gave the product (20%) as a dark brown solid, which gives a deep red solution in acetone.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2[3,5\text{-}N_2C_6H_3(CH_3)_2]][BF_4]$ (2c). This was synthesized analogously with **2b** by using $[3,5\text{-}(CH_3)_2C_6H_3N_2][BF_4]$ (66 mg, 0.30 mmol) and stirring for 2 h at 35 °C. The solution changed from yellow to dark reddish brown. No solid could be isolated, only a reddish brown oil being obtained in low yield. This was identified by a comparison of its properties and IR spectrum with those of **2a** and **2b**.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(2,6\text{-}N_2C_6H_3Cl_2)][BF_4]$ (2d). This was prepared similarly in 43% yield, mp 124–125 °C, as a brown-orange microcrystalline solid. Anal. Calcd for $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(2,6\text{-}N_2C_6H_3Cl_2)][BF_4]$: C, 37.25; H, 2.22; N, 6.21. Found: C, 37.16; H, 2.40; N, 6.15.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2[2,6\text{-}N_2C_6H_3(NO_2)_2]][BF_4]$ (2e). This was prepared similarly in 20% yield, mp 104–105 °C, as a brown microcrystalline solid and characterized by IR.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ (1a) with $NaBH_4$. This reaction was carried out similarly with the reaction of **1b** described next. The color changed from red-brown to a bright, deep orange-red, and the IR spectrum of the hexane extract showed the presence of the new diazene complex $[CpRe(CO)_2(p\text{-}NHNC_6H_4CH_3)]$ (**3a**) together with a significant amount of the dinitrogen complex $[CpRe(CO)_2(N_2)]$ (**4**). The solution is very air and temperature labile, and a GC–MS analysis showed only two GC peaks in addition to solvent, having parent ions at m/e 92 (toluene) and 334, 336 (**4**).

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ (1b) with $NaBH_4$. To **1b** (100 mg) dissolved in a 1:1 mixture of THF and water (3 mL) was added a stoichiometric amount of solid $NaBH_4$, and the mixture was stirred at 0 °C for 15 min under N_2. An instantaneous reaction occurred, with considerable gas evolution, and the color changed from red-orange to a bright, deep orange. The solution was cooled to −50 °C, and the viscous mass so formed was extracted with cold hexane and filtered. The IR spectrum of the hexane extract showed the presence of the diazene complex $[CpRe(CO)_2(p\text{-}NHNC_6H_4OCH_3)]$ (**3b**) and a very small amount of the dinitrogen complex $[CpRe(CO)_2(N_2)]$ (**4**). When the very air and temperature sensitive solution was cooled, the diazene complex was isolated as a dark red solid, mp 73 (darkens), 83 °C dec. The GC–MS analysis showed only two GC peaks in addition to solvent, having parent ions at m/e 108 (anisole) and 334, 336 (**4**).

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ (1d) with $NaBH_4$. This was carried out as described above for **1b**. The color change from dark green to blood red and the IR of the blood red hexane extract showed the presence of the new diazene complex $[CpRe(CO)_2(p\text{-}NHNC_6H_4NEt_2)]$ (**3d**), plus a very small amount of the dinitrogen complex **4**. Evaporation of the solvent under reduced pressure afforded a blood red microcrystalline solid, mp 55 (darkens), 82 °C dec. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHNC_6H_4N(C_2H_5)_2]]$: C, 42.15; H, 4.13; N, 8.68. Found: C, 39.11; H, 4.12; N, 8.49. The GC–MS of the solution showed only two components, having parent ions at m/e 149 ($C_6H_5NEt_2$) and 334, 336 (**4**). A direct-injection MS of the solid **3d** similarly showed only these two components and no parent peak for **3d** even when the spectrum was obtained at 15 eV and a low inlet temperature (90 °C).

Reaction of $[CpRe(CO)_2(3,5\text{-}N_2C_6H_3Me_2)][BF_4]$ (1g) with $NaBH_4$. This reaction was carried out as described above for **1b**. The color changed from reddish brown to bright, deep orange-red. The IR spectrum of the hexane extract showed the presence of the new diazene complex $[(\eta^5\text{-}C_5H_5)Re(CO)_2(3,5\text{-}NHNC_6H_3Me_2)]$ (**3g**) and a significant amount of the dinitrogen complex **4**. The GC–MS spectrum of this solution showed only two components with parent ions at m/e 106 and 334, 336, which correspond to $1,3\text{-}(CH_3)_2C_6H_4$ and the dinitrogen complex (**4**).

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Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (2a) with $NaBH_4$. To **2a** (100 mg) dissolved in a mixture of 1:1 THF/H_2O (3 mL) was added a 1:1 stoichiometric amount of solid $NaBH_4$, and the mixture was stirred at 0 °C for 15 min under N_2. The reaction took place instantaneously, with considerable gas evolution, and the color of the solution changed from red-orange to dark red-violet. After 15 min the solution was cooled to −50 °C, and a viscous mass was obtained. The products were extracted with cool hexane, and the IR spectrum of this dark red-violet solution showed the presence of the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2)]$ (**5**) (ν(CO) 1975 vs, 1920 vs; ν(NN) 2170 vs cm^{-1})[4] and a new complex with strong carbonyl bands at 1958 and 1900 cm^{-1}. Evaporation of the deep red-violet hexane solution to dryness under vacuum at −30 °C gave a deep red-violet, very air- and temperature-sensitive solid that decomposes at about −20 °C. The low-temperature ^1H NMR spectrum (in $CDCl_3$) of this solid was very broad but showed a band at δ 13.70, which tentatively is assigned as the N–H resonance of a diazene complex analogous to those of the rhenium series.

The broadening of the NMR is ascribed to the presence of Mn(II) species formed in the reaction. The ESR spectrum exhibited a multiline resonance identical with the ESR of aqueous $MnCl_2$.

Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2[3,5\text{-}N_2C_6H_3(CH_3)_2]][BF_4]$ (2c) with $NaBH_4$. This reaction was carried out as described for compound **2a**. The color changed from orange-red to a much deeper orange-red, and the IR spectrum of the orange-red hexane solution showed the presence of the dinitrogen complex **5**, plus a new complex with ν(CO) bands at 1957 and 1901 cm^{-1}. This very air- and temperature-sensitive complex, which could not be isolated, is tentatively suggested to be the diazene complex. No resonance assignable to δ(NH) could be discerned in the extremely paramagnetically broadened ^1H NMR. The ESR spectrum was identical with that for the reaction of **2a**.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4Me)][BF_4]$ (1a) with CH_3Li. To a suspension of **1a** in hexane (20 mL) was added by syringe excess methyllithium (1.3 M in Et_2O), and the mixture was stirred for 30 min at room temperature under N_2. A fast reaction took place, and the hexane solution became red, while a light brown solid precipitated out of the solution.

The IR spectrum of the hexane solution showed the presence of the new hydrazido(2−) complex $[CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4CH_3)]$ (**6a**) plus the dinitrogen complex **4**. The hexane solution was separated and concentrated in vacuo to ca. 4 mL. Dark red air-stable crystals of the hydrazido(2−) complex **6a** were obtained by cooling this solution to −12 °C in the freezer. The dinitrogen complex **4** remained in solution.

The precipitate was a mixture of $LiBF_4$ and a monocarbonyl complex (by IR), which has been tentatively identified as the acetyl complex $[CpRe(CO)(COCH_3)(p\text{-}N_2C_6H_4Me)]$ (**7a**) and obtained in impure form by repeated crystallization from CH_2Cl_2–hexane: IR (CH_2Cl_2) 1952 s (ν(CO)), 1640 s, br cm^{-1} (acyl).

Reactions of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1b), $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ (1d), and $[CpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (1e) with CH_3Li. These reactions were carried out under conditions identical with those described above, to give the new hydrazido(2−) complexes $[CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]]$ (**6b**), $[CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4NEt_2]]$ (**6d**), and $[CpRe(CO)_2[o\text{-}NN(CH_3)C_6H_4CF_3]]$ (**6e**) as dark red air-stable solids and the corresponding acetyl complexes **7b**, **7d**, and **7e** as impure light brown air-sensitive solids.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (1b) with PhLi. To a solution of **1b** (60 mg, 0.11 mmol) in a mixture of 1:1 hexane–CH_2Cl_2 (10 mL) was added by syringe an excess of PhLi (1.95 M in cyclohexane–Et_2O (70:30)), and the mixture was stirred at room temperature for 30 min under N_2. A fast reaction took place, the solution became yellow-orange, and a brown-orange solid precipitated. The IR spectrum of the solution showed the presence of only the dinitrogen complex **4**. The precipitate was a mixture of $LiBF_4$ and a monocarbonyl complex (IR), which tentatively was identified as the benzoyl complex $[CpRe(CO)(COPh)(p\text{-}N_2C_6H_4OMe)]$: IR ($CH_2Cl_2$) 1962 s ($\nu$(CO)), 1644 s, br cm^{-1} (benzoyl).

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ (1d) with *n*-BuLi. To a solution of **1d** (60 mg, 0.105 mmol) in a mixture of 1:1 hexane–acetone (10 mL) was added an excess of *n*-BuLi (2.4 M in hexane) with a syringe, and the mixture was stirred at room temperature for 30 min under N_2. The reaction was instantaneous, and the color changed from dark green to red-brown. The IR spectrum of this solution showed the presence of a monocarbonyl-containing product only. Addition of excess hexane produced precipitation of an orange-brown air-sensitive solid, which gave a dark red solution in CH_2Cl_2. This new complex was tentatively identified as the acyl complex $[(\eta^5\text{-}C_5H_5)Re(CO)(CO\text{-}n\text{-}Bu)(p\text{-}N_2C_6H_4NEt_2)]$. The IR spectrum showed only one terminal ν(CO) band (1938 vs cm^{-1}) and strong and broad bands at 1660–1600 cm^{-1}.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ (1d) with HCl(g). Dry HCl(g) was bubbled into a solution of **1d** (60 mg, 0.105 mmol) in CH_2Cl_2 (10 mL) for a few minutes at room temperature. An instantaneous reaction took place, the color changed from dark green to reddish brown, and a reddish brown oil precipitated out. An orange-brown solid was isolated by washing the oil with hexane at least two times and identified as the adduct $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]\cdot HCl$: IR ($CH_2Cl_2$) 2095 vs, 2038 vs ($\nu$(CO)), 1752 vs, br cm^{-1} (ν(NN)) (1725 vs, br ($\nu(^{15}N^{14}N)$)). Anal. Calcd for $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]\cdot HCl$: C, 33.64; H, 3.30; N, 6.92. Found: C, 32.25; H, 3.57; N, 6.58. This adduct readily loses HCl to regenerate the aryldiazenido complex. None of the other rhenium aryldiazenido complexes **1** react with HCl(g).

Reaction of $[CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4Me]]$ (6a) with HBF_4. To a solution of **6a** in CH_2Cl_2 or $CHCl_3$ (10 mL) was added dry HBF_4 in Et_2O, and the mixture was stirred at room temperature for 20–30 min under N_2. A fast reaction took place, the color changed from red-orange to deep red, and precipitation of an air-stable dark red solid was completed by the addition of diethyl ether. It was easily recrystallized as dark red diamond-shaped crystals from $CHCl_3$–Et_2O; mp 155–158 °C dec. Anal. Calcd for $[CpRe(CO)_2[p\text{-}NHN(CH_3)C_6H_4Me]][BF_4]$ (**8a**): C, 34.03; H, 3.02; N, 5.29. Found: C, 33.85; H, 3.11; N, 4.95. IR (CH_2Cl_2): 2002 vs, 1936 vs cm^{-1} (ν(CO)). ^1H NMR ($(CD_3)_2CO$): δ 16.5 s, br (NH), 7.26 d, 7.58 d (C_6H_4), 6.41 s (Cp), 3.24 s (NCH_3), 2.26 s (CH_3). A $CHCl_3$ solution of **8a**, when stirred with solid Na_2CO_3 (4 h), quantitatively regenerated compound **6a** (IR spectrum).

Reaction of $[CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]]$ (6b) with HBF_4. To a solution of **6b** in CH_2Cl_2 or $CHCl_3$ (10 mL) was added dry HBF_4 in Et_2O, and the mixture was stirred at room temperature for 20–30 min under nitrogen. The color rapidly changed from red-orange to deep red, and a dark red solid precipitated. Ether was added, the supernatant liquid removed, and the precipitate washed several times with ether and then dried in a stream of N_2. It was recrystallized from chloroform–ether; mp 158–159 °C dec. Anal. Calcd for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NHN(CH_3)C_6H_4OMe]][BF_4]$ (**8b**): C, 33.03; H, 2.94; N, 5.14. Found: C, 31.04; H, 2.80; N, 5.03. IR ($CHCl_3$): 2001 vs, 1933 vs cm^{-1} (ν(CO)). The ^1H NMR ($CDCl_3$) revealed two sets of resonances due to solution conformers [δ 15.72 s (NH), 7.45 d, 6.94 d (C_6H_4), 6.17 s (Cp), 3.83 s (OCH_3), 3.09 s (NCH_3) (conformer 1); 16.11 s (NH), 7.42 d, 7.08 d (C_6H_4), 6.04 s (Cp), 3.91 s (OCH_3), 3.21 s (NCH_3) (conformer 2)] in approximate 2:1 ratio (conformer 1:conformer 2). In the NMR of the $^{15}N(1)H$ complex $[^{15}N^1]$**8b**, formed by protonation of $[^{15}N^1]$**6b**, the NH resonances of both conformers appear as doublets with $^1J(^{15}NH)$ = 78 Hz.

X-ray Structure Determination for $CpRe(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]$ (3b). A crystal suitable for data collection, obtained by slow evaporation of a hexane solution at room temperature, was mounted on a glass fiber. Precession and Weissenberg methods were used to determine the space group and approximate cell dimensions. Accurate cell dimensions were determined by least-squares refinement of 22 accurately centered reflections (2θ = 27.0–36.0°, λ(Mo $K\alpha_1$) = 0.70926 Å). Data were collected with a Picker FACS-1 automatic four-circle diffractometer with a graphite monochromator and a scintillation counter with pulse-height discrimination. Symmetrical θ–2θ scans were used, while stationary-crystal, stationary-counter background counts were taken for 10% of the scan time at each scan limit. The background-corrected intensity and associated error of each reflection were determined by the peak profile method of Grant and Gabe.[8] Intensity measurement of 2 standards every 70 reflections showed no evidence of crystal deterioration or instability of the detection system. Intensities (≤50°) were measured for 2605 independent reflections, of which 2178 were classed as observed [$I \geq 2.3\sigma(I)$]. Relevant data are listed in Table I.

The Re atom was located by conventional Patterson synthesis. All remaining nonhydrogen atoms were located in a subsequent difference Fourier synthesis. These atoms were refined until no further im-

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(8) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1977**, *11*, 114.

Table I. Crystal Data and Data Collection Conditions for Dicarbonyl(η^5-cyclopentadienyl)[N^2-methyl-N^2-(p-methoxyphenyl)hydrazido(2−)-N^1]rhenium

formula	$C_{15}H_{15}ReO_3N_2$	V, Å^3	1478.73
space group	$P2_1/c$	Z	4
a, Å	5.895 (1)	D_o, g cm^{-3}	2.02 (2)
b, Å	21.096 (4)	D_c, g cm^{-3}	2.055
c, Å	12.829 (2)	cryst dimens, mm	0.08 × 0.08 × 0.18
β, deg	112.05 (1)		

temp, °C	20
μ, cm^{-1}	87.08
takeoff angle, deg	3
scan speed, deg in 2θ min^{-1}	2
bkgd	10% of total scan on both sides
scan width, deg	$1.6 + 0.692 \tan \theta$
reflctns ($3° < 2\theta < 50°$)	2605
obsd reflctns $I > 2.3\sigma(I)$	2178
R	0.037
R_w	0.040

Table II. Final Atomic Coordinates for $[(\eta^5\text{-}C_5H_5)Re(CO)_2[p\text{-}NN(CH_3)C_6H_4OMe]]^a$

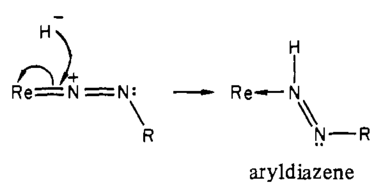
atom	x	y	z
Re	21915 (6)	16330 (2)	38679 (3)
C(1)	−295 (17)	2086 (4)	2749 (8)
C(2)	4108 (18)	2360 (5)	3921 (8)
C(3)	3379 (20)	1537 (5)	5800 (7)
C(4)	893 (18)	1641 (5)	5371 (8)
C(5)	−248 (19)	1119 (5)	4655 (8)
C(6)	1583 (20)	692 (5)	4688 (8)
C(7)	3896 (20)	940 (5)	5384 (8)
C(8)	2764 (17)	1677 (5)	1249 (8)
C(9)	5261 (16)	682 (4)	1780 (7)
C(10)	6437 (18)	802 (4)	1044 (7)
C(11)	7924 (17)	329 (5)	885 (8)
C(12)	8228 (17)	−221 (5)	1403 (8)
C(13)	7081 (18)	−350 (5)	2141 (8)
C(14)	5574 (18)	98 (4)	2310 (8)
C(15)	10372 (21)	−1223 (5)	1791 (9)
N(1)	3563 (13)	1125 (4)	2991 (6)
N(2)	3844 (14)	1162 (4)	2048 (6)
O(1)	−1848 (14)	2382 (4)	2090 (7)
O(2)	5277 (16)	2810 (4)	4009 (8)
O(3)	9760 (14)	−651 (4)	1169 (6)

[a] Fractional atomic coordinates are $\times 10^5$ for Re and $\times 10^4$ for C, N, and O. Estimated standard deviations in the least significant figures are given in parentheses.

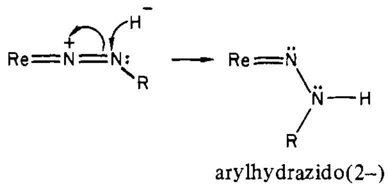
provement in the model was obtained. At this stage cyclopentadienyl and phenyl hydrogen atoms were included in the refinement, fixed in their calculated positions, with isotropic temperature factors proportional to those of their parent carbon atoms. A subsequent difference Fourier synthesis clearly revealed the positions of the remaining methyl hydrogen atoms, which were subsequently included in fixed positions with appropriate temperature factors.

The final difference map was flat (less than 3 times the standard error associated with the map) apart from two peaks close to the Re atom (6 times the error in the map). Gauss–Seidel block-diagonal least-squares refinement, with all nonhydrogen atoms anisotropic, gave final agreement values of $R = 0.037$ and $R_w = 0.040$ [$R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ for 190 variables. Lorentz, polarization, and absorption corrections have been applied; transmission coefficients varied over the range 0.197–0.372. Unit weights have been applied. Scattering factors were taken from ref 9. The computer programs used were those belonging to ref 10. Final positional parameters are listed in Table II. Thermal parameters (Table A), calculated hydrogen positions (Table B), intermolecular distances (Table C), and observed and calculated structure factors (Table D) are available as supplementary material.

Scheme I



Scheme II



Results and Discussion

Synthesis. In a previous paper,[4] we reported the synthesis of a series of aryldiazenido derivatives of tricarbonyl(methylcyclopentadienyl)manganese and the related rhenium aryldiazenido compound $[CpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ from the hydridotriphenylsilyl derivatives $(MeCp)MnH(CO)_2SiPh_3$ and $CpReH(CO)_2SiPh_3$, respectively. In the case of rhenium (but not manganese[4]) the direct reaction of an arenediazonium salt with the THF derivative[6] $CpRe(CO)_2THF$ (obtainable as a crystalline solid) is a simpler method and yields the aryldiazenido complexes $[CpRe(CO)_2N_2R][BF_4]$ (**1**: R = C_6H_4X with X = (**a**) p-CH_3, (**b**) p-OMe, (**c**) o-OMe, (**d**) p-NEt_2, (**e**) o-CF_3; R = $C_6H_3X_2$ with X_2 = (**f**) 2,6-dimethyl, (**g**) 3,5-dimethyl), listed in Table III, in better than 95% yield. The two ν(CO) absorptions that occur at 2090 and 2030 cm^{-1} (CH_2Cl_2) in the o-CF_3 derivative **1e** are lowered when the benzene ring is substituted by more electron-releasing groups, to as much as 2058 and 1995 cm^{-1} (CH_2Cl_2) in the p-NEt_2 derivative **1d**. The value of ν(NN), which is 1760 cm^{-1} (CH_2Cl_2) in **1e**, is simultaneously raised in these other derivatives, becoming as high as 1836 cm^{-1} (CH_2Cl_2) in the 2,6-dimethyl derivative **1f**. The assignment of ν(NN) has been confirmed by ^{15}N isotopic substitution at the metal-bound nitrogen position, N(1), in **1a**, **1b**, and **1d**, which causes an observed lowering by 30–36 cm^{-1}. Steric, as well as electronic, effects evidently influence the increase in ν(NN) in 2,6-disubstituted derivatives as indicated by the high values (ca. 1824–1828 cm^{-1}) of the manganese compounds **2d** and **2e** having electron-withdrawing –Cl and –NO_2 groups in these positions. From the similarity in spectroscopic and chemical properties, the rhenium aryldiazenido complexes are clearly structurally similar to the manganese ones and in particular possess aryldiazenido ligands coordinated in the singly bent geometry I (cf. X-ray structure for **2a**).[4] These rhenium aryldiazenido complexes **1** react instantaneously in 1:1 THF–water solution near 0 °C with a stoichiometric amount of sodium borohydride to yield compounds **3** (Table IV) containing the substituted phenyldiazene ligand (HNNR) along with varying amounts of the dinitrogen complex $CpRe(CO)_2(N_2)$ (**4**). This is, to our knowledge, the first instance in which an aryldiazenido ligand has been found capable of conversion to an identifiable aryldiazene ligand by hydride attack. The aryldiazene ligand is, however, a long-established and frequently encountered species in diazonium complex chemistry, usually arising either by insertion of a

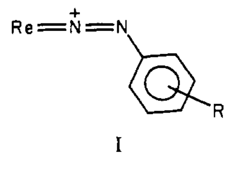


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Table III. Infrared ν(CO) and ν(NN) Data for Rhenium and Manganese Aryldiazenido Complexes

compd	solvent[a]	ν(CO)[b]	ν(NN)[b]
$[CpRe(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ (1a)	CH_2Cl_2	2080 vs, 2021 vs	1769 vs, br (1733 vs)[d]
	acetone	2075 vs, 2018 vs	*c*
$[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ (1b)	CH_2Cl_2	2078 vs, 2020 vs	1770 vs, br (1735 vs)[d]
	acetone	2078 vs, 2012 vs	*c*
$[CpRe(CO)_2(o\text{-}N_2C_6H_4OCH_3)][BF_4]$ (1c)	CH_2Cl_2	2070 vs, 2010 vs	1790 vs, br
	acetone	2062 vs, 2005 vs	*c*
$[CpRe(CO)_2[p\text{-}N_2C_6H_4N(C_2H_5)_2]][BF_4]$ (1d)	CH_2Cl_2	2058 vs, 1995 vs	1762 vs, br (1732 vs)[d]
	acetone	2060 vs, 1990 vs	*c*
$[CpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (1e)	CH_2Cl_2	2090 vs, 2030 vs	1760 vs, br
	acetone	2082 vs, 2023 vs	*c*
$[CpRe(CO)_2[2,6\text{-}N_2C_6H_3(CH_3)_2]][BF_4]$ (1f)	CH_2Cl_2	2070 vs, 2000 vs	1836 vs, br
	acetone	2068 vs, 1995 vs	*c*
$[CpRe(CO)_2[3,5\text{-}N_2C_6H_3(CH_3)_2]][BF_4]$ (1g)	CH_2Cl_2	2082 vs, 2024 vs	1775 vs, br
	acetone	2082 vs, 2022 vs	*c*
$[MeCpMn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (2a)	$CHCl_3$	2090 vs, 2045 vs	1795 vs, br
	acetone	2083 vs, 2041 vs	*c*
$[MeCpMn(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ (2b)	$CHCl_3$	2090 vs, 2044 vs	1794 vs, br
	acetone	2085 vs, 2040 vs	*c*
$[MeCpMn(CO)_2[3,5\text{-}N_2C_6H_3(CH_3)_2]][BF_4]$ (2c)	CH_2Cl_2	2086 vs, 2042 vs	1812 vs, br
	acetone	2085 vs, 2043 vs	*c*
$[MeCpMn(CO)_2[2,6\text{-}N_2C_6H_3Cl_2]][BF_4]$ (2d)	CH_2Cl_2	2095 vs, 2048 vs	1824 vs, br
	acetone	2090 vs, 2045 vs	*c*
$[MeCpMn(CO)_2[2,6\text{-}N_2C_6H_3(NO_2)_2]][BF_4]$ (2e)	CH_2Cl_2	2105 vs, 2060 vs	1828 vs, br
	acetone	2104 vs, 2062 vs	*c*

[a] Measured in CaF_2 cells; some of the solutions react with alkali halide windows.[4] [b] Frequencies in cm^{-1}. Abbreviations: vs, very strong; br, broad; MeCp, η^5-$CH_3C_5H_4$; Cp, η^5-C_5H_5. [c] Band obscured by solvent absorption. [d] $\nu(^{15}N^{14}N)$.

Table IV. IR and ^{1}H NMR Data for Rhenium Aryldiazene Complexes

		^{1}H NMR[b]			
compd	ν(CO)[a]	Cp	aryl	NH	other
$[CpRe(CO)_2(p\text{-}NHNC_6H_4CH_3)]$ (3a)	1938, 1876	5.61 s	7.24 d 7.39 d	15.70 s	2.26 s (CH_3)
$[CpRe(CO)_2(p\text{-}NHNC_6H_4OCH_3)]$ (3b)	1938, 1874	5.61 s	6.95 d 7.46 d	15.46 s	3.86 s (OCH_3)
$[CpRe(CO)_2(p\text{-}NHNC_6H_4NEt_2)]$ (3d)	1932, 1869	5.40 s	6.60 d 7.31 d	14.80[c] s	1.09 t (CH_3) 3.40 q (CH_2)
$[CpRe(CO)_2(3,5\text{-}NHNC_6H_3Me_2)]$ (3g)	1940, 1877				
$[MeCpMn(CO)_2(o\text{-}NHNC_6H_4CF_3)]$	1958, 1900			13.70 s, br	
$[MeCpMn(CO)_2(3,5\text{-}NHNC_6H_3Me_2)]$	1957, 1901				

[a] In cm^{-1} for hexane solution; all bands are very strong. [b] In acetone-d_6 at −30 °C; all values in ppm. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet. [c] 14.82 d in ^{15}N(1)H derivative; $^1J(^{15}NH)$ = 69 Hz.

diazonium ion into a metal–hydride bond[11] or by protonation of a doubly bent aryldiazenido ligand.[12] Presumably, only a singly bent aryldiazenido ligand can be attacked by H^- in this way, though it is conceivable that either an aryldiazene (Scheme I) or an arylhydrazido(2−) (Scheme II) ligand could result (cf. CH_3^- attack, below). Nevertheless, in those cases that we know of, where aryldiazenido compounds have been reacted with borohydride (e.g., ref 12), reduction to a hydrido complex tends to have occurred instead.

The products in the present case have been unambiguously identified by NMR to contain the aryldiazene ligand (with the hydrogen bound at N(1)). The NH resonance occurs well downfield (ca. δ 15), at the lower end of the range, ca. 11–15 ppm, observed for many other aryldiazenes,[11,13] and the resonance is split into a sharp doublet ($^1J(^{15}NH)$ = 69 Hz) in the spectrum of the ^{15}N(1) derivative $[CpRe(CO)_2(p\text{-}^{15}NHNC_6H_4NEt_2)]$ ([^{15}N^1]**1d**). This coupling constant compares with $^1J(^{15}NH)$ values observed for a number of other aryldiazene complexes such as $RhCl_3(p\text{-}^{15}NHNC_6H_4OMe)(PPh_3)_2$ (65 Hz),[13] $OsCl_2(p\text{-}^{15}NHNC_6H_4Me)(CO)(PPh_3)_2$ (67 Hz),[13] and $[RuCl(^{15}NHNPh)(CO)_2(PPh_3)_2][ClO_4]$ (65 Hz).[14] In the IR spectrum, two ν(CO) bands occur, which are lowered substantially from the corresponding positions in the aryldiazenido complexes, for example, to 1932 vs, 1869 vs cm^{-1} in the *p*-NEt_2 derivative **3d**. The position of ν(NN) has not yet been unambiguously identified. In attempts to obtain a mass spectral identification by GC–MS, only two GC fractions were observed, with *m/e* values corresponding to the dinitrogen complex **4** and the arene, respectively, presumably as a result of thermal decomposition of the aryldiazene complex **3** in the GC. This has been shown to occur by monitoring a heated KBr disk of **3b** by IR, where the ν(CO) bands of **3b** become smoothly replaced by those of **4**, and an odor of anisole is produced:

$$\underset{\mathbf{3}}{[CpRe(CO)_2(NHNR)]} \rightarrow \underset{\mathbf{4}}{[CpRe(CO)_2(N_2)]} + RH$$

The manganese aryldiazenido complexes also react with $NaBH_4$, but the reactions are more complicated. The dinitrogen complex $[MeCpMn(CO)_2(N_2)]$ (**5**) was positively identified, but the IR spectrum shows an additional pair of strong ν(CO) bands (e.g., at 1958, 1900 cm^{-1} for the reaction of **2a**) due to another dicarbonyl compound. We tentatively suggest that these may be correlated with a low-field NMR signal at δ 13.70 as indicating the formation of the analogous diazene complex $[MeCpMn(CO)_2(o\text{-}NHNC_6H_4CF_3)]$. Furthermore, the broadness of the NMR and the presence of

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[13] Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2713.

[14] Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369.

Table V. Analytical, MS, IR, and NMR Data for the Hydrazido(2–) Complexes 6

		anal.[a]					^{1}H NMR[h]			
compd	color, mp, °C	% C	% H	% N	m/e[b]	ν(CO)[d]	Cp	C_6H_4	$N(CH_3)$	other
[$CpRe(CO)_2[p$-$NN(CH_3)C_6H_4Me]$] (**6a**)	dk red, 132–135 dec	40.82 (38.92)	3.40 (3.36)	6.40 (6.17)	440, 442	1953, 1881[e] 1936, 1855[f] 1937, 1855[g]	5.85 s	7.12 s	3.79 s	2.28 s (Me)
[$CpRe(CO)_2[p$-$NN(CH_3)C_6H_4OMe]$] (**6b**)	dk red, 148	39.39 (39.17)	3.28 (3.24)	6.13 (5.90)	456, 458[c]	1952, 1877[e] 1938, 1857[f] 1942, 1859[g]	5.86 s	6.84 d 7.20 d	3.78[i] s	3.81[i] s (OMe)
[$CpRe(CO)_2[p$-$NN(CH_3)C_6H_4NEt_2]$] (**6d**)	dk red, 89	43.37 (42.56)	4.42 (4.34)	8.43 (8.22)	497, 499	1946, 1875[e] 1930, 1850[f]	5.79 s	6.56 d 7.12 d	3.80 s	3.34 q (CH_2) 1.15 t (CH_3)

[a] Calculated values in parentheses. [b] Re isotopes 185 (37.07%), 187 (62.93%). [c] High-resolution spectrum yielded the exact mass values 456.0611 and 458.0638 (calculated 456.0607 and 458.0637). [d] In cm^{-1}; all bands very strong. [e] Hexane solution. [f] CH_2Cl_2 solution. [g] $CHCl_3$ solution. [h] 100 MHz; solvents are $CDCl_3$ (for **6a** and **6d**) and CD_2Cl_2 (for **6b**). Abbreviations: s, singlet, d, doublet; t, triplet; q, quartet. [i] $N(CH_3)$ and OMe assignments could be reversed.

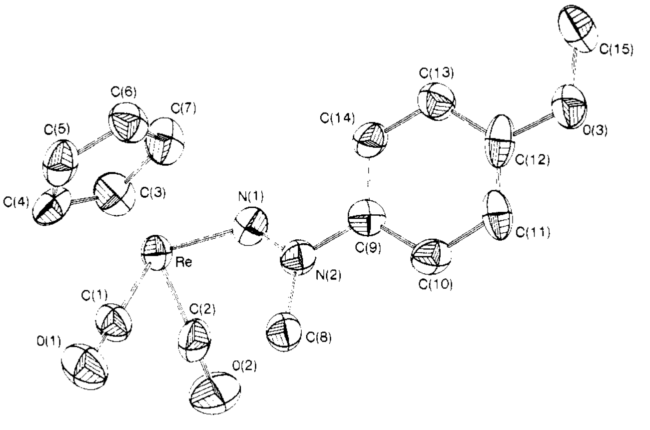


Figure 1. Perspective view of the complex [$(\eta^5$-$C_5H_5)Re(CO)_2[p$-$NN(CH_3)C_6H_4OMe]$] (**6b**).

Table VI. Bond Parameters[a] for [$(\eta^5$-$C_5H_5)Re(CO)_2[p$-$NN(CH_3)C_6H_4OMe]$]

(a) Distances (Å)

Re–C(1)	1.883 (9)	C(6)–C(7)	1.420 (15)
Re–C(2)	1.890 (10)	C(7)–C(3)	1.444 (15)
Re–C(3)	2.318 (9)	N(1)–N(2)	1.283 (10)
Re–C(4)	2.327 (9)	N(2)–C(8)	1.466 (11)
Re–C(5)	2.314 (10)	N(2)–C(9)	1.433 (11)
Re–C(6)	2.337 (9)	C(9)–C(10)	1.388 (13)
Re–C(7)	2.337 (9)	C(10)–C(11)	1.392 (13)
Re–N(1)	1.937 (7)	C(11)–C(12)	1.316 (16)[c]
Re–CR[b]	1.992	C(12)–C(13)	1.382 (13)
C(1)–O(1)	1.17 (1)	C(13)–C(14)	1.369 (13)
C(2)–O(2)	1.15 (1)	C(14)–C(9)	1.386 (13)
C(3)–C(4)	1.376 (15)	C(12)–O(3)	1.390 (12)
C(4)–C(5)	1.430 (15)	O(3)–C(15)	1.417 (14)
C(5)–C(6)	1.394 (15)		

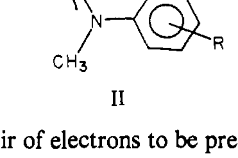
(b) Angles (Deg)

C(1)–Re–C(2)	84.2 (4)	Re–N(1)–N(2)	138.1 (6)
C(1)–Re–N(1)	102.3 (4)	N(1)–N(2)–C(8)	121.9 (7)
C(1)–Re–CR[b]	126.5	N(1)–N(2)–C(9)	118.5 (7)
C(2)–Re–N(1)	95.5 (4)	C(8)–N(2)–C(9)	119.6 (7)
C(2)–Re–CR[b]	126.4	N(2)–C(9)–C(10)	121.4 (8)
N(1)–Re–CR[b]	114.6	N(2)–C(9)–C(14)	119.5 (8)
		C(9)–C(10)–C(11)	118.2 (9)
Re–C(1)–O(1)	177.2 (9)	C(10)–C(11)–C(12)	122.1 (9)
Re–C(2)–O(2)	176.4 (9)	C(11)–C(12)–C(13)	120.8 (9)
C(3)–C(4)–C(5)	107.9 (9)	C(11)–C(12)–O(3)	116.3 (8)
C(4)–C(5)–C(6)	107.8 (9)	C(13)–C(12)–O(3)	123 (1)
C(5)–C(6)–C(7)	109.3 (9)	C(12)–C(13)–C(14)	119.0 (9)
C(6)–C(7)–C(3)	105.5 (9)	C(13)–C(14)–C(9)	120.9 (8)
C(7)–C(3)–C(4)	109.4 (9)	C(14)–C(9)–C(10)	119.1 (8)
		C(12)–O(3)–C(15)	118.8 (8)

[a] Analysis of the internal consistency of the phenyl and cyclopentadienyl rings suggests that standard errors in their bond parameters derived from least squares have been underestimated by a factor of 1.5–2.0. [b] CR denotes the centroid of the cyclopentadienyl ring. [c] This value is significantly lower than expected. Close examination of atoms C(11) and C(12) does not indicate the reason for this discrepancy.

a broad, multiline ESR resonance showed that the reaction was accompanied by the formation of paramagnetic manganese species, probably of Mn(II). We were not able to obtain the manganese diazenes, which appeared to be extremely air and temperature sensitive, pure and free from paramagnetic contamination for further studies.

Contrasting with the reaction of H^-, which gives the N(1)H product, the rhenium aryldiazenido complexes **1** react with CH_3^- to give N(2)-methylated derivatives, the N^2-aryl-N^2-methylhydrazido(2–)-N^1 complexes [$CpRe(CO)_2[NN(Me)R]$] (**6**). Competing reactions also occur, resulting in formation of the dinitrogen complex **4** (presumed to be via nucleophilic displacement at the benzene ring) and a monocarbonyl compound tentatively identified as the acetyl complex [$CpRe(CO)(COMe)(N_2R)$] (**7**) (due to attack at a carbonyl). The latter type seems to be formed also in reactions with PhLi and *n*-BuLi, and these compounds are being investigated further. Qualitatively, the proportion of dinitrogen complex increased in the order of benzene substituents: *o*-CF_3 > *p*-OMe > *p*-Me > *p*-NEt_2. The hydrazido(2–) complexes **6** are dark red, air-stable solids, all soluble in organic solvents, and have ν(CO) values ca. 1950 vs and 1880 vs cm^{-1} (hexane). They have been completely characterized by IR, NMR, and mass spectral data (Table V) and by an X-ray crystal structure determination on **6b** (see below). The hydrazido(2–) ligand is bound to the metal in the highly unusual bent geometry II,



II

suggesting a lone pair of electrons to be present on N(1). This is entirely consistent with the reactivity, since protonation at N(1) occurs on addition of HBF_4 to yield the cationic hydrazido(1–) complexes [$CpRe(CO)_2[NHN(Me)R]$][BF_4] (**8**) as air-stable, dark red crystals. The hydrazido(2–) complex can be easily and completely regenerated by treatment with Na_2CO_3. The protonation is accompanied by an increase in the ν(CO) positions (e.g., to near 2000 vs and 1935 vs cm^{-1} in the *p*-CH_3 and *p*-OCH_3 derivatives **8a** and **8b**), and δ(NH) occurs near 16 in the NMR. The site of protonation has been confirmed by $^{15}N(1)$ isotopic substitution in [$^{15}N^1$]**8b** with the observed coupling constant $^1J(^{15}NH)$ = 78 Hz. We have evidence for the existence of stereoisomers in solution in $CDCl_3$ (but not in $(CD_3)_2CO$) at room temperature for these complexes, since each resonance in the NMR of, for example, **8b**

Table VII. Least-Squares Planes Calculations[a]

Planes

plane	atoms defining plane	equation	χ^2
1	C(3)–C(7)	$0.4068X + 0.4687Y - 0.7841Z + 4.2161 = 0$	2.80
2	C(9)–C(14)	$-0.5370X - 0.3704Y - 0.7579Z + 3.3347 = 0$	2.30
3	C(8), C(9), N(1), N(2)	$-0.7166X - 0.5458Y - 0.4342Z + 3.3124 = 0$	0.00
4	Re, C(2), N(1)	$-0.4201X + 0.3372Y - 0.8425Z + 2.4733 = 0$	
5	Re, C(1), N(1)	$-0.6802X - 0.7312Y - 0.0514Z + 2.3669 = 0$	
6	C(11), C(14), O(3)	$-0.5838X - 0.4456Y - 0.6787Z + 3.3617 = 0$	

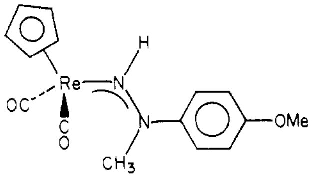
plane	dev of atoms from the plane, Å
1	C(3), 0.00 (1); C(4), −0.01 (1); C(5), 0.01 (1); C(6), −0.01 (1); C(7), 0.00 (1)
2	C(9), −0.006 (9); C(10), 0.00 (1); C(11), 0.00 (1); C(12), 0.00 (1); C(13), −0.01 (1); C(14), 0.01 (1)

Dihedral Angles between Planes

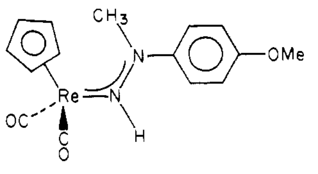
plane A	plane B	angle, deg	plane A	plane B	angle, deg	plane A	plane B	angle, deg
1	3	101.9	3	4	61.1	2	3	23.6
1	4	49.6	3	5	24.7	2	6	6.8
1	5	125.4	4	5	85.3			

[a] *X*, *Y*, and *Z* are the orthogonal coordinates (Å) with *X* along the *a* axis, *Y* in the *a*–*b* plane, and *Z* along the *c** axis.

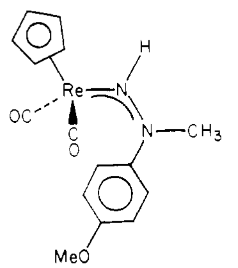
occurs as two unequal sets of signals of consistent relative intensity, which we ascribe to the structures III and IV (rather than V or VI in which steric crowding occurs). Further work on the structural characterization of these hydrazido(1−) complexes and an NMR study of their stereoisomerism will be reported in a future paper.



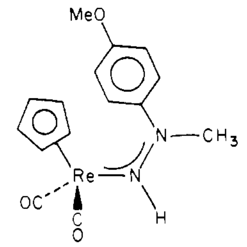
III



IV



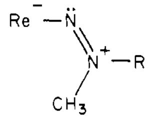
V



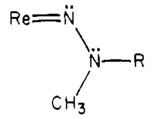
VI

Description of the Structure of [CpRe(CO)$_2$[*p*-NN(CH$_3$)C$_6$H$_4$OMe]] (6b). The crystal structure consists of four discrete molecules per unit cell. The molecular structure and numbering scheme are shown in Figure 1, while bond distances and angles are contained in Table VI. The shortest intermolecular contact is 2.37 (1) Å, between O(3) and H(11); other intermolecular distances have been included in the supplementary material (Table C). The rhenium atom lies in an irregular tetrahedral environment, provided by two carbonyl ligands, the centroid of an η^5-C$_5$H$_5$ ligand and N(1) of a *N*^{2}-(methoxyphenyl)-*N*^{2}-methylhydrazido(2−)-*N*^{1} ligand. The "tetrahedral angles" range widely from 84.2 (4)° for C(1)–Re–C(2) to 126.5 (4)° for C(1)–Re–CR.[15] The Re–C(carbonyl) distances (Re–C(1) = 1.883 (9) Å and Re–C(2) = 1.890 (10) Å) are not significantly different from one another and have typical values, similar to those found in related compounds,[16-19] e.g., in CpRe(CO)$_2$HSiPh$_3$ (9)[19] Re–C(carbonyl)$_{av}$ = 1.88 (1) Å and in [Cp(CO)$_2$Re=C(C$_6$H$_5$)P(CH$_3$)$_3$][BCl$_4$] (**10**)[18] Re–C(carbonyl)$_{av}$ = 1.91 Å. The average Re–C(cyclopentadienyl) distance is 2.327 (9) Å, which is comparable to values found in other compounds, viz., for **9**[19] Re–C(cyclopentadienyl)$_{av}$ = 2.30 Å, while for **10**[18] Re–C(cyclopentadienyl)$_{av}$ = 2.31 (2) Å.

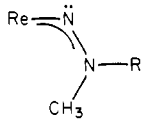
The principal chemical features elucidated by the structure are that methylation of the aryldiazenido ligand in **1b** has occurred at N(2) to generate a hydrazido(2−) ligand and, furthermore, that this ligand is coordinated to the metal through N(1) in an "end-on" fashion with a distinctly bent Re–N(1)–N(2) geometry (angle at N(1) = 138.1 (6)°). This is only the second example of a hydrazido(2−) complex known to have this geometry, and the metrical details closely parallel those of the first example [Cp$_2$WH(*p*-NNHC$_6$H$_4$F)][PF$_6$].[20] Thus, the Re–N(1) distance (1.937 (7) Å) is probably lengthened over that in the aryldiazenido compound,[21] whereas the N(1)–N(2) length (1.28 (1) Å) is intermediate between typical single (1.40 Å)[22,23] and double (1.23 Å)[24] bonds. The structure seems to be best described in valence terms by IX, intermediate between the formal structures VII and VIII. The



VII



VIII



IX

observed bent geometry contrasts with the totally linear (or nearly so) M–N–N skeleton more frequently observed in hydrazido(2−) complexes of Mo,[25,26] W,[27,28] and Re.[29] The

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(15) CR is the centroid of the Cp ring.

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(21) There has been no structural determination of the rhenium aryldiazenido complexes **1**, though these are expected to be structurally analogous to the manganese aryldiazenido complexes **2**, for which a structure determination (on **2a**) shows an exceedingly short Mn–N bond length of 1.693 (7) Å.[4] The Re–N bond length is 1.77 (2) Å in the aryldiazenido complex ReCl$_2$(N$_2$Ph)(PMe$_2$Ph)$_3$.[29]

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reason for the nonlinearity in the present case is clear. As in the tungsten example,[20] the metal thereby acquires an 18-electron count, which would be exceeded if the lone pair on N(1) were to donate to Re also, to make the ReNN skeleton linear. By contrast, such a donation is required to *establish* the 18-electron count in the Mo, W, and Re complexes cited above possessing linear MNN skeletons.

It is instructive to compare the dimensions of the rhenium–hydrazido(2–) group in the two determined structures possessing linear and nonlinear geometries. In $[ReCl_2(NH_3)(N_2HPh)(PMe_2Ph)_2]Br$, the values observed for the linear Re–N–N system[29] are Re–N = 1.75 (1) Å, N–N = 1.28 (2) Å, and Re–N–N = 172 (1)°. Thus, the Re–N distance is considerably shorter than in the present case, consistent with this notion that the linearity is due to the nitrogen atom donating to Re the (otherwise) lone pair of electrons, thus increasing the multiple bonding to the Re atom. In both cases, however, the N–N bonds are not significantly different in length (and are slightly longer than a typical double-bond length). If the Re–N distance to the NH_3 ligand in ref 29 (2.200 (13) Å) can be taken as representative of a single bond, then it appears that a considerable degree of Re–N multiple bonding exists in the aryldiazenido complex and in both the linear and the bent hydrazido(2–) complexes.

Table VII lists the results of mean-plane calculations. The most striking features are as follows: (i) The geometry at N(2) is strictly planar (plane 3) due to the delocalization of the ReN(1)N(2) π system (the Re atom lies only 0.156 Å out of this plane). (ii) The phenyl ring (plane 2) is not coplanar with plane 3 but is twisted to make a dihedral angle of ca. 24°, probably to relieve intermolecular contacts between H(10) and the CH_3 group on N(2) (note that the H(10)–H(83) distance is only 1.85 Å); this may be compared with the nearly planar arrangement found in the tungsten compound,[20] where a N(2)H group is present instead of $N(2)CH_3$. (iii) Plane 3, that of the hydrazido(2–) ligand skeleton, does not bisect the angle at Re formed by the two carbonyl groups; rather, the hydrazido plane is twisted toward C(1)O(1) as can be seen from the smaller dihedral angle made with plane 5 (ca. 25°) compared to that with plane 4 (ca 61°). The reason for this twisted arrangement is not presently clear.

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Registry No. **1a**, 81028-25-3; **1b**, 81028-27-5; **1c**, 81028-29-7; **1d**, 81028-31-1; **1e**, 73838-58-1; **1f**, 81028-33-3; **1g**, 81028-35-5; **2a**, 81028-37-7; **2b**, 81028-39-9; **2c**, 81028-41-3; **2d**, 81028-43-5; **2e**, 81028-45-7; **3a**, 81045-30-9; **3b**, 81028-46-8; **3d**, 81028-47-9; **3g**, 81028-48-0; **4**, 36543-62-1; **5**, 73838-59-2; **6a**, 81028-49-1; **6b**, 81028-50-4; **6d**, 81028-51-5; **6e**, 81045-31-0; **7a**, 81028-52-6; **7b**, 81028-53-7; **7d**, 81028-54-8; **7e**, 81028-55-9; **8a**, 81028-57-1; **8b**, 81028-59-3; $MeCpMn(CO)_2(o\text{-}NHNC_6H_4CF_3)$, 81028-60-6; $MeCpMn(CO)_2(3,5\text{-}NHNC_6H_3Me_2)$, 81028-61-7; $CpRe(CO)(COPh)(p\text{-}N_2C_6H_4OMe)$, 81028-62-8; $(\eta^5\text{-}C_5H_5)Re(CO)(CO\text{-}n\text{-}Bu)(p\text{-}N_2C_6H_4NEt_2)$, 81028-63-9; $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]\cdot HCl$, 81028-64-0; $CpRe(CO)_2THF$, 59423-86-8; $(\eta^5\text{-}C_5H_5)Re(CO)_3$, 12079-73-1; $(\eta^5\text{-}CH_3C_5H_4)MnH(CO)_2SiPh_3$, 32628-49-2.

Supplementary Material Available: Thermal parameters (Table A), calculated hydrogen positions (Table B), intermolecular distances (Table C), and observed and calculated structure factors (Table D) (19 pages). Ordering information is given on any current masthead page.

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Aryldiazenido, Aryldiazene, and Arylhydrazido Complexes. Low-Temperature (–100 °C) X-ray Structural Characterization of Nonlinear Tungsten–Arylhydrazido(2–) Coordination in $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$ and a Comparison of the Reactions of Cp_2WH_2 and $CpRe(CO)_2H_2$ with Arenediazonium Ions

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The structure of $[Cp_2WH(p\text{-}NNHC_6H_4F)][PF_6]\cdot Me_2CO$ has been determined by single-crystal X-ray crystallography at –100 °C. The compound crystallizes in the space group $P2_1/c$ with a = 10.270 (3) Å, b = 10.591 (2) Å, c = 21.041 (5) Å, β = 107.35 (2)°, and Z = 4. The calculated and measured densities are 1.953 and 1.94 (1) g cm^{-3}, respectively. On the basis of 2479 observed, three-dimensional, X-ray counter-measured intensities with $I > 2.3\sigma(I)$ in the range $3° \leq 2\theta \leq 45°$ (Mo Kα), the structure was solved and refined by full-matrix, least-squares methods to $R = 0.035$ and $R_w = 0.043$. The environment of the tungsten atom in the cation is that of a very flattened tetrahedron, with the W atom displaced only 0.224 Å out of the plane defined by N(1) and the centroids of the two Cp rings, presumably toward the hydride ligand (which was not located). The p-fluorophenylhydrazido(2–) ligand is bound to W with a distinctly nonlinear W–N(1)–N(2) skeleton, with W–N(1) = 1.837 (7) Å, N(1)–N(2) = 1.315 (9) Å, and W–N(1)–N(2) = 146.4 (5)°. Unsuccessful attempts were made to synthesize other examples of metal–hydrazido(2–) complexes which might also contain nonlinear M–N–N skeletons by reacting p-fluorobenzenediazonium ion with related compounds $Cp_2W(Ph)H$ and $CpRe(CO)_2H_2$.

Introduction

Structural studies of aryldiazenido complexes have, by now, firmly established that this ligand may, in its coordination to transition metals, display a variety of skeletal geometries of which two, the "singly bent" (I) and "doubly bent" (II), modes are most common.[1] In simple terms, these geometries can

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