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Aryldiazene, Aryldiazenido, and Hydrazine Complexes of Manganese. Preparation, Characterization, and X-ray Crystal Structures of $[Mn(CO)_3(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2]BF_4$ and $[Mn(CO)_3(NH_2NH_2)\{PPh(OEt)_2\}_2]BPh_4$ Derivatives

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Aryldiazene complexes $[Mn(CO)_3(ArN{=}NH)P_2]BF_4$ (**1**, **2**) and $[\{Mn(CO)_3P_2\}_2(\mu\text{-}HN{=}NArArN{=}NH)](BF_4)_2$ (**3**, **4**) [$P = PPh(OEt)_2$, PPh_2OEt; $Ar = C_6H_5$, $2\text{-}CH_3C_6H_4$, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$; $ArAr = 4,4'\text{-}C_6H_4C_6H_4$, $4,4'\text{-}(2\text{-}CH_3)C_6H_3C_6H_3(2\text{-}CH_3)$, $4,4'\text{-}C_6H_4CH_2C_6H_4$] were prepared by reacting hydride species $MnH(CO)_3P_2$ with the appropriate aryldiazonium cations in CH_2Cl_2 or acetone solutions at −80 °C. The compounds were characterized by IR, ^1H and ^{31}P NMR spectra (with ^{15}N isotopic substitution), and a single-crystal X-ray structure determination. The complex $[Mn(CO)_3(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2]BF_4$ (**1c**) crystallizes in the space group $C2/c$ with $a = 31.857(5)$ Å, $b = 11.119(2)$ Å, $c = 22.414(3)$ Å, $\beta = 97.82(1)°$, and $Z = 8$. Treatment of aryldiazene compounds **1**−**4** with NEt_3 gave the pentacoordinate aryldiazenido $[Mn(CO)_2(ArN_2)P_2]$ (**5**, **6**) and $[\{Mn(CO)_2P_2\}_2(\mu\text{-}N_2ArArN_2)]$ (**7**, **8**) [$P = PPh(OEt)_2$, PPh_2OEt; $Ar = C_6H_5$, $4\text{-}CH_3C_6H_4$; $ArAr = 4,4'\text{-}C_6H_4C_6H_4$, $4,4'\text{-}(2\text{-}CH_3)C_6H_3C_6H_3\text{-}(2\text{-}CH_3)$] derivatives. Protonation reactions of these aryldiazenido complexes **5**−**8** with HCl afforded the aryldiazene $[MnCl(CO)_2(ArN{=}NH)P_2]$ (**9**) and $[\{MnCl(CO)_2P_2\}_2(\mu\text{-}HN{=}NArArN{=}NH)]$ (**10**) derivatives. Hydrazine complexes $[Mn(CO)_3(RNHNH_2)P_2]BPh_4$ (**11**, **12**) [$P = PPh(OEt)_2$, PPh_2OEt; $R = H$, CH_3, C_6H_5, $4\text{-}NO_2C_6H_4$] were prepared by allowing hydride species $MnH(CO)_3P_2$ to react first with triflic acid and then with the appropriate hydrazine. Their characterization by IR, ^1H and ^{31}P NMR spectra, and an X-ray crystal structure determination is reported. The compound $[Mn(CO)_3(NH_2NH_2)\{PPh(OEt)_2\}_2]BPh_4$ (**11a**) crystallizes in the space group $P\bar{1}$ with $a = 13.772(3)$ Å, $b = 14.951(4)$ Å, $c = 13.319(3)$ Å, $\alpha = 104.47(1)°$, $\beta = 100.32(1)°$, $\gamma = 111.08(1)°$, and $Z = 2$. Oxidation reactions of hydrazine compounds **11** and **12** with $Pb(OAc)_4$ at −40 °C gave stable aryldiazene $[Mn(CO)_3(RN{=}NH)P_2]BPh_4$ and thermally unstable (upon reaching −40 °C) diazene $[Mn(CO)_3(HN{=}NH)P_2]BPh_4$ derivatives.

Introduction

There is current interest in the chemistry of aryldiazo, aryldiazene, and hydrazine complexes[1−3] due to different factors including the possible relevance in the dinitrogen fixation process, the influence that the central metal and the ancillary ligand may have in determining the different coordination modes of the "diazo" groups, and the potential properties of these derivatives toward oxidation, reduction, protonation, and deprotonation reactions.

Our interest in this field has been mainly devoted to metal complexes of the iron family, and a number of studies on the synthesis and reactivity of both mono and bis forms of aryldiazene and aryldiazenido derivatives of the type $[MH(ArN{=}NH)P_4]^+$, $[M(ArN{=}NH)_2P_4]^{2+}$, $[M(ArN_2)P_4]^+$, and $[M(ArN_2)_2P_3]^{2+}$ ($M = Fe$, Ru, Os; $P =$ phosphite) have been recently reported.[4] These results prompted us to extend our studies to include other metal complexes such as those of manganese which result to be, as Mn(I), isoelectronic with the iron(II) family and whose "diazo" and hydrazine chemistry is relatively little studied[5−12] as compared to other transition metals.[1] A perusal of the literature showed, in fact, that while some stable and well-characterized aryldiazenido complexes,

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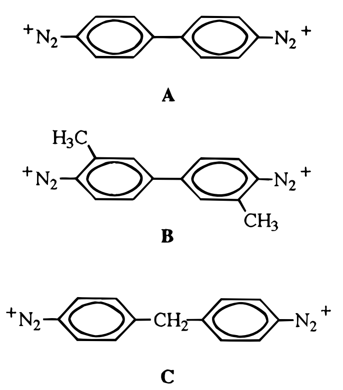
Chart 1



$[Mn(\eta^5\text{-}RC_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4R')]BF_4$ ($R = CH_3$, H; $R' = CF_3$, F, H),[5] $Mn(CO)_n(N_2Ph)(PPh_3)_{4-n}$ ($n = 2, 3$),[8,10] $MnX(N_2Ph)_2(PPh_3)_2$,[10] $[Mn(CO)(N_2Ph)_2(PPh_3)_2]PF_6$,[10] and $[(PhNN)Mn(CO)_4]_2$,[12] have been described, very few examples of both diazene and hydrazine complexes have been reported. Apart from stable dimeric complexes with a diazene bridge of the type $\eta^5\text{-}C_5H_5Mn(CO)_2HN{=}NHCr(CO)_5$[7] and $[\eta^5\text{-}C_5H_5Mn(CO)_2]_2(\mu\text{-}C_6H_5N{=}NH)$[9] and the related unstable mononuclear ones, only two brief reports, one on aryldiazene[10] and the other on hydrazine[13] derivatives of manganese, appear in the literature. It seems therefore desirable to begin a systematic study of the "diazo" chemistry of this metal, and so in this paper we report the synthesis and characterization of new aryldiazene, aryldiazenido, and hydrazine complexes of manganese stabilized by phosphonite $PPh(OEt)_2$ and phosphinite PPh_2OEt ligands. These studies include the use of the bis(diazonium) cations $[N_2ArArN_2]^{2+}$ of the types **A**−**C** (Chart 1), which gave dinuclear complexes, as well as the first X-ray crystal structure determinations of an aryldiazene and a hydrazine derivative of manganese.

Experimental Section

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere dry box. Once isolated, the complexes were found to be relatively stable in air but were stored under an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuumtight storage flasks. The phosphites $PPh(OEt)_2$ and PPh_2OEt were prepared by the method of Rabinowitz and Pellon.[14] Diazonium salts were obtained in the usual way.[15] The related bis(diazonium) $[N_2ArArN_2](BF_4)_2$ [ArAr = 4,4′-$C_6H_4C_6H_4$, **A**; 4,4′-(2-CH_3)$C_6H_3C_6H_3$(2-CH_3), **B**; 4,4′-$C_6H_4CH_2C_6H_4$, **C**] salts (Chart 1) were prepared by treating the amine precursors $H_2NArArNH_2$ with $NaNO_2$ as described in the literature for the common mono(diazonium) salts.[15] The labeled diazonium tetrafluoroborates $[C_6H_5N{\equiv}^{15}N]BF_4$ and $[4,4'\text{-}^{15}N{\equiv}NC_6H_4C_6H_4N{\equiv}^{15}N](BF_4)_2$ were prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the appropriate amine. Alternatively, the $[C_6H_5{}^{15}N{\equiv}N]BF_4$ salt was obtained from $NaNO_2$ and $C_6H_5{}^{15}NH_2$. The hydrazines $C_6H_5NHNH_2$, CH_3NHNH_2, 4-$NO_2C_6H_4NHNH_2$, and $(CH_3)_2NNH_2$ were Aldrich products used as received. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.[16] $Mn_2(CO)_{10}$ (Aldrich), $HBF_4{\cdot}Et_2O$ (54% solution), and triflic acid (Aldrich) were used as purchased. Triethylamine was dried with CaH_2 and distilled before use. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Digilab Bio-Rad FTS-40 spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. ^1H and ^{13}C spectra are referred to internal tetramethylsilane, while $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The conductivities of 10^{-3} M solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83 instrument.

Synthesis of Complexes. The hydride $MnH(CO)_5$ was prepared from $Mn_2(CO)_{10}$ according to the procedure previously reported.[17] The hydride species $MnH(CO)_3P_2$, $MnH(CO)_2P_3$, and $MnH(CO)P_4$ [P = $PPh(OEt)_2$ and PPh_2OEt] were instead prepared by substitution of the carbonyl ligands in the $MnH(CO)_5$ derivative following a method that will be reported in a forthcoming paper.[18] The $MnH(CO)_3$(dppe) complex was obtained as previously described.[19]

$[Mn(CO)_3(ArN{=}NH)P_2]BF_4$ (1, 2) [Ar = C_6H_5 (a), 4-$CH_3C_6H_4$ (b), 2-$CH_3C_6H_4$ (c); P = $PPh(OEt)_2$ (1), PPh_2OEt (2)]. A solid sample of the appropriate hydride $MnH(CO)_3P_2$ (1 mmol) and solid aryldiazonium tetrafluoroborate $[ArN_2]BF_4$ (1 mmol) were mixed together in a 25-mL three-necked round-bottomed flask and cooled to about −80 °C. Dichloromethane (10 mL) was slowly added, and the resulting mixture was brought to room temperature and stirred for 3 h. Removal of the solvent under reduced pressure gave an oil which was treated with 2 mL of ethanol. By cooling of the resulting solution to −25 °C yellow microcrystals slowly separated out which were collected and crystallized from ethanol; yield ≥80%. Anal. Calcd for **1a**: C, 47.83; H, 4.98; N, 3.85. Found: C, 48.04; H, 4.91; N, 3.71. Mp: 87 °C. $\Lambda_M = 87.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **1b**: C, 48.54; H, 5.16; N, 3.77. Found: C, 48.42; H, 5.31; N, 3.82. Mp: 97 °C. $\Lambda_M = 99.5\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **1c**: C, 48.54; H, 5.16; N, 3.77. Found: C, 48.76; H, 5.06; N, 3.68. Mp: 123 °C. $\Lambda_M = 92.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **2b**: C, 56.60; H, 4.75; N, 3.47. Found: C, 56.57; H, 4.88; N, 3.56. Mp: 131 °C. $\Lambda_M = 85.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **2c**: C, 56.60; H, 4.75; N, 3.47. Found: C, 56.77; H, 4.71; N, 3.52. Mp: 137 °C. $\Lambda_M = 91.0\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Mn(CO)_3(4\text{-}CH_3OC_6H_4N{=}NH)P_2]BPh_4$ (1d, 2d). These complexes were prepared like the related **1** and **2** but using an excess of $NaBPh_4$ (2 mmol, 0.68 g) in ethanol (5 mL) as the precipitating agent; yield ≥80%. Anal. Calcd for **1d**: C, 65.46; H, 5.90; N, 2.83. Found: C, 65.84; H, 5.98; N, 2.89. $\Lambda_M = 51.3\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **2d**: C, 70.60; H, 5.54; N, 2.66. Found: C, 70.78; H, 5.67; N, 2.75. $\Lambda_M = 53.8\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[Mn(CO)_3(C_6H_5N{=}^{15}NH)\{PPh(OEt)_2\}_2]BF_4$ ($1a_1$) and $[Mn(CO)_3(C_6H_5{}^{15}N{=}NH)\{PPh(OEt)_2\}_2]BF_4$ ($1a_2$). These complexes were prepared like the related **1a** using the labeled $[C_6H_5N{\equiv}^{15}N]BF_4$ and $[C_6H_5{}^{15}N{\equiv}N]BF_4$ aryldiazonium salts, respectively; yield ≥80%. Anal. Calcd for **$1a_1$**: C, 47.76; H, 4.97; N, 3.98. Found: C, 47.81; H, 4.89; N, 3.86. Mp: 87 °C. $\Lambda_M = 82.8\ \Omega^{-1}\ mol^{-1}\ cm^2$. Calcd for **$1a_2$**: C, 47.76; H, 4.97; N, 3.98. Found: C, 47.68; H, 4.84; N, 3.80. Mp: 87 °C. $\Lambda_M = 92.0\ \Omega^{-1}\ mol^{-1}\ cm^2$.

$[\{Mn(CO)_3P_2\}_2(\mu\text{-}HN{=}NArArN{=}NH)](BF_4)_2$ (3, 4) [P = $PPh(OEt)_2$ (3), PPh_2OEt (4); ArAr = 4,4′-$C_6H_4C_6H_4$ (a), 4,4′-(2-CH_3)-$C_6H_3C_6H_3$(2-CH_3) (c)]. A 25-mL three-necked round-bottomed flask was charged with a solid sample of the appropriate hydride $MH(CO)_3P_2$ (1 mmol) and of the bis(diazonium) salt $[N_2ArArN_2](BF_4)_2$ (0.5 mmol) and cooled to about −80 °C. Acetone (10 mL) was added, and the resulting mixture was brought to room temperature and stirred for 6 h.

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The solvent was removed under reduced pressure giving an oil which was triturated with 5 mL of ethanol. A red solid slowly separated out which was filtered and crystallized from ethanol; yield ≥90%. Anal. Calcd for **3a**: C, 47.89; H, 4.85; N, 3.85. Found: C, 47.93; H, 4.94; N, 3.79. Mp: 165 °C. $\Lambda_M = 175\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **3c**: C, 48.61; H, 5.03; N, 3.78. Found: C, 48.25; H, 5.17; N, 3.71. Mp: 168 °C. $\Lambda_M = 182\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **4a**: C, 56.16; H, 4.46; N, 3.54. Found: C, 55.87; H, 4.38; N, 3.46. Mp: 156 °C. $\Lambda_M = 178\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **4c**: C, 56.67; H, 4.63; N, 3.48. Found: C, 56.51; H, 4.70; N, 3.58. Mp: 157 °C. $\Lambda_M = 191\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

$[\mathrm{Mn(CO)_3\{PPh(OEt)_2\}_2}]_2(\mu\text{-}4,4'\text{-}\mathrm{HN{=}NC_6H_4CH_2C_6H_4N{=}NH})(\mathrm{BPh_4})_2$ (3e). This complex was prepared like the related **3** but using an excess of $\mathrm{NaBPh_4}$ in ethanol as the precipitating agent; yield ≥90%. Anal. Calcd: C, 66.47; H, 5.84; N, 2.90. Found: C, 66.60; H, 5.96; N, 2.81. $\Lambda_M = 121\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

$[\{\mathrm{Mn(CO)_3(PPh(OEt)_2)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{H^{15}N{=}NC_6H_4C_6H_4N{=}^{15}NH})](\mathrm{BF_4})_2$ (3a$_1$) and $[\{\mathrm{Mn(CO)_3(PPh_2OEt)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{H^{15}N{=}NC_6H_4\text{-}C_6H_4N{=}^{15}NH})]\ (\mathrm{BF_4})_2$ (4a$_1$). These complexes were prepared like the related **3a** and **4a** using the labeled $[4,4'\text{-}^{15}\mathrm{N{\equiv}NC_6H_4C_6H_4N{\equiv}^{15}N}](\mathrm{BF_4})_2$ bis(diazonium) salt; yield ≥90%. Anal. Calcd for **3a$_1$**: C, 47.82; H, 4.84; N, 3.98. Found: C, 47.75; H, 4.72; N, 3.87. Mp: 165 °C. $\Lambda_M = 184\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **4a$_1$**: C, 56.08; H, 4.45; N, 3.66. Found: C, 56.24; H, 4.53; N, 3.59. Mp: 155 °C. $\Lambda_M = 172\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

$\mathrm{Mn(CO)_2(ArN_2)P_2}$ (5, 6) [Ar = $\mathrm{C_6H_5}$ (a), 4-$\mathrm{CH_3C_6H_4}$ (b); P = $\mathrm{PPh(OEt)_2}$, (5), $\mathrm{PPh_2OEt}$ (6)]. An excess of triethylamine (5 mmol, 0.70 mL) was added to a solution of the appropriate diazene complex $[\mathrm{Mn(CO)_3(ArN{=}NH)P_2}]\mathrm{BF_4}$ (1 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$, and the reaction mixture was stirred for 2 h. The solvent was removed under reduced pressure giving a red oil which was treated with 2 mL of ethanol. The resulting solution was cooled to 0 °C and vigorously stirred until an orange solid separated out which was filtered out and crystallized from ethanol; yield ≥80%. Anal. Calcd for **5a**: C, 54.91; H, 5.76; N, 4.57. Found: C, 54.53; H, 5.65; N, 4.49. Calcd for **5b**: C, 55.60; H, 5.95; N, 4.47. Found: C, 55.78; H, 5.87; N, 4.55. Mp: 61 °C. Calcd for **6b**: C, 64.35; H, 5.40; N, 4.06. Found: C, 64.57; H, 5.49; N, 4.10. Mp: 123 °C.

$\mathrm{Mn(CO)_2(C_6H_5N{\equiv}^{15}N)\{PPh(OEt)_2\}_2}$ (5a$_1$). This compound was prepared like **5a** starting from the labeled complex $[\mathrm{Mn(CO)_3\text{-}(C_6H_5N{=}^{15}NH)\{PPh(OEt)_2\}_2}]\mathrm{BF_4}$ (**1a$_1$**); yield ≥80%. Anal. Calcd: C, 54.82; H, 5.75; N, 4.73. Found: C, 54.58; H, 5.83; N, 4.80.

$[\mathrm{Mn(CO)_2P_2}]_2(\mu\text{-}\mathrm{N_2ArArN_2})$ (7, 8) [ArAr = 4,4′-$\mathrm{C_6H_4C_6H_4}$, (a), 4,4′-(2-$\mathrm{CH_3}$)$\mathrm{C_6H_3C_6H_3}$(2-$\mathrm{CH_3}$) (c); P = $\mathrm{PPh(OEt)_2}$ (7) $\mathrm{PPh_2OEt}$ (8)]. These binuclear complexes were prepared like the related mononuclear **5** and **6** by deprotonation with triethylamine of the corresponding bis(diazene) $[\{\mathrm{Mn(CO)_3P_2}\}_2(\mu\text{-}\mathrm{HN{=}NArArN{=}NH})](\mathrm{BF_4})_2$ (**3**, **4**) derivatives in $\mathrm{CH_2Cl_2}$; yield ≥90%. Anal. Calcd for **7a**: C, 55.00; H, 5.60; N, 4.58. Found: C, 54.82; H, 5.48; N, 4.67. Mp: 132 °C. Calcd for **7c**: C, 55.69; H, 5.80; N, 4.48. Found: C, 55.86; H, 5.86; N, 4.43. Mp: 100 °C. Calcd for **8c**: C, 64.45; H, 5.26; N, 4.06. Found: C, 64.22; H, 5.12; N, 4.13. Mp: 143 °C.

$[\mathrm{Mn(CO)_2\{PPh(OEt)_2\}_2}]_2(\mu\text{-}4,4'\text{-}^{15}\mathrm{N{\equiv}NC_6H_4C_6H_4N{\equiv}^{15}N})$ (7a$_1$). This complex was prepared like **7a** starting from the labeled $[\{\mathrm{Mn\text{-}(CO)_3(PPh(OEt)_2)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{H^{15}N{=}NC_6H_4\text{-}C_6H_4N{=}^{15}NH})](\mathrm{BF_4})_2$ (**3a$_1$**)-derivative; yield ≥90%. Anal. Calcd: C, 54.91; H, 5.60; N, 4.74. Found: C, 54.78; H, 5.52; N, 4.81. Mp: 132 °C.

$[\mathrm{MnCl(CO)_2(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2}]$ (9b). A solution of $\mathrm{Mn(CO)_2(4\text{-}CH_3C_6H_4N_2)[PPh(OEt)_2]_2}$ (**5b**) (0.3 mmol, 0.19 g) in 10 mL of $\mathrm{CH_2Cl_2}$ was cooled to −80 °C, and HCl in solution of diethyl ether (0.3 mmol, 3 mL of a 0.1 M solution) was added. [The solution of HCl was prepared by treating $\mathrm{(CH_3)_3SiCl}$ in diethyl ether with an equimolar amount of $\mathrm{CH_3OH}$.] The reaction mixture was brought to room temperature and stirred for 2 h, and then the solvent was removed under reduced pressure. The oil obtained was treated with 2 mL of ethanol and the resulting solution stirred at 0 °C until a red solid slowly separated out which was filtered and crystallized from ethanol; yield ≥70%. Anal. Calcd: C, 52.54; H, 5.78; N, 4.23. Found: C, 52.76; H, 5.63; N, 4.34. Mp: 107 °C.

$[\mathrm{MnCl(CO)_2\{PPh(OEt)_2\}_2}]_2(\mu\text{-}4,4'\text{-}\mathrm{H^{15}N{=}NC_6H_4C_6H_4N{=}^{15}NH})$ (10a$_1$). This complex was prepared like the related mononuclear **9b** by treating the labeled $[\mathrm{Mn(CO)_2\{PPh(OEt)_2\}_2}]_2(\mu\text{-}4,4'\text{-}^{15}\mathrm{N{\equiv}NC_6H_4\text{-}C_6H_4N{\equiv}^{15}N})$ (**7a$_1$**) complex with HCl in a 1:2 molar ratio; yield ≥85%. Anal. Calcd: C, 51.82; H, 5.44; N, 4.47. Found: C, 52.12; H, 5.39; N, 4.35. Mp: 111 °C.

$[\mathrm{Mn(CO)_3(RNHNH_2)P_2}]\mathrm{BPh_4}$ (11, 12) [R = H (a), $\mathrm{CH_3}$ (b); P = $\mathrm{PPh(OEt)_2}$ (11), $\mathrm{PPh_2OEt}$ (12)]. A solution of the appropriate hydride $\mathrm{MnH(CO)_3P_2}$ (1 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$ was cooled to −80 °C and treated with an equimolar amount of $\mathrm{CF_3SO_3H}$ (1 mmol, 88.5 μL). The reaction mixture was brought to room temperature, stirred for about 2 h, and cooled again to −80 °C. An excess of the appropriate hydrazine (3 mmol) was added to the solution which was brought to 20 °C and stirred for 12−14 h. The solvent was removed under reduced pressure giving an oil which was treated with 5 mL of ethanol. The addition of an excess of $\mathrm{NaBPh_4}$ (2 mmol, 0.68 g) in 2 mL of ethanol caused the precipitation of a yellow solid, which was filtered out and crystallized from $\mathrm{CH_2Cl_2}$ (2 mL)/ethanol (8 mL); yield ≥80%. Anal. Calcd for **11a**: C, 63.67; H, 6.14; N, 3.16. Found: C, 63.59; H, 6.21; N, 3.23. Mp: 119 °C. $\Lambda_M = 65.0\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **11b**: C, 64.01; H, 6.27; N, 3.11. Found: C, 64.38; H, 6.22; N, 3.17. Mp: 108 °C. $\Lambda_M = 60.7\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **12a**: C, 69.48; H, 5.72; N, 2.95. Found: C, 69.67; H, 5.68; N, 3.05. Mp: 122 °C. $\Lambda_M = 59.2\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **12b**: C, 69.72; H, 5.85; N, 2.90. Found: C, 69.51; H, 5.83; N, 2.97. Mp: 121 °C. $\Lambda_M = 61.4\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

$[\mathrm{Mn(CO)_3(RNHNH_2)P_2}]\mathrm{BPh_4}$ (11, 12) [R = $\mathrm{C_6H_5}$ (c), 4-$\mathrm{NO_2C_6H_4}$ (d); P = $\mathrm{PPh(OEt)_2}$ (11), $\mathrm{PPh_2OEt}$ (12)]. These complexes were prepared like the related hydrazine derivatives by treating $\mathrm{MnH(CO)_3P_2}$ (1 mmol) with an equivalent amount of $\mathrm{CF_3SO_3H}$ (1 mmol, 88.5 μL) and then with a slight excess (1.1 mmol) of the appropriate hydrazine. The resulting solution was stirred for 3 h giving, after workup, green microcrystals of the product in about 80% yield. Anal. Calcd for **11c**: C, 66.12; H, 6.07; N, 2.91. Found: C, 66.39; H, 5.96; N, 2.85. Mp: 123 °C. $\Lambda_M = 62.2\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **11d**: C, 63.11; H, 5.80; N, 4.17. Found: C, 62.90; H, 5.72; N, 4.22. Mp: 95 °C. $\Lambda_M = 59.8\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **12c**: C, 71.35; H, 5.69; N, 2.73. Found: C, 71.55; H, 5.72; N, 2.78. Mp: 125 °C. $\Lambda_M = 63.7\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$. Calcd for **12d**: C, 68.36; H, 5.36; N, 3.92. Found: C, 68.22; H, 5.47; N, 3.84. Mp: 98 °C. $\Lambda_M = 64.1\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

$[\mathrm{Mn(CO)_3\{(CH_3)_2NNH_2\}\{PPh(OEt)_2\}_2}]\mathrm{BPh_4}$ (11e). This complex was prepared like the related **11** and **12** using an excess of the hydrazine $\mathrm{(CH_3)_2NNH_2}$ with respect to the starting $\mathrm{MnH(CO)_3P_2}$ compound (5:1 ratio) and stirring the reaction mixture for 24 h; yield ≥80%. Anal. Calcd: C, 64.34; H, 6.39; N, 3.06. Found: C, 64.02; H, 6.51; N, 3.11. Mp: 99 °C. $\Lambda_M = 58.9\ \Omega^{-1}\ \mathrm{mol}^{-1}\ \mathrm{cm}^2$.

Oxidation Reactions. The oxidation of the hydrazine complexes **11** and **12** was carried out with $\mathrm{Pb(OAc)_4}$ under an inert atmosphere in $\mathrm{CH_2Cl_2}$ at −40 °C. In a typical experiment a $\mathrm{CH_2Cl_2}$ solution (10 mL) of the appropriate hydrazine complex (0.2 mmol) was placed in a three-necked 25 mL flask fitted with a solid-addition side arm containing $\mathrm{Pb(OAc)_4}$ (0.21 mmol, 93 mg). The system was cooled to −40 °C, and the $\mathrm{Pb(OAc)_4}$ was added portionwise to the cold stirred solution in about 20−30 min. The solution was filtered and the solvent removed under vacuum to give an orange oil which was treated with 5 mL of ethanol. By vigorous stirring of the resulting solution, an orange solid separated out which was filtered out and dried under vacuum; yield ≥80%.

X-ray Structure Determination of $[\mathrm{Mn(CO)_3(4\text{-}CH_3C_6H_4N{=}NH)\text{-}\{PPh(OEt)_2\}_2}]\mathrm{BF_4}$ (1b) and $[\mathrm{Mn(CO)_3(NH_2NH_2)\{PPh(OEt)_2\}_2}]\mathrm{BPh_4}$ (11a). The crystallographic data and the final *R* indices for the two compounds **1b** and **11a** are summarized in Table 2. Both structures were solved by direct methods (SIR92)[20] and refined on F^2 using SHELXL93.[21] All the non-hydrogen atoms were refined anisotropically. For compound **1b** an empirical absorption correction was applied after the last isotropic refinement, according to the method of Walker and Stuart.[22] In each case the hydrogen atoms bonded to N atoms were located from ΔF maps and refined isotropically, whereas the remaining ones were included at calculated positions and refined as

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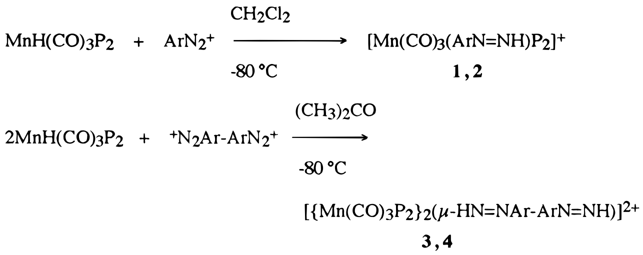
Scheme 1[a]



[a] P = PPh(OEt)$_2$ (**1**, **3**), PPh$_2$OEt (**2**, **4**); Ar = C$_6$H$_5$ (**a**), 4-CH$_3$C$_6$H$_4$ (**b**), 2-CH$_3$C$_6$H$_4$ (**c**), 4-CH$_3$OC$_6$H$_4$ (**d**), ArAr = 4,4′-C$_6$H$_4$C$_6$H$_4$ (**a**), 4,4′-(2-CH$_3$)C$_6$H$_3$C$_6$H$_3$(2-CH$_3$) (**c**), 4,4′-C$_6$H$_4$CH$_2$C$_6$H$_4$ (**e**).

riding atoms with their thermal parameters set up to 1.2 times the values of the parent atoms (1.5 times for methyl groups).

PARST95[23] and ZORTEP[24] were used for geometric calculations and drawings. All calculations were performed on an ENCORE91 station at the Centro di Studi per la Strutturistica Diffrattometrica del CNR in Parma, Italy.

Results and Discussion

Aryldiazene and Aryldiazenido Complexes. Hydride tricarbonyl species MnH(CO)$_3$P$_2$ react quickly with both mono- and bis(aryldiazonium) cations to give the diazene derivatives [Mn(CO)$_3$(ArN=NH)P$_2$]$^+$ (**1**, **2**) and [{Mn(CO)$_3$P$_2$}$_2$(μ-HN=NArArN=NH)]$^{2+}$ (**3**, **4**) which were isolated in high yields as BF$_4^-$ or BPh$_4^-$ salts and characterized (Scheme 1). Crucial for the successful preparation of both mono- and binuclear complexes is the use of an exact stoichiometric ratio between the reagents and a low temperature at the start of the reaction. Otherwise, a large amount of decomposition products or oily substances were found in the final reaction products.

Other manganese hydrides with a carbonyl−phosphine ratio different from 3:2 of the type MnH(CO)$_2$P$_3$ and MnH(CO)P$_4$ [P = PPh(OEt)$_2$ and PPh$_2$OEt] were also reacted with aryldiazonium cations, but in every case no aryldiazene complex was isolated. Monitoring the progress of the reactions by ^{1}H NMR spectra revealed the initial formation of a diazene compound which, however, resulted to be very unstable in solution and was not isolated. Instead, the hydride MnH(CO)$_3$(dppe) (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) reacted with ArN$_2^+$ to give [Mn(CO)$_3$(ArN=NH)(dppe)]BF$_4$, but the compound resulted to be impure and decomposed when crystallization was attempted. However, despite the absence of good analytical data, the IR (ν(CO) at 2029 m, 1951 s, and 1919 s cm^{-1} in KBr) and the ^{1}H NMR spectra [N*H* at δ 14.17 (s, br) and 4-C*H*$_3$C$_6$H$_4$ at δ 2.20 (s) ppm in CD$_2$Cl$_2$ at 25 °C] confirm the proposed formulation. It seems, therefore, that both the stoichiometry of the complexes and the nature of the phosphine ligands are important in determining the stability of the diazene ligand bonded to a manganese center. In fact, although the insertion reaction of the aryldiazonium cation into the Mn−H bond seems to proceed with all the tested hydrides, only with the tricarbonyl fragment Mn(CO)$_3$P$_2$ containing phosphonite PPh(OEt)$_2$ and phosphinite PPh$_2$OEt ligands can stable aryldiazene complexes be obtained. Probably, the greater Π-acceptor properties of our phosphites as compared with tertiary phosphine ligands play an important role in stabilizing the aryldiazene ligand bonded to the Mn(CO)$_3$P$_2$ fragment. It seems, in fact, that only a delicate balancing of steric and electronic factors of the ancillary ligands allows stable aryldiazene complexes of manganese to be prepared.

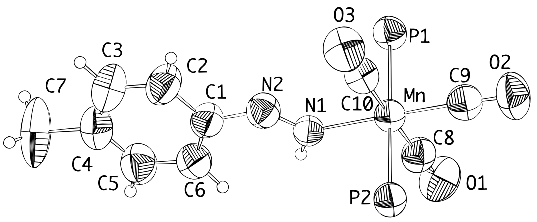
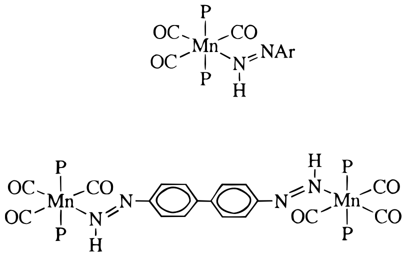


Figure 1. Perspective drawing of compound **1b**, with anisotropic thermal displacement parameters represented as ellipsoids at the 40% level of probability. Phenyl and ethoxy groups have been omitted for clarity.

Chart 2



Complexes **1**−**4** are yellow or orange solids, diamagnetic, and stable in the air both as solids and in solutions of polar organic solvents, where they behave as 1:1 (**1**, **2**) or 2:1 (**3**, **4**) electrolytes.[25] Some spectroscopic properties are reported in Table 1.

Diagnostic for the presence of the diazene ligand in both mono- and binuclear complexes was the high-frequency ^{1}H NMR signal of the NH proton at 14.09−13.33 ppm, which is split into a sharp doublet in the labeled compounds **1a$_1$**, **1a$_2$**, and **3a$_1$**. The values for both the $^1J_{^{15}\mathrm{NH}}$ and the $^2J_{^{15}\mathrm{NH}}$ of 65 and 3.8 Hz, respectively, were also determined, and these data[1,4,26] further support the proposed formulation.

The infrared spectra of both the mono- and the dinuclear aryldiazene complexes **1**−**4** show three ν(CO) bands between 2079 and 1939 cm^{-1}, two of which are of strong intensity and one medium, suggesting the presence of three carbonyl ligands in a *mer* position. Furthermore, the broad signal that appears at room temperature in the ^{31}P{^{1}H} NMR spectra resolves into a sharp singlet at −90 °C, in agreement with the presence of two magnetically equivalent phosphine ligands. On these bases a *mer*−*trans* geometry (Chart 2) similar to that found in the solid state for **1b** (Figure 1) can be proposed in solution for all the aryldiazene derivatives. This similar geometry observed for both the mononuclear and binuclear diazene complexes agrees with the other spectroscopic properties (νCO and ^{1}H NMR data) which result, in all cases, as strictly comparable.

The broad signal observed at room temperature for the ^{31}P{^{1}H} NMR spectra seems to indicate a fluxional process which may involve the aryldiazene ligand or the simple interexchange of the positions of the phosphite groups. A switch in the Mn−N bond of the ArN=NH ligand from NH to NC can be excluded on the basis of the diazene ^{1}H NMR spectra, which result in being sharp between +20 and −90 °C in the ^{15}N-labeled compounds **1a$_1$**, **3a$_1$**, and **4a$_1$**. A restricted rotation of the aryldiazene ligand as the temperature is changed cannot be excluded, and the broad ^{31}P NMR spectra observed at +20 °C may suggest a slow rotation of the ArN=NH group at this temperature. This feature, however, contrasts with the ^{1}H NMR

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Table 1. IR and NMR Data for Manganese Complexes

no.	compd	IR[a]		^{1}H NMR[b,c]		^{31}P{^{1}H} NMR[b,d]
		ν, cm^{-1}	assgnt	δ (J (Hz))	assgnt	δ
1a	$[\mathrm{Mn(CO)_3(C_6H_5N{=}NH)\{PPh(OEt)_2\}_2]BF_4}$	2062 m, 1981 s, 1948 s	ν(CO)	14.04 (s)	$\mathrm{N}H$	189 (s, br)
				4.18 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				1.42 (t)	$\mathrm{POCH_2C}H_3$	
1a$_1$	$[\mathrm{Mn(CO)_3(C_6H_5N{=}^{15}NH)\{PPh(OEt)_2\}_2]BF_4}$	2063 m, 1983 s, 1952 s	ν(CO)	14.01 (d) $({}^1J_{^{15}\mathrm{NH}} = 65)$	$\mathrm{N}H$	189 (s, br)
				4.18 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				1.40 (t)	$\mathrm{POCH_2C}H_3$	
1a$_2$	$[\mathrm{Mn(CO)_3(C_6H_5{}^{15}N{=}NH)\{PPh(OEt)_2\}_2]BF_4}$	2062 m, 1984 s, 1951 s	ν(CO)	14.00 (d) $({}^2J_{^{15}\mathrm{NH}} = 3.8)$	$\mathrm{N}H$	189 (s, br)
				4.18 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	189.9 (s)[e]
				1.40 (t)	$\mathrm{POCH_2C}H_3$	
1b	$[\mathrm{Mn(CO)_3(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2]BF_4}$	2063 m, 1983 s, 1950 s	ν(CO)	13.83 (s)	$\mathrm{N}H$	188 (s, br)
				4.16 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				2.35 (s)	$\mathrm{C}H_3$	
				1.39 (t)	$\mathrm{POCH_2C}H_3$	
1c	$[\mathrm{Mn(CO)_3(2\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2]BF_4}$	2059 m, 1983 s, 1953 s	ν(CO)	13.93 (s)	$\mathrm{N}H$	189 (s, br)
				4.19 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				2.46 (s)	$\mathrm{C}H_3$	
				1.41 (t)	$\mathrm{POCH_2C}H_3$	
1d	$[\mathrm{Mn(CO)_3(4\text{-}CH_3OC_6H_4N{=}NH)\{PPh(OEt)_2\}_2]BPh_4}$	2064 m, 1983 s, 1960 s	ν(CO)	13.39 (s)	$\mathrm{N}H$	188 (s, br)
				4.15 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				3.85 (s)	$\mathrm{OC}H_3$	
				1.38 (t)	$\mathrm{POCH_2C}H_3$	
2b	$[\mathrm{Mn(CO)_3(4\text{-}CH_3C_6H_4N{=}NH)(PPh_2OEt)_2]BF_4}$	2073 m, 1978 s, 1939 s	ν(CO)	13.74 (s)	$\mathrm{N}H$	162 (s, br)
				3.69 (qi)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				2.35 (s)	$\mathrm{C}H_3$	
				1.17 (t)	$\mathrm{POCH_2C}H_3$	
2c	$[\mathrm{Mn(CO)_3(2\text{-}CH_3C_6H_4N{=}NH)(PPh_2OEt)_2]BF_4}$	2060 m, 1982 s, 1956 s	ν(CO)	13.81 (s)	$\mathrm{N}H$	163 (s, br)
				3.70 (qi)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				2.26 (s)	$\mathrm{C}H_3$	
				1.18 (t)	$\mathrm{POCH_2C}H_3$	
2d	$[\mathrm{Mn(CO)_3(4\text{-}CH_3OC_6H_4N{=}NH)(PPh_2OEt)_2]BPh_4}$	2060 m, 1979 s, 1954 s	ν(CO)	13.33 (s)	$\mathrm{N}H$	163 (s, br)
				3.68 (qi)	$\mathrm{POC}H_2\mathrm{CH}_3$	167.7 (s)[e]
				3.84 (s)	$\mathrm{OC}H_3$	
				1.16 (t)	$\mathrm{POCH_2C}H_3$	
3a	$[\{\mathrm{Mn(CO)_3(PPh(OEt)_2)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{HN{=}NC_6H_4C_6H_4N{=}NH)](BF_4)_2}$	2067 m, 1986 s, 1950 s	ν(CO)	14.09 (s)	$\mathrm{N}H$	188 (s, br)
				4.19 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				1.41 (t)	$\mathrm{POCH_2C}H_3$	
3a$_1$	$[\{\mathrm{Mn(CO)_3(PPh(OEt)_2)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{H^{15}N{=}NC_6H_4C_6H_4N{=}^{15}NH)](BF_4)_2}$	2068 m, 1987 s, 1947 s	ν(CO)	14.09 (d) $({}^1J_{^{15}\mathrm{NH}} = 65)$	$\mathrm{N}H$	188 (s, br)
				4.19 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	189.9 (s)[e]
				1.41 (t)	$\mathrm{POCH_2C}H_3$	
3c	$[\{\mathrm{Mn(CO)_3(PPh(OEt)_2)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{HN{=}N(2\text{-}CH_3)C_6H_3C_6H_3(2\text{-}CH_3)N{=}NH\}](BF_4)_2}$	2061 m, 1982 s, 1952 s	ν(CO)	13.95 (s)	$\mathrm{N}H$	188 (s, br)
				4.19 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				2.52 (s)	$\mathrm{C}H_3$	
				1.40 (t)	$\mathrm{POCH_2C}H_3$	
3e	$[\{\mathrm{Mn(CO)_3(PPh(OEt)_2)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{HN{=}NC_6H_4CH_2C_6H_4N{=}NH)](BPh_4)_2}$	2062 m, 1983 s, 1964 s	ν(CO)	13.88 (s)	$\mathrm{N}H$	191 (s, br)
				4.16 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				3.97 (s)	$-\mathrm{C}H_2-$	
				1.37 (t)	$\mathrm{POCH_2C}H_3$	
4a	$[\{\mathrm{Mn(CO)_3(PPh_2OEt)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{HN{=}NC_6H_4C_6H_4N{=}NH)](BF_4)_2}$	2062 m, 1987 s, 1945 s	ν(CO)	14.02 (s)	$\mathrm{N}H$	162 (s, br)
				3.72 (qi)	$\mathrm{POC}H_2\mathrm{CH}_3$	163.1 (s)[e]
				1.19 (t)	$\mathrm{POCH_2C}H_3$	
4a$_1$	$[\{\mathrm{Mn(CO)_3(PPh_2OEt)_2}\}_2(\mu\text{-}4,4'\text{-}\mathrm{H^{15}N{=}NC_6H_4C_6H_4N{=}^{15}NH)](BF_4)_2}$	2064 m, 1986 s, 1945 s	ν(CO)	14.02 (d) $({}^1J_{^{15}\mathrm{NH}} = 65)$	$\mathrm{N}H$	162 (s, br)
				3.72 (qi)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				1.20 (t)	$\mathrm{POCH_2C}H_3$	
4c	$[\{\mathrm{Mn(CO)_3(PPh_2OEt)_2}\}_2\{\mu\text{-}4,4'\text{-}\mathrm{HN{=}N(2\text{-}CH_3)C_6H_3C_6H_3(2\text{-}CH_3)N{=}NH\}](BF_4)_2}$	2062 m, 1984 s, 1950 s	ν(CO)	13.88 (s)	$\mathrm{N}H$	162 (s, br)
				3.72 (qi)	$\mathrm{POC}H_2\mathrm{CH}_3$	
				2.34 (s)	$\mathrm{C}H_3$	
				1.20 (t)	$\mathrm{POCH_2C}H_3$	
5a	$\mathrm{Mn(CO)_2(C_6H_5NN)\{PPh(OEt)_2\}_2}$	1943 s, 1864 s	ν(CO)	3.75−3.60 (m)[f]	$\mathrm{POC}H_2\mathrm{CH}_3$	203 (s, br)[f]
		1625 m, 1560 m	ν(NN)	0.78 (t)	$\mathrm{POCH_2C}H_3$	
		1574	ν'(NN)[g]			
5a$_1$	$\mathrm{Mn(CO)_2(C_6H_5N^{15}N)\{PPh(OEt)_2\}_2}$	1943 s, 1864 s	ν(CO)	4.02 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	203 (s, br)
		1611 m, 1544 m	ν(NN)	1.24 (t)	$\mathrm{POCH_2C}H_3$	
		1555	ν'(NN)			
5b	$\mathrm{Mn(CO)_2(4\text{-}CH_3C_6H_4NN)\{PPh(OEt)_2\}_2}$	1937 s, 1866 s	ν(CO)	4.00 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	203 (s, br)
		1623 m, 1559 m	ν(NN)	2.28 (s)	$\mathrm{C}H_3$	201.9 (s)[e]
		1590	ν'(NN)	1.23 (t)	$\mathrm{POCH_2C}H_3$	
6b	$\mathrm{Mn(CO)_2(4\text{-}CH_3C_6H_4NN)(PPh_2OEt)_2}$	1923 s, 1843 s	ν(CO)	3.99 (qi)	$\mathrm{POC}H_2\mathrm{CH}_3$	176 (s, br)
		1623 m, 1560 m	ν(NN)	2.23 (s)	$\mathrm{C}H_3$	
				1.28 (t)	$\mathrm{POCH_2C}H_3$	
7a	$[\mathrm{Mn(CO)_2\{PPh(OEt)_2\}_2]_2(\mu\text{-}4,4'\text{-}NNC_6H_4C_6H_4NN)}$	1941 s, 1861 s	ν(CO)	4.05 (m)	$\mathrm{POC}H_2\mathrm{CH}_3$	203 (s, br)
		1614 m, 1564 m	ν(NN)	1.27 (t)	$\mathrm{POCH_2C}H_3$	201.4 (s)[e]
		1576	ν'(NN)			

Table 1. (Continued)

		IR[a]		^{1}H NMR[b,c]		^{31}P{^{1}H} NMR[b,d]
no.	compd	ν cm^{-1}	assgnt	δ (J (Hz))	assgnt	δ
7a$_1$	$[\mathrm{Mn(CO)_2\{PPh(OEt)_2\}_2}]_2(\mu\text{-}4,4'\text{-}^{15}\mathrm{NNC_6H_4C_6H_4N}^{15}\mathrm{N})$	1940 s, 1861 s	ν(CO)	4.06 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	203 (s, br)
		1607 m, 1546 m	ν(NN)	1.27 (m)	$\mathrm{POCH_2C}H_3$	
		1553	ν'(NN)			
7c	$[\mathrm{Mn(CO)_2\{PPh(OEt)_2\}_2}]_2\{\mu\text{-}4,4'\text{-}$ $\mathrm{NN(2\text{-}CH_3)C_6H_3C_6H_3(2\text{-}CH_3)NN}\}$	1944 s, 1863 s	ν(CO)	4.05 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	203 (s, br)
		1617 m, 1577 m	ν(NN)	2.22 (s)	$\mathrm{C}H_3$	
		1594	ν'(NN)	1.27 (t)	$\mathrm{POCH_2C}H_3$	
8c	$[\mathrm{Mn(CO)_2(PPh_2OEt)_2}]_2\{\mu\text{-}4,4'\text{-}$ $\mathrm{NN(2\text{-}CH_3)C_6H_3C_6H_3(2\text{-}CH_3)NN})$	1931 s, 1850 s	ν(CO)	4.04 (qi)	$\mathrm{POC}H_2\mathrm{CH_3}$	176 (s, br)
		1617 m, 1577 m	ν(NN)	1.99 (s)	$\mathrm{C}H_3$	
		1590	ν'(NN)	1.32 (t)	$\mathrm{POCH_2C}H_3$	
9b	$\mathrm{MnCl(CO)_2(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2}$[h]	1951 s, 1884 s	ν(CO)	13.52 (s)	$\mathrm{N}H$	191 (s, br)
				4.70−3.80 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	
				2.28 (s)	$\mathrm{C}H_3$	
				1.35, 1.33, 1.27 (t)	$\mathrm{POCH_2C}H_3$	
10a$_1$	$[\mathrm{MnCl(CO)_2\{PPh(OEt)_2\}_2}]_2(\mu\text{-}4,4'\text{-}$ $\mathrm{H}^{15}\mathrm{N{=}NC_6H_4C_6H_4N{=}}^{15}\mathrm{NH})$	1956 s, 1888 s	ν(CO)	13.70 (d) ($^1J_{^{15}\mathrm{NH}} = 60$)	$\mathrm{N}H$	190 (s, br)
				4.25−3.80 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	191.5 (s)[e]
				1.37, 1.29 (t)	$\mathrm{POCH_2C}H_3$	
11a	$[\mathrm{Mn(CO)_3(NH_2NH_2)\{PPh(OEt)_2\}_2}]\mathrm{BPh_4}$	2057 m, 1968 s, 1944 s	ν(CO)	4.06 (m)[i]	$\mathrm{POC}H_2\mathrm{CH_3}$	187 (s, br)[i]
		3348 m, 3294 m, 3262 w, 3222 m	ν(NH)	2.78 (m)	$\mathrm{MnN}H_2\mathrm{NH_2}$	
		1617 m	δ(NH$_2$)	2.28 (m)	$\mathrm{MnNH_2N}H_2$	
				1.39 (t)	$\mathrm{POCH_2C}H_3$	
11b	$[\mathrm{Mn(CO)_3(CH_3NHNH_2)\{PPh(OEt)_2\}_2}]\mathrm{BPh_4}$	2063 m, 1971 s, 1935 s	ν(CO)	4.10 (m)[i]	$\mathrm{POC}H_2\mathrm{CH_3}$	187 (s, br)[i]
		3318 m, 3270 m, 3192 w	ν(NH)	3.12 (m)	$\mathrm{N}H_2$	
				2.50 (m)	$\mathrm{N}H\mathrm{CH_3}$	
				1.99 (d) ($^3J_{\mathrm{HH}} = 6$)	$\mathrm{NHC}H_3$	
				1.41 (t)	$\mathrm{POCH_2C}H_3$	
11c	$[\mathrm{Mn(CO)_3(C_6H_5NHNH_2)\{PPh(OEt)_2\}_2}]\mathrm{BPh_4}$	2061 m, 1975 s, 1946 s	ν(CO)	5.75 (t)	$\mathrm{C_6H_5N}H$	188 (s, br)
		3341 m, 3298 m	ν(NH)	5.10 (m)	$\mathrm{N}H_2$	184.7 (s)[e]
		1602 w	δ(NH$_2$)	4.30 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	
				1.42 (t)	$\mathrm{POCH_2C}H_3$	
11d	$[\mathrm{Mn(CO)_3(4\text{-}NO_2C_6H_4NHNH_2)\{PPh(OEt)_2\}_2}]\mathrm{BPh_4}$	2063 m, 1986 s, 1947 s	ν(CO)	6.68 (t)	$-\mathrm{C_6H_4N}H$	190 (s, br)
		3366 w, 3242 m	ν(NH)	5.46 (m)	$\mathrm{N}H_2$	
				4.27 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	
				1.42 (t)	$\mathrm{POCH_2C}H_3$	
11e	$[\mathrm{Mn(CO)_3\{(CH_3)_2NNH_2\}\{PPh(OEt)_2\}_2}]\mathrm{BPh_4}$	2056 m, 1969 s, 1944 s	ν(CO)	4.23 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	186 (s, br)
		3283 m	ν(NH)	3.59 (s, br)	$\mathrm{N}H_2$	
				2.34 (s)	$\mathrm{N(C}H_3)_2$	
				1.43 (t)	$\mathrm{POCH_2C}H_3$	
12a	$[\mathrm{Mn(CO)_3(NH_2NH_2)(PPh_2OEt)_2}]\mathrm{BPh_4}$	2050 m, 1964 s, 1935 s	ν(CO)	3.60 (m)[i]	$\mathrm{POC}H_2\mathrm{CH_3}$	160 (s, br)[i]
		3338 w, 3276 w, 3253 m	ν(NH)	2.98 (m)	$\mathrm{MnN}H_2\mathrm{NH_2}$	158.5 (s)[e]
		1610 m	δ(NH$_2$)	2.32 (t)	$\mathrm{MnNH_2N}H_2$	
				1.15 (t)	$\mathrm{POCH_2C}H_3$	
12b	$[\mathrm{Mn(CO)_3(CH_3NHNH_2)(PPh_2OEt)_2}]\mathrm{BPh_4}$	2054 m, 1972 s, 1941 s	ν(CO)	3.66 (m, br)[i]	$\mathrm{POC}H_2\mathrm{CH_3}$	160 (s, br)[i]
		3315 w, 3256 m	ν(NH)	3.14 (m)	$\mathrm{N}H_2$	
		1605 m	δ(NH$_2$)	2.64 (m)	$\mathrm{N}H\mathrm{CH_3}$	
				1.98 (d) ($^3J_{\mathrm{HH}} = 6$)	$\mathrm{NHC}H_3$	
				1.21 (t)	$\mathrm{POCH_2C}H_3$	
12c	$[\mathrm{Mn(CO)_3(C_6H_5NHNH_2)(PPh_2OEt)_2}]\mathrm{BPh_4}$	2047 m, 1958 s, 1947 s	ν(CO)	5.58 (t)	$\mathrm{C_6H_5N}H$	161 (s, br)
		3363 w, 3285 w	ν(NH)	4.80 (m)	$\mathrm{N}H_2$	
		1616 m	δ(NH$_2$)	3.75 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	
				1.18 (t)	$\mathrm{POCH_2C}H_3$	
12d	$[\mathrm{Mn(CO)_3(4\text{-}NO_2C_6H_4NHNH_2)(PPh_2OEt)_2}]\mathrm{BPh_4}$	2054 m, 1973 s, 1954 s	ν(CO)	6.48 (t)	$-\mathrm{C_6H_4N}H$	166 (s, br)
		3320 w, 3264 m, 3229 m	ν(NH)	3.75 (m)	$\mathrm{POC}H_2\mathrm{CH_3}$	
				4.93 (m)	$\mathrm{N}H_2$	
				1.18 (t)	$\mathrm{POCH_2C}H_3$	

[a] In KBr pellets. [b] At room temperature in $(\mathrm{CD_3})_2\mathrm{CO}$. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% $\mathrm{H_3PO_4}$. [e] At −90 °C. [f] In $\mathrm{C_6D_6}$. [g] For calculation see ref 34. [h] ^{13}C{^{1}H} NMR, δ ($\mathrm{CD_2Cl_2}$): 227.4 t, 215.7 t (CO); 151−118 m (phenyl); 62.8 s (CH$_2$); 16.2 s (CH$_3$). [i] In $\mathrm{CD_2Cl_2}$.

spectra of the same diazene ligand and was never observed in previously reported aryldiazene complexes[4] or in the related hydrazine derivatives **11** and **12**. Therefore, it is plausible to assume that the fluxional process simply results in the interexchange of the position of the P ligands at room temperature, and the freezing of this change as the temperature is lowered results in a static structure with equivalent phosphorus *nuclei* (sharp singlet) at −90 °C.

A previously reported example of aryldiazene complex of the type $\mathrm{CpMn(CO)_2(PhN{=}NH)}$ was obtained by successive nucleophilic and electrophilic attack by LiPh and H$^+$ on $\mathrm{CpMn(CO)_2N_2}$ and was formulated as containing the MnN(Ph)=NH moiety where the phenyl is located on Nα adjacent to the manganese.[9] The compound is, however, thermally unstable and decomposed at −30 °C like the related dinuclear[9] derivative $[\mathrm{CpMn(CO)_2}]_2(\mu\text{-PhN{=}NH})$. Other aryldiazene complexes of manganese are only cited, either as an intermediate in the preparation of $\mathrm{Mn(CO)_2(PhN_2)(PPh_3)_2}$[10] or as a very unstable species in the NaBH$_4$ reduction[27] of $[(\eta^5\text{-}\mathrm{CH_3C_5H_4})\mathrm{Mn(CO)_2}(o\text{-}$

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(27) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1982**, *21*, 2578.

Table 2. Crystallographic Data for Compounds $[Mn(CO)_3(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2]BF_4$ (**1b**) and $[Mn(CO)_3(NH_2NH_2)\{PPh(OEt)_2\}_2]BPh_4$ (**11a**)

compd	$[Mn(CO)_3(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2]BF_4$	$[Mn(CO)_3(NH_2NH_2)\{PPh(OEt)_2\}_2]BPh_4$
chem formula	$C_{30}H_{38}BF_4MnN_2O_7P_2$	$C_{47}H_{54}BMnN_2O_7P_2$
fw	742.33	888.65
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a, Å	31.857(5)	13.772(3)
b, Å	11.119(2)	14.951(4)
c, Å	22.414(3)	13.319(3)
α, deg	90	104.47(1)
β, deg	97.82(1)	100.32(1)
γ, deg	90	111.08(1)
T, °C	22	22
λ, Å	0.710 69	0.710 69
V, Å^3	7866(2)	2365(1)
Z	8	2
ρ_{calcd}, g cm^{-3}	1.254	1.245
μ(Mo Kα), cm^{-1}	4.77	3.96
$R_1(F_o)$, w$R_2(F_o^2)^a$	0.0708, 0.3600	0.0511, 0.1730

[a] $R_1 = \Sigma|F_o - F_c|/\Sigma(F_o)$, calculated only on reflections with $F_o > 4\sigma(F_o)$; $wR_2 = \sqrt{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(w(F_o^2)^2]}$, calculated on all reflections.

Table 3. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses

$[Mn(CO)_3(4\text{-}CH_3C_6H_4N{=}NH)\{PPh(OEt)_2\}_2]BF_4$

Mn−P1	2.263(2)	O1−C8	1.136(11)
Mn−P2	2.263(2)	O2−C9	1.156(12)
Mn−N1	1.984(7)	O3−C10	1.141(11)
Mn−C8	1.855(9)	N1−N2	1.263(10)
Mn−C9	1.803(9)	N2−C1	1.438(11)
Mn−C10	1.847(9)		
C9−Mn−C10	92.4(4)	P1−Mn−C9	90.0(3)
C8−Mn−C10	179.2(4)	P1−Mn−C8	89.2(2)
C8−Mn−C9	87.3(4)	P1−Mn−N1	89.8(2)
N1−Mn−C10	88.8(3)	P1−Mn−P2	177.9(1)
N1−Mn−C9	178.7(4)	Mn−N1−N2	125.1(5)
N1−Mn−C8	91.4(3)	Mn−C8−O1	175.1(8)
P2−Mn−C10	92.0(3)	Mn−C9−O2	176.4(8)
P2−Mn−C9	90.3(3)	Mn−C10−O3	178.8(8)
P2−Mn−C8	88.8(2)	N1−N2−C1	119.8(7)
P2−Mn−N1	89.8(2)	N2−C1−C6	125.2(8)
P1−Mn−C10	90.0(3)	N2−C1−C2	115.2(7)

$[Mn(CO)_3(NH_2NH_2)\{PPh(OEt)_2\}_2]BPh_4$

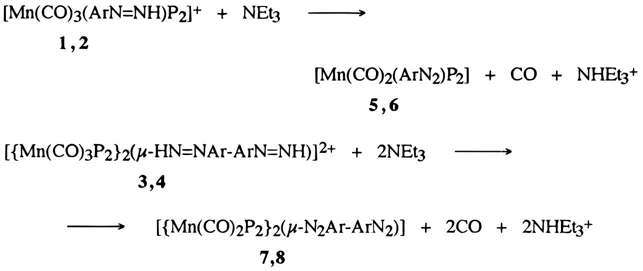
Mn−P1	2.273(1)	O1−C1	1.135(3)
Mn−P2	2.266(1)	O2−C2	1.153(3)
Mn−N1	2.125(2)	O3−C3	1.138(2)
Mn−C1	1.859(2)	N1−N2	1.455(3)
Mn−C2	1.799(3)	Mn−C3	1.849(2)
C2−Mn−C3	89.7(1)	P1−Mn−C3	90.0(1)
C1−Mn−C3	179.1(1)	P1−Mn−C2	90.9(1)
C1−Mn−C2	89.7(1)	P1−Mn−C1	89.4(1)
N1−Mn−C3	90.7(1)	P1−Mn−N1	88.5(1)
N1−Mn−C2	179.2(1)	P1−Mn−P2	178.0(0)
N1−Mn−C1	89.9(1)	Mn−N1−N2	117.4(2)
P2−Mn−C3	92.0(1)	Mn−C1−O1	176.5(2)
P2−Mn−C2	89.1(1)	Mn−C2−O2	179.2(2)
P2−Mn−C1	88.6(1)	Mn−C3−O3	177.0(2)
P2−Mn−N1	91.5(1)		

$N_2C_6H_4CF_3)]BF_4$, and therefore our compounds **1**−**4** seem to be the first stable and well-characterized aryldiazene complexes of manganese.

Preliminary studies on the chemical properties of these manganese complexes **1**−**4** showed that the diazene ligand is rather inert to substitution by several ligands such as CO, isocyanides, and phosphites and the starting complex can be, for example, recovered with high yield (≥90%) after 10−12 h of reaction with CO (1 atm) or an excess of isocyanide. The use of longer reaction times as well as reflux conditions is limited, however, by decomposition of the starting derivatives **1**−**4**.

Treatment of both mono- (**1**, **2**) and bis(diazene) (**3**, **4**) complexes with base resulted in a color change from yellow or orange to red with the formation of the aryldiazenido derivatives $[Mn(CO)_2(ArN_2)P_2]$ (**5**, **6**) and $[\{Mn(CO)_2P_2\}_2(\mu\text{-}N_2ArArN_2)]$ (**7**, **8**), which were isolated and characterized (Scheme 2). The ammonium cation $NHEt_3^+$ is also formed during the reaction course and can be recovered in an equivalent amount as the BPh_4^- salt from a CH_2Cl_2 solution. Furthermore, evolution of gas (CO) was also observed and the complexes **5**−**8** were obtained in almost quantitative yield (≥90%) in agreement with the stoichiometry reported in Scheme 2.

Scheme 2[a]



$$\underset{\mathbf{1,2}}{[Mn(CO)_3(ArN{=}NH)P_2]^+} + NEt_3 \longrightarrow \underset{\mathbf{5,6}}{[Mn(CO)_2(ArN_2)P_2]} + CO + NHEt_3^+$$

$$\underset{\mathbf{3,4}}{[\{Mn(CO)_3P_2\}_2(\mu\text{-}HN{=}NAr\text{-}ArN{=}NH)]^{2+}} + 2NEt_3 \longrightarrow \underset{\mathbf{7,8}}{[\{Mn(CO)_2P_2\}_2(\mu\text{-}N_2Ar\text{-}ArN_2)]} + 2CO + 2NHEt_3^+$$

[a] P = $PPh(OEt)_2$ (**5**, **7**), PPh_2OEt (**6**, **8**); R = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**), ArAr = 4,4′-$C_6H_4C_6H_4$ (**a**), 4,4′-(2-CH_3)$C_6H_3C_6H_3$(2-CH_3) (**c**).

The complexes are air-stable red-orange solids, diamagnetic, and moderately soluble in both polar and nonpolar organic solvents and nonelectrolytes. The infrared spectra show in the ν(CO) region, for both mono- and dinuclear derivatives, two strong bands at 1944−1843 cm^{-1}, in agreement with two carbonyl ligands in a mutually *cis* position. Furthermore, in the νNN region of the aryldiazenido ligand, two medium-intensity bands are present at 1625−1617 cm^{-1} and at 1577−1559 cm^{-1}, respectively, which are both shifted at a lower frequency in the corresponding labeled compounds $\mathbf{5a_1}$ and $\mathbf{7a_1}$. The presence of two or more ν(NN) bands for complexes containing only one aryldiazenido group is a feature previously observed for several derivatives, and it was demonstrated that these bands result from resonance interaction of ν(NN) with the weak vibrational mode of the attached phenyl group:[28] This probably applies to our derivatives. The values of the imperturbated ν'(NN) were also calculated[28] and fall in the range 1594−1576 cm^{-1} (Table 1). A comparison of these ν(NN) values with those of other aryldiazenido complexes whose crystal structure is known[2b,4b,29] does not allow us to unambiguously assign a coordination mode for the ArN_2 ligand, *i.e.* a singly-bent or a double-bent geometry. The 1594−1576 cm^{-1}

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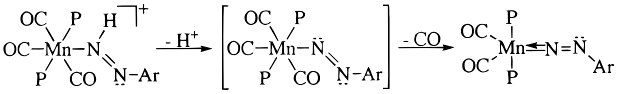
(28) Haymore, B. L.; Ibers, J. A.; Meek, D. W. *Inorg. Chem.* **1975**, *14*, 541.

Scheme 3



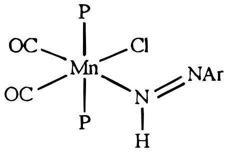
frequency represents, in fact, a borderline case also for the empirical rule proposed by Haymore and Ibers[30] for which the observed and corrected νNN frequencies fall into at least two groups, those above and below 1550−1530 cm^{-1}, with those above characteristic of a singly-bent aryldiazenido ligand. In fact, if we hypothesize the presence of a singly-bent ArN_2^+ ligand bonded to a formal Mn(1−) d^8 central metal, the observed pentacoordination results as being plausible and the complex may be compared with related iron(0) $[Fe(CO)_2(PPh_3)_2(C_6H_5N_2)]BF_4$[29a] and $[Fe(ArN_2)P_4]BPh_4$[4b] [P = P(OEt)$_3$, PPh(OEt)$_2$] or cobalt(I)[31] $[Co(ArN_2)P_4](BPh_4)_2$ derivatives which show, however, a higher νN_2 frequency [1660−1760 cm^{-1} for Fe(0) and 1770−1790 cm^{-1} for Co(I)] than our compounds **5**−**7**.

A doubly-bent ArN_2^- ligand should be obtained, instead, as the first deprotonation product (Scheme 3) of the $[Mn(CO)_3(ArN{=}NH)P_2]^+$ cation, giving an aryldiazenido(1−) complex with a formal Mn(1+) d^6 central metal in an octahedral environment. The dissociation of one ligand (CO) observed in our case does not seem, however, plausible for such a configuration, but rather there is a rearrangement of the ArN_2^- ligand to ArN_2^+ and concurrent formal reduction of the central metal to Mn(1−) giving a pentacoordinate complex. In the absence of an X-ray crystal structure, due to the poor quality of the obtained crystals, no reliable assignment can be made, therefore, on the singly- or doubly-bent coordination mode of the diazo ligand as well as on the geometry of the complexes. The $^{31}P\{^1H\}$ NMR spectra of compounds **5**−**8** indicate, in fact, only that the two phosphines are magnetically equivalent (only one singlet present at low temperature) and do not give further structural information.

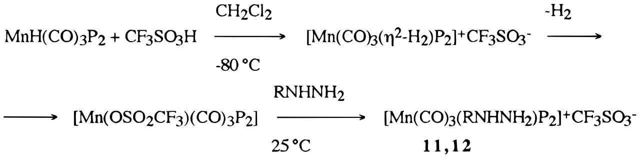
The previously reported aryldiazenido complexes of manganese whose X-ray structure are known both contain a singly-bent ArNN ligand, but they are difficult to compare with our compounds **5**−**8** because one of them is the dinuclear[12] compound $[Mn(CO)_4(C_6H_5N_2)]_2$ with two bridging ArN_2 groups and the other is the cationic[5] $[(\eta^5\text{-}CH_3C_6H_4)(CO)_2(o\text{-}N_2C_6H_4\text{-}CF_3)]BF_4$ complex containing a formal Mn(1+) in an octahedral environment.

Aryldiazenido complexes **5**−**8** react with an equimolar amount of HCl in CH_2Cl_2 at −80 °C to give the new aryldiazene complexes $[MnCl(CO)_2(ArN{=}NH)P_2]$ which, in the case of Ar = 4-$CH_3C_6H_4$, **9b**, was isolated in the solid state and characterized. Furthermore, in order to determine the nitrogen site of the protonation, we treated the labeled $[Mn(CO)_2\{PPh(OEt)_2\}_2]_2(\mu\text{-}4,4'\text{-}^{15}N{\equiv}NC_6H_4C_6H_4N{\equiv}^{15}N)$ (**7a$_1$**) complex with HCl and observed that the protonation takes place on the N1 nitrogen atom affording $[MnCl(CO)_2\{PPh(OEt)_2\}_2]_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4C_6H_4N{=}^{15}NH)$ (**10a$_1$**) as the final solid compound. Finally, the deprotonation reaction of the chloro−diazene $[MnCl(CO)_2(ArN{=}NH)P_2]$ (**9b**) with triethylamine gives the aryldiazenido $[Mn(CO)_2(ArN_2)P_2]$, which was also isolated as a solid. The infrared spectra of the new aryldiazenes show two νCO bands at 1984−1950 cm^{-1}, in agreement with the presence of two carbonyls in the mutually *cis* position. Furthermore, the $^{13}C\{^1H\}$ NMR spectra suggest the magnetic unequivalence of the two CO ligands showing two triplets at δ 227.4 and at δ 215.7 ppm in the carbonyl carbon region. Taking into account that in the temperature range +30 to −90 °C the $^{31}P\{^1H\}$ NMR spectra appear as sharp singlets, a *cis*-geometry of the type shown in Chart 3 seems to be present in solution for the new chloro−aryldiazene **9** derivatives.

Chart 3



Scheme 4[a]



$$MnH(CO)_3P_2 + CF_3SO_3H \xrightarrow[-80\ ^\circ C]{CH_2Cl_2} [Mn(CO)_3(\eta^2\text{-}H_2)P_2]^+CF_3SO_3^- \xrightarrow{-H_2} [Mn(OSO_2CF_3)(CO)_3P_2] \xrightarrow[25\ ^\circ C]{RNHNH_2} \underset{\mathbf{11,12}}{[Mn(CO)_3(RNHNH_2)P_2]^+CF_3SO_3^-}$$

[a] P = PPh(OEt)$_2$ (**11**), PPh$_2$OEt (**12**); R = H (**a**), CH_3 (**b**), Ph (**c**), 4-$NO_2C_6H_4$ (**d**).

Hydrazine Complexes. Treatment of the hydrides $MnH(CO)_3P_2$ first with triflic acid and then with the appropriate hydrazine afforded the new $[Mn(CO)_3(RNHNH_2)P_2]^+$ (**11**, **12**) derivatives which were isolated as BPh_4^- salts and characterized (Scheme 4). Studies on this reaction by ^1H NMR showed that the protonation of $MnH(CO)_3P_2$ species at low temperature probably proceeds with the formation of the dihydrogen cation $[Mn(CO)_3(\eta^2\text{-}H_2)P_2]^+$ which is thermally unstable and gives, after loss of H_2, the triflate complex $[Mn(OSO_2CF_3)(CO)_3P_2]$. This complex is a good precursor of hydrazine derivatives including the disubstituted $(CH_3)_2NNH_2$ hydrazine compound $[Mn(CO)_3\{(CH_3)_2NNH_2\}\{PPh(OEt)_2\}_2]BPh_4$ (**11e**). The triflate complex $[Mn(OSO_2CF_3)(CO)_3\{PPh(OEt)_2\}_2]$ was also isolated as a nonelectrolyte yellow solid and shows the νCO bands at 2057 m, 1966 s, and 1930 s cm^{-1}. Only one resonance at 157.6 ppm was observed in the $^{31}P\{^1H\}$ NMR spectra (C_6D_6), while the proton signals are as follows (C_6D_6, δ): 7.60−6.70 (phenyl), 3.10 (m, CH_2), 0.62 (t, CH_3). However, diagnostic for the presence of the η^1-O-coordination of the triflate ion in the complex is the characteristic band at 1320 cm^{-1} present in the IR spectra.[32]

All the hydrazine complexes are pale-yellow or green air-stable solids, diamagnetic, and 1:1 electrolytes.[25] Some of their spectroscopic properties are reported in Table 1. The infrared spectra confirm the presence of the hydrazine ligand showing the characteristic ν(NH) bands of medium or weak intensity at 3366−3192 cm^{-1} and in some case also the $\delta(NH_2)$ absorption at 1616−1602 cm^{-1}. Furthermore, in the ν(CO) region three bands are present (two strong and one medium) between 2063 and 1935 cm^{-1} suggesting that the three carbonyl ligands are in a *mer* position.

In the ^1H NMR spectra the hydrazine $RNHNH_2$ proton signals are present as broad multiplets between 6.48 and 2.28 ppm and have been clearly assigned by careful integration and decoupling experiments (Table 1). In the case of the $[Mn(CO)_3(NH_2NH_2)P_2]BPh_4$ (**11a**, **12a**) complexes both the signals of the coordinated and free NH_2 protons appear in the ^1H spectra, so

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(29) (a) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 1369. (b) Cowie, M.; Haymore, B. L.; Ibers, J. A. *Ibid.* **1975**, *14*, 2617. (c) McArdle, J. V.; Schultz, A. J.; Corden, B. J.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 1676. (d) Gaughan, A. P.; Haymore, B. L.; Ibers, J. A.; Myers, W. H.; Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6859. (e) Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Gilchrist, A. B.; Sutton, D. *J. Chem. Soc., Dalton Trans.* **1977**, 373.

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(31) Albertin, G.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1986**, 2551.

(32) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.

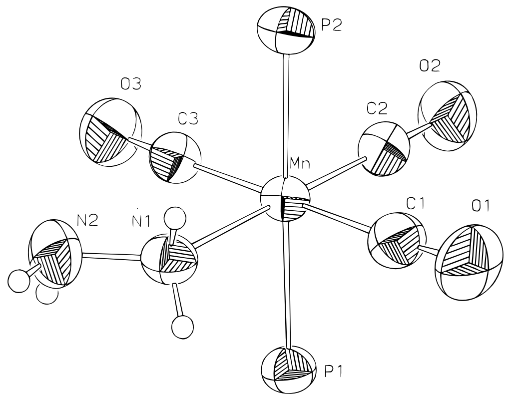
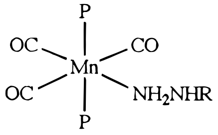
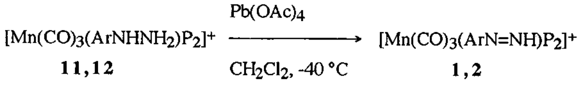


Figure 2. Perspective drawing of compound **11a**, with anisotropic thermal displacement parameters represented as ellipsoids at the 50% level of probability. Phenyl and ethoxy groups have been omitted for clarity.

Chart 4



Scheme 5[a]



[a] P = PPh(OEt)$_2$, PPh$_2$OEt; Ar = C_6H_5, 4-$NO_2C_6H_4$.

excluding the presence of a dimeric complex with the NH_2NH_2 bridging ligand.

In the temperature range between +30 and −90 °C the ^{31}P-{^{1}H} NMR spectra show a sharp singlet indicating the magnetic equivalence of the phosphine ligand as in the geometry shown in Chart 4. Such a geometry for the hydrazine complex **11a** has been confirmed by an X-ray crystal structure determination whose ORTEP is shown in Figure 2.

Arylhydrazine complexes [Mn(CO)$_3$(ArNHNH$_2$)P$_2$]BPh$_4$ (**11c,d**, **12c,d**) react with an equimolar amount of Pb(OAc)$_4$ at −40 °C in CH_2Cl_2 to give the corresponding aryldiazene derivatives [Mn(CO)$_3$(ArN=NH)P$_2$]$^+$ (**1**, **2**) which can be isolated in good yields and characterized (Scheme 5). The lead tetraacetate acts as oxidant on the coordinate arylhydrazine giving the aryldiazene ligand, which remains bonded to manganese. The related complexes [Mn(CO)$_3$(ArN=NH)P$_2$]BPh$_4$ show spectroscopic properties identical to those of samples prepared by reacting the hydride MnH(CO)$_3$P$_2$ with aryldiazonium cations, and these features, together with the analytical data, strongly support the proposed formulation.

These results prompted us to attempt to prepare the diazene HN=NH complexes by oxidation with Pb(OAc)$_4$ of the hydrazine [Mn(CO)$_3$(NH$_2$NH$_2$)P$_2$]BPh$_4$ derivatives. The reaction proceeds easily at a temperature below −40 °C to give a red solution from which we were able to isolate only a red oil. This oil is thermally unstable and slowly decomposes above −40 °C both as an oil and in CH_2Cl_2 solution giving the starting hydrazine compound [Mn(CO)$_3$(NH$_2$NH$_2$)P$_2$]BPh$_4$ and other unidentified products. However, the ^{1}H NMR spectra registered on an oxidized sample of **11a** prepared below −40 °C showed, beside the phosphite signals, a rather broad signal at 19.0 ppm (in CH_2Cl_2) attributable to a NH proton of a diazene ligand. The ^{31}P{^{1}H} spectra of the same sample appear as only one resonance at 193.5 ppm. Unfortunately, the compound is too unstable for a complete characterization, but the spectroscopic data seem to support the presence of a diazene ligand in a complex of the type [Mn(CO)$_3$(HN=NH)P$_2$]$^+$ or, more probably, of the type [{Mn(CO)$_3$P$_2$}$_2$(μ-HN=NH)]$^{2+}$ as suggested by the presence of only one NH signal in the ^{1}H NMR spectra.

The formation of the starting hydrazine complex **11a** from the hypothesized diazene [Mn(CO)$_3$(HN=NH)P$_2$]$^+$ can also be observed in the NMR tube increasing the sample temperature from −40 °C, and this may be due to the known disproportionation reaction[7,33] of the diazene complexes affording the [Mn(CO)$_3$(NH$_2$NH$_2$)P$_2$]$^+$ cation and a very unstable N_2 derivative of the type [Mn(CO)$_3$(N$_2$)P$_2$]$^+$, which was not detected. The formation of the hydrazine complexes from the solution containing the diazene derivative may therefore be considered as a further support for the presence of the HN=NH ligand in the oxidized complexes. The easy oxidation of the RNHNH$_2$ ligand seems to be, however, the only reaction shown by compounds **11** and **12**, which are robust complexes rather inert to the substitution of the ligand or to the deprotonation with an excess of base (NEt$_3$ or LiOH) to give hydrazido(1−) derivatives. Also treatment with H_2 (1 atm) does not give any reaction, and the starting hydrazine complexes can be recovered unchanged after 48 h of stirring under H_2 at room temperature.

X-ray Crystal Structures. Perspective drawings of compounds [Mn(CO)$_3$(4-CH$_3$C$_6$H$_4$N=NH){PPh(OEt)$_2$}$_2$]BF$_4$ (**1b**) and [Mn(CO)$_3$(NH$_2$NH$_2$){PPh(OEt)$_2$}$_2$]BPh$_4$ (**11a**) are shown in Figures 1 and 2. The two compounds differ only in the nature of the azo ligand (*p*-tolyldiazene in **1b** and hydrazine in **11a**) and in the counteranion (BF_4^- and BPh_4^-, respectively). Both crystal structures are the result of the packing of discrete cations and anions, which interact only by means of electrostatic and dispersive forces.

In both complex cations the coordination polyhedron of the Mn(I) atom is a distorted octahedron, with the two phosphite ligands *trans* to each other and one carbonyl group *trans* to the terminal hydrazinic moiety. The bond distance between this carbonyl group and the central metal is significantly affected by the *trans* influence of the azo group, and in both compounds this distance is about 0.05 Å shorter than the Mn−C distances involving the two carbonyl groups in *trans* to each other. Accordingly, the corresponding C−O distances follow the opposite trend and the strenghtening of approximately 0.05 Å of the Mn−C bond results in a weakening of about 0.015 Å of the C−O bond.

The different nature of the diazo ligand in the two cations is responsible for the relevant differences in the Mn−N [1.984(7) and 2.125(2) Å] and N−N distances [1.263(10) and 1.455(2) Å] (compounds **1b** and **11a**, respectively). These differences derive from the different bonding conditions of the N atoms in the two ligands: while for terminal hydrazine an sp^3 hybridization is present, the aryldiazene ligand shows an sp^2 hybridization, as already observed in similar compounds.[4b] In both complexes the apical phosphorus atoms can be regarded as equivalent with respect to the diazo moiety, which lies in the equatorial plane of the coordination octahedron within less than 0.1 Å. The displacement of N2 from the least-squares equatorial defined by N1 and the three coordinated carbonyls is 0.05 Å for the hydrazino and 0.08 Å for the aryldiazenido compounds, respectively. With respect to the Mn−N bond, the diazo group is *cis* to C3−O3 [C3−Mn−N1−N2 = 2.1(2)°] in the hydrazino and to C10−O3 [C10−Mn−N1−N2 = 5.2(7)°] in the aryldiazene compound. In the latter, the aryl group and the metal atom are *trans* to each other with reference to the N=N bond [Mn−N1−N2−C1 = 173.9(6)°]. The aryl plane forms a dihedral

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(33) Sellmann, D.; Brandl, A.; Endell, R. *J. Organomet. Chem.* **1975**, *90*, 309.

angle of 16.0(4)° with the plane of the diazene bond, evidence of the lack of resonance of the double-bond character between the sp^2 nitrogens and the ring system.

Up to now, only seven complexes[3c,34] between a transition metal and a terminal hydrazine have been studied by X-ray diffraction, and compound **11a** is the first case which contains Mn.

Conclusions. We have reported in this contribution that aryldiazene cations of manganese of the type $[Mn(CO)_3(ArN{=}NH)P_2]^+$ can be prepared both by an insertion reaction of an aryldiazonium cation into the Mn−H bond of the hydride species $MnH(CO)_3P_2$ and by an oxidation reaction with lead tetraacetate of the arylhydrazine complexes $[Mn(CO)_3(RNHNH_2)P_2]BPh_4$. Crucial for the stabilization of the ArN=NH ligand seems to be the coordination to the $Mn(CO)_3P_2$ fragment containing phosphonite $PPh(OEt)_2$ and phosphinite PPh_2OEt ligands, and this fragment also allows dinuclear bis(diazene) $[\{Mn(CO)_3P_2\}_2(\mu\text{-}HN{=}NArArN{=}NH)](BF_4)_2$ derivatives to be prepared. The first structural parameters for both an aryldiazene **1b** and a hydrazine **11a** complex of manganese are also reported. Among the properties shown by the aryldiazene complexes **1**−**4** can be cited the easy deprotonation reaction giving new pentacoordinate aryldiazenido complexes $[Mn(CO)_2(ArN_2)P_2]$ and $[\{Mn(CO)_2P_2\}_2(\mu\text{-}N_2Ar\text{-}ArN_2)]$, which can be protonated at the N1 nitrogen atom by treatment with HCl to give new $[MnCl(CO)_2(ArN{=}NH)P_2]$ aryldiazene derivatives.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1b** and **11a** are available on the Internet only. Access information is given on any current masthead page.

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