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Preparation of new ‘diazo’ complexes of manganese stabilised by phosphite ligands

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Abstract

A series of mono- and binuclear aryldiazene complexes $[Mn(ArN{=}NH)(CO)_nP_{5-n}]BPh_4$ and $[\{Mn(CO)_nP_{5-n}\}_2(\mu\text{-}HN{=}NAr\text{–}ArN{=}NH)](BPh_4)_2$ [$P = P(OMe)_3$, $P(OEt)_3$ or $P(OPh)_3$; $Ar = C_6H_5$, $4\text{-}CH_3C_6H_4$; $Ar\text{–}Ar = 4,4'\text{-}C_6H_4\text{–}C_6H_4$, $4,4'\text{-}C_6H_4\text{–}CH_2\text{–}C_6H_4$; $n = 1$, 2 or 3] were prepared by allowing hydride species $MnH(CO)_nP_{5-n}$ to react with the appropriate aryldiazonium salts at −80°C. Characterisation of the complexes by IR and variable-temperature ^1H-, ^{31}P-, ^{15}N-NMR spectra (with ^{15}N isotopic substitution) are reported. Treatment of aryldiazene derivatives containing both the tricarbonyl $Mn(CO)_3P_2$ and the dicarbonyl $Mn(CO)_2P_3$ fragments with NEt_3 affords the pentacoordinate dicarbonyl aryldiazenido $Mn(ArN_2)(CO)_2P_2$ and $[Mn(CO)_2P_2]_2(\mu\text{-}N_2Ar\text{–}ArN_2)$ derivatives. Instead, the aryldiazene bonded to the monocarbonyl fragment $Mn(CO)P_4$ is unreactive towards base and does not give aryldiazenido species. Hydrazine complexes $[Mn(RNHNH_2)(CO)_nP_{5-n}]BPh_4$ [$R = H$, CH_3 or C_6H_5; $P = P(OMe)_3$, $P(OEt)_3$ or $P(OPh)_3$; $n = 1$, 2 or 3] were prepared by reacting hydride species $MnH(CO)_nP_{5-n}$ first with Brønsted acid (HBF_4 or CF_3SO_3H) and then with an excess of the appropriate hydrazine. The binuclear complex $[\{Mn(CO)_3[P(OEt)_3]_2\}_2(\mu\text{-}NH_2NH_2)](BPh_4)_2$ was also prepared. Oxidation reactions of phenylhydrazine cations $[Mn(C_6H_5NHNH_2)(CO)_nP_{5-n}]^+$ with $Pb(OAc)_4$ at −40°C give the phenyldiazene $[Mn(C_6H_5N{=}NH)(CO)_nP_{5-n}]^+$ derivatives, whereas the oxidation of methylhydrazine $[Mn(CH_3NHNH_2)(CO)_nP_{5-n}]^+$ complexes allows the synthesis of the first methyldiazene $[Mn(CH_3N{=}NH)(CO)\{P(OMe)_3\}_4]BPh_4$ derivative of manganese. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Manganese; Diazene; Diazenido; Hydrazine; Dinuclear compounds

1. Introduction

The chemistry of diazenido, RN_2, diazene, RN=NH, and hydrazine, $RNHNH_2$, complexes of transition metals has been studied extensively [1–3] in the past 25 years, not only for their relevance in the nitrogen fixation process, but also for the interesting chemical and structural properties that these classes of compounds may exhibit and the potential reactions involving the NN single and multiple bond.

Numerous complexes of various metals have been prepared [1–3] and much work has been addressed to study the structure and reactivity of these important classes of compounds, in an attempt to determine the influence of the central metal, its oxidation state and the nature of the ancillary ligand on the properties of the ‘diazo’ ligands. However, the influence of the various factors on the properties of these complexes has not still been completely rationalised and much remains unknown about the chemistry of coordinate ‘diazo’ molecules.

We are active in this field and have reported extensively on the synthesis and reactivity of ‘diazo’ complexes of the iron family [4]. Recently, we have also begun study on the Mn triad and reported [5] the synthesis and some reactions of aryldiazene, aryldiazenido and hydrazine complexes of manganese, which are stabilised by the $Mn(CO)_3P_2$ fragment containing phosphonite, $PPh(OEt)_2$, and phosphinite, PPh_2OEt ligands. In order to determine the influence of the phosphine ligand on the properties of ‘diazo’ complexes of manganese, the chemistry of which is rather restricted [6], we extended these studies to include phosphite $P(OR)_3$ ($R = Me$, Et or Ph) as ancillary ligands. The results of these studies are reported here.

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2. Experimental

2.1. General considerations and physical measurements

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 vacuum-tight storage flasks. Phosphites $P(OMe)_3$ and $P(OEt)_3$ (Aldrich) were purified by distillation under nitrogen; $P(OPh)_3$ was used as received. Diazonium salts were obtained in the usual way [7]. Related di-diazonium $[N_2Ar–ArN_2](BF_4)_2$ ($Ar–Ar = 4,4'-C_6H_4–C_6H_4$; $4,4'-C_6H_4–CH_2–C_6H_4$) salts were prepared by treating amine precursors $H_2NAr–ArNH_2$ with $NaNO_2$, as described in the literature for common mono-diazonium salts [7]. Labelled diazonium tetrafluoroborate $[C_6H_5N{\equiv}^{15}N]BF_4$ and $[4,4'-{}^{15}N{\equiv}NC_6H_4–C_6H_4-N{\equiv}^{15}N](BF_4)_2$ were prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the appropriate amine. Hydrazines CH_3NHNH_2 and $C_6H_5NHNH_2$ were Aldrich products used as received. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method [8]. $Mn_2(CO)_{10}$ (Aldrich), $HBF_4·Et_2O$ (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 Nicolet Magna 750 FTIR spectrophotometer. NMR spectra (^1H, ^{13}C, ^{31}P, ^{15}N) 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; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. ^{15}N spectra refer to external $CH_3^{15}NO_2$, with downfield shifts considered positive. The SWAN-MR software package [9] was used to treat NMR data. The conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25°C were measured with a Radiometer CDM 83 instrument.

2.2. Synthesis of complexes

The pentacarbonyl species $MnH(CO)_5$ [10a] and the hydrides $MnH(CO)_3[P(OEt)_3]_2$, $MnH(CO)_2[P(OEt)_3]_3$ and $MnH(CO)[P(OEt)_3]_4$ [10b] were prepared according to the procedures previously reported.

2.2.1. $MnH(CO)[P(OMe)_3]_4$

A solution of $MnH(CO)_5$ (2.55 g, 13 mmol) in 50 cm^3 of toluene was treated, under argon, with an excess of $P(OMe)_3$ (11.2 cm^3, 90 mmol) and the mixture was irradiated for 20 h at room temperature (r.t.) in a Pyrex Schlenk flask, using a standard 400 W, medium-pressure mercury arc lamp. The solvent was removed under reduced pressure, giving an oil which was treated with 5 cm^3 of ethanol. By slow cooling to −25°C of the resulting solution, a white solid separated out, which was filtered and dried under vacuum; yield ≥60%. It may be noted that a shorter irradiation time (8–12 h) gives a mixture of $MnH(CO)[P(OMe)_3]_4$ and $MnH(CO)_2[P(OMe)_3]_3$, from which we were not able to separate the dicarbonyl, owing its decomposition during attempts at chromatographic separation.

Anal. Calc. for $C_{13}H_{37}MnO_{13}P_4$: C, 26.9; H, 6.4. Found: C, 26.8; H, 6.6%. $\delta_H(CD_2Cl_2$, 298 K) 3.56 (36 H, br, CH_3), −8.72 (1 H, qi, hydride, $J_{PH} = 50$ Hz); $\delta_P(CD_2Cl_2$, 298 K) 199.7 (s). IR, cm^{-1} (KBr) 1866 (s) $\nu(CO)$.

2.2.2. $MnH(CO)_2[P(OPh)_3]_3$

An excess of $P(OPh)_3$ (22 cm^3, 70 mmol) was added to a solution of $MnH(CO)_5$ (2.55 g, 13 mmol) in 50 cm^3 of toluene and the solution was irradiated with a standard 400 W, medium-pressure mercury arc lamp for 48 h. The solvent was removed under reduced pressure and the resulting oil chromatographed on a silica gel column (length 60 cm, diameter 4 cm) using as eluent a mixture of petroleum ether (40–70°C) and benzene in a 10:1 ratio. The first eluate (~650 cm^3) allowed us to separate the tricarbonyl $MnH(CO)_3[P(OPh)_3]_2$ (yield ≥ 30%); from the second eluate (650 cm^3), after evaporation of the solvent and treatment with 3 cm^3 of ethanol of the resulting oil, a white solid of $MnH(CO)_2[P(OPh)_3]_3$ separated out, which was filtered and dried under vacuum; yield ≥35%

Anal. Calc. for $C_{56}H_{46}MnO_{11}P_3$: C, 64.5; H, 4.5. Found: C, 64.7; H, 4.4%. $\delta_H(C_6D_6$, 298 K) 7.40–6.50 (45 H, m, Ph), A_2BX spin system, δ_X −7.89 (X = hydride), $J_{AX} = 50$, $J_{BX} = 70$ Hz; $\delta_P(C_6D_6$, 298 K) A_2B spin system, δ_A 178.5, δ_B 171.3, $J_{AB} = 102$ Hz. IR, cm^{-1} (KBr) 1978 (s), 1920 (s) $\nu(CO)$.

2.2.3. $MnH(CO)_3P_2$ [$P = P(OMe)_3$ or $P(OPh)_3$]

An excess of the appropriate phosphite (39 mmol) was added to a solution of $MnH(CO)_5$ (2.55 g, 13 mmol) in 30 cm^3 of toluene and the reaction mixture was refluxed for 90 min. The solvent was removed under reduced pressure and the oil obtained was triturated with 10 cm^3 of ethanol. By cooling to −25°C of the resulting solution, white microcrystals of the product separated out, which were collected and dried under vacuum; yield ≥70%

Anal. Calc. for $C_9H_{19}MnO_9P_2$ ($MnH(CO)_3[P(OMe)_3]_2$): C, 27.9; H, 4.9. Found: C, 27.7; H, 5.0%. $\delta_H(C_6D_6$, 298 K) 3.42 (18 H, t, CH_3), −8.16 (1 H, t, hydride, $J_{PH} = 44$ Hz); $\delta_P(C_6D_6$, 298 K) 194.0 (s, br). IR, cm^{-1} (KBr) 2023 (m), 1940 (s), 1925 (s) $\nu(CO)$.

Anal. Calc. for $C_{39}H_{31}MnO_9P_2$ ($MnH(CO)_3[P(OPh)_3]_2$): C, 61.6; H, 4.1. Found: C, 61.7; H, 4.2%. δ_H(C_6D_6, 298 K) 7.30–6.80 (30 H, m, Ph), −8.09 (1 H, t, hydride, $J_{PH} = 50$ Hz); δ_P(C_6D_6, 298 K) 183.6 (s). IR, cm^{-1} (KBr) 2075 (m), 1980 (s), 1956 (s) ν(CO).

*2.2.4. $[Mn(C_6H_5N{=}NH)(CO)P_4]BPh_4$ (**1**), $[Mn(C_6H_5N{=}NH)(CO)_2P_3]BPh_4$ (**2**), $[Mn(C_6H_5N{=}NH)(CO)_3P_2]BPh_4$ (**3**) [P = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**) or $P(OPh)_3$ (**c**)]*

In a 25 cm^3 three-necked round-bottomed flask were placed a solid sample of the appropriate hydride $MnH(CO)_nP_{5-n}$ ($n = 1$, 2, 3) (1 mmol) and solid $[C_6H_5N_2]BF_4$ (0.192 g, 1 mmol) and the flask cooled to −196°C. Dichloromethane (10 cm^3) was added and the reaction mixture, brought to r.t., was stirred for 2 h. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol (3 cm^3). The addition of an excess of $NaBPh_4$ (0.68 g, 2 mmol) in 2 cm^3 of ethanol to the resulting solution caused the separation of a yellow solid, the precipitation of which was completed by cooling to −25°C of the reaction mixture. The solid was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥80%; Λ_M/S cm^2 mol^{-1} = 52.7 for **1a**, 55.0 for **1b**, 49.6 for **2b**, 51.3 for **2c**, 50.8 for **3a**, 58.8 for **3b**.

Anal. Calc. for $C_{43}H_{62}BMnN_2O_{13}P_4$ (**1a**): C, 51.4; H, 6.2; N, 2.8. Found: C, 51.2; H, 6.2; N, 2.7%.

Anal. Calc. for $C_{55}H_{86}BMnN_2O_{13}P_4$ (**1b**): C, 56.2; H, 7.4; N, 2.4. Found: C, 56.2; H, 7.5; N, 2.5%.

Anal. Calc. for $C_{50}H_{71}BMnN_2O_{11}P_3$ (**2b**): C, 58.0; H, 6.9; N, 2.7. Found: C, 58.2; H, 6.8; N, 2.6%.

Anal. Calc. for $C_{86}H_{71}BMnN_2O_{11}P_3$ (**2c**): C, 70.4; H, 4.9; N, 1.9. Found: C, 70.2; H, 4.8; N, 1.9%.

Anal. Calc. for $C_{39}H_{44}BMnN_2O_9P_2$ (**3a**): C, 57.7; H, 5.5; N, 3.5. Found: C, 57.8; H, 5.4; N, 3.4%.

Anal. Calc. for $C_{45}H_{56}BMnN_2O_9P_2$ (**3b**): C, 60.3; H, 6.3; N, 3.1. Found: C, 60.2; H, 6.5; N, 3.0%.

*2.2.5. $[Mn(C_6H_5N{=}NH)(CO)_3\{P(OPh)_3\}_2]BF_4$ (**3c**)*

This complex was prepared exactly like related compounds **1**–**3**, but was separated as BF_4 salt; yield ≥ 65%; Λ_M/S^2 cm^2 mol^{-1} = 90.4.

Anal. Calc. for $C_{45}H_{36}BF_4MnN_2O_9P_2$: C, 56.8; H, 3.8; N, 2.9. Found: C, 56.6; H, 3.9; N, 2.9%.

*2.2.6. $[Mn(4\text{-}CH_3C_6H_4N{=}NH)(CO)\{P(OEt)_3\}_4]BPh_4$ (**1*b**)*

This complex was prepared exactly like related phenyldiazene compound **1b**; yield ≥80%; Λ_M/S cm^2 mol^{-1} = 57.1.

Anal. Calc. for $C_{56}H_{88}BMnN_2O_{13}P_4$: C, 56.7; H, 7.5; N, 2.4. Found: C, 56.5; H, 7.3; N, 2.3%.

*2.2.7. $[Mn(C_6H_5N{=}^{15}NH)(CO)\{P(OEt)_3\}_4]BPh_4$ (**1b**$_1$), $[Mn(C_6H_5N{=}^{15}NH){-}(CO)_2\{P(OEt)_3\}_3]BPh_4$ (**2b**$_1$), $[Mn(C_6H_5N{=}^{15}NH)(CO)_3\{P(OEt)_3\}_2]BPh_4$ (**3b**$_1$)*

These complexes were prepared like related complexes **1b**, **2b** and **3b** using the labelled $(C_6H_5N{\equiv}^{15}N)BF_4$ aryldiazonium salt; yield ≥80%.

*2.2.8. $[\{Mn(CO)P_4\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$ (**4**), $[\{Mn(CO)_2P_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$ (**5**) or $[\{Mn(CO)_3P_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$ (**6**) [P = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**) or $P(OPh)_3$ (**c**)]*

Solid samples of the appropriate hydrides (1 mmol) and of the bis(aryldiazonium) salt $(4,4'\text{-}N_2C_6H_4{-}C_6H_4N_2)(BF_4)_2$ (0.191 g, 0.5 mmol) were placed in a 25 cm^3 three-necked round-bottomed flask and cooled to −196°C. Acetone (10 cm^3) or a mixture $(CH_3)_2CO{:}CH_2Cl_2$ in ratio 1:1 (10 cm^3) was slowly added and the resulting solution brought to r.t. and stirred for 4 h. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol (2 cm^3). The addition of an excess of $NaBPh_4$ (0.68 g, 2 mmol) to the resulting solution caused, after cooling to −25°C, the separation of a yellow solid which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥85%; Λ_M/S cm^2 mol^{-1} = 114.2 for **4a**, 119.7 for **4b**, 123.1 for **5b**, 122.5 for **5c**, 99.6 for **6a**, 107.4 for **6b**.

Anal. Calc. for $C_{86}H_{122}B_2Mn_2N_4O_{26}P_8$ (**4a**): C, 51.5; H, 6.1; N, 2.8. Found: C, 51.3; H, 6.2; N, 2.7%.

Anal. Calc. for $C_{110}H_{170}B_2Mn_2N_4O_{26}P_8$ (**4b**): C, 56.4; H, 7.3; N, 2.4. Found: C, 56.2; H, 7.3; N, 2.3%.

Anal. Calc. for $C_{100}H_{140}B_2Mn_2N_4O_{22}P_6$ (**5b**): C, 58.1; H, 6.8; N, 2.7. Found: C, 58.2; H, 6.7; N, 2.6%.

Anal. Calc. for $C_{172}H_{140}B_2Mn_2N_4O_{22}P_6$ (**5c**): C, 70.5; H, 4.8; N, 1.9. Found: C, 70.3; H, 4.7; N, 1.8%.

Anal. Calc. for $C_{78}H_{86}B_2Mn_2N_4O_{18}P_4$ (**6a**): C, 57.7; H, 5.3; N, 3.5. Found: C, 57.6; H, 5.4; N, 3.6%.

Anal. Calc. for $C_{90}H_{110}B_2Mn_2N_4O_{18}P_4$ (**6b**): C, 60.4; H, 6.2; N, 3.1 Found: C, 60.6; H, 6.0; N, 3.0%.

*2.2.9. $[\{Mn(CO)[P(OEt)_3]_4\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}CH_2{-}C_6H_4N{=}NH)](BPh_4)_2$ (**4*b**)*

This complex was prepared exactly like related compound **4b** using the bis(aryldiazonium) salt $(4,4'\text{-}N_2C_6H_4{-}CH_2{-}C_6H_4N_2)(BF_4)_2$ as reagent; yield ≥80%; Λ_M/S cm^2 mol^{-1} = 113.7.

Anal. Calc. for $C_{112}H_{174}B_2Mn_2N_4O_{26}P_8$: C, 56.7; H, 7.4; N, 2.4. Found: C, 56.6; H, 7.5; N, 2.3%.

*2.2.10. $[\{Mn(CO)[P(OEt)_3]_4\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BPh_4)_2$ (**4b**$_1$)*

This compound was prepared exactly like related **4b** using the labelled $(4,4'\text{-}^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N)(BF_4)_2$ aryldiazonium salt; yield ≥85%.

2.2.11. $Mn(C_6H_5N_2)(CO)_2[P(OPh)_3]_2$ (**7c**), $[Mn(CO)_2P_2]_2(\mu\text{-}4,4'\text{-}N_2C_6H_4\text{–}C_6H_4N_2)$ (**8**) [$P = P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**) or $P(OPh)_3$ (**c**)]

An excess of triethylamine (0.69 cm^3, 5 mmol) was added to a solution of the appropriate aryldiazene complex $[Mn(C_6H_5N{=}NH)(CO)_3P_2]BPh_4$ or $[\{Mn(CO)_3P_2\}_2(\mu\text{ - }4,4'\text{ - }HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$ (1 mmol) in 10 cm^3 of CH_2Cl_2 and the reaction mixture stirred for about 2 h. The solvent was removed under reduced pressure, giving an oil which was triturated with benzene (5 cm^3). A white solid of $(NHEt_3)BPh_4$ slowly separated out from the resulting solution, which was collected by filtration and rejected. The solution was evaporated to dryness, giving a reddish–brown oil which was treated with 2 cm^3 of ethanol. By cooling of the resulting solution to − 25°C, orange microcrystals of the product were obtained, which were filtered and dried under vacuum; yield ≥ 75%.

Anal. Calc. for $C_{44}H_{35}MnN_2O_8P_2$ (**7c**): C, 63.2; H, 4.2; N, 3.4. Found: C, 63.0; H, 4.1; N, 3.5%.

Anal. Calc. for $C_{28}H_{44}Mn_2N_4O_{16}P_4$ (**8a**): C, 36.3; H, 4.8; N, 6.1. Found: C, 36.4; H, 4.7; N, 6.0%.

Anal. Calc. for $C_{40}H_{68}Mn_2N_4O_{16}P_4$ (**8b**): C, 43.9; H, 6.3; N, 5.1. Found: C, 43.7; H, 6.3; N, 5.3%.

Anal. Calc. for $C_{88}H_{68}Mn_2N_4O_{16}P_4$ (**8c**): C, 63.2; H, 4.1; N, 3.4. Found: C, 63.1; H, 4.2; N, 3.3%.

2.2.12. $Mn(C_6H_5N{\equiv}^{15}N)(CO)_2[P(OPh)_3]_2$ (**7c$_1$**)

This compound was prepared exactly like related **7c** by treatment of the labelled compound $[Mn(C_6H_5N{=}^{15}NH)(CO)_3\{P(OPh)_3\}_2]BPh_4$ with NEt_3; yield ≥ 75%.

2.2.13. $[Mn(NH_2NH_2)(CO)P_4]BPh_4$ (**9**), $[Mn(NH_2NH_2)(CO)_2P_3]BPh_4$ (**10b**), $[Mn(NH_2NH_2)(CO)_3P_2]BPh_4$ (**11**) [$P = P(OMe)_3$ (**a**) or $P(OEt)_3$ (**b**)]

To a solution of the appropriate hydride $MnH(CO)_nP_{5-n}$ ($n = 1$, 2, 3) (0.83 mmol), in 10 cm^3 of CH_2Cl_2 cooled to − 196°C, an equimolar amount of $HBF_4{\cdot}Et_2O$ (119 μl of a 54%° solution in Et_2O, 0.83 mmol) was added and the reaction mixture, brought to r.t., was stirred for 1 h. The solution was again cooled to − 196°C, treated with a slight excess of NH_2NH_2 (28.9 μl, 0.92 mmol), and then brought to r.t. After 3 h of stirring, the solvent was removed under reduced pressure, giving an oil which was triturated with ethanol (3 cm^3). The addition of an excess of $NaBPh_4$ (0.68 g, 2 mmol) caused the separation of a pale yellow solid which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥ 55%; Λ_M/S cm^2 mol^{-1} = 50.3 for **9a**, 55.9 for **9b**, 58.0 for **10b**, 54.8 for **11a**, 58.3 for **11b**.

Anal. Calc. for $C_{37}H_{60}BMnN_2O_{13}P_4$ (**9a**): C, 47.8; H, 6.5; N, 3.0. Found: C, 47.6; H, 6.6; N, 2.9%.

Anal. Calc. for $C_{49}H_{84}BMnN_2O_{13}P_4$ (**9b**): C, 53.6; H, 7.7; N, 2.6. Found: C, 53.8; H, 7.6; N, 2.5%.

Anal. Calc. for $C_{44}H_{69}BMnN_2O_{11}P_3$ (**10b**): C, 55.0; H, 7.2; N, 2.9. Found: C, 54.9; H, 7.2; N, 3.0%.

Anal. Calc. for $C_{33}H_{42}BMnN_2O_9P_2$ (**11a**): C, 53.7; H, 5.7; N, 3.8. Found: C, 53.6; H, 5.7; N, 3.7%.

Anal. Calc. for $C_{39}H_{54}BMnN_2O_9P_2$ (**11b**): C, 57.0; H, 6.6; N, 3.4. Found: C, 56.8; H, 6.5; N, 3.5%.

2.2.14. $[Mn(CH_3NHNH_2)(CO)P_4]BPh_4$ (**12**), $[Mn(CH_3NHNH_2)(CO)_2P_3]BPh_4$ (**13b**) [$P = P(OMe)_3$ (**a**) or $P(OEt)_3$ (**b**)]

A solution of the appropriate hydride $MnH(CO)_nP_{5-n}$ ($n = 1$, 2) (0.83 mmol) in 10 cm^3 of CH_2Cl_2 was cooled to − 196°C and treated with an equimolar amount of $HBF_4{\cdot}Et_2O$ (119 μl of a 54% solution in Et_2O, 0.83 mmol). The reaction mixture was brought to r.t., stirred for 1 h and again cooled to − 196°C. An excess of CH_3NHNH_2 (133 μL, 2.5 mmol) was then added, and the reaction mixture brought to r.t. and stirred for about 20 h. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol (5 cm^3) containing an excess of $NaBPh_4$ (0.68 g, 2 mmol). A pale yellow solid separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥ 60%; Λ_M/S cm^2 mol^{-1} = 60.2 for **12a**, 58.5 for **12b**, 56.8 for **13b**.

Anal. Calc. for $C_{38}H_{62}BMnN_2O_{13}P_4$ (**12a**): C, 48.3; H, 6.6; N, 3.0. Found: C, 48.5; H, 6.5; N, 3.1%.

Anal. Calc. for $C_{50}H_{86}BMnN_2O_{13}P_4$ (**12b**): C, 54.0; H, 7.8; N, 2.5. Found: C, 54.2; H, 7.7; N, 2.4%.

Anal. Calc. for $C_{45}H_{71}BMnN_2O_{11}P_3$ (**13b**): C, 55.5; H, 7.3; N, 2.9. Found: C, 55.3; H, 7.2; N, 3.0%.

2.2.15. $[Mn(C_6H_5NHNH_2)(CO)P_4]BPh_4$ (**14**), $[Mn(C_6H_5NHNH_2)(CO)_3P_2]BPh_4$ (**15a**) [$P = P(OMe)_3$ (**a**) or $P(OEt)_3$ (**b**)]

These complexes were prepared following the method used for the related NH_2NH_2 and CH_3NHNH_2 derivatives **9**–**13**: the appropriate hydride (0.83 mmol), in 10 cm^3 of CH_2Cl_2, was treated first with an equimolar amount of $HBF_4{\cdot}Et_2O$ (**14a**) or CF_3SO_3H (**14b** and **15a**) and then with a slight excess (91 μl, 0.92 mmol) of $C_6H_5NHNH_2$. The compounds were crystallised from CH_2Cl_2 and ethanol; yield ≥ 65%; Λ_M/S cm^2 mol^{-1} = 54.4 for **14a**, 59.0 for **14b**, 57.6 for **15a**.

Anal. Calc. for $C_{43}H_{64}BMnN_2O_{13}P_4$ (**14a**): C, 51.3; H, 6.4; N, 2.8. Found: C, 51.5; H, 6.3; N, 2.9%.

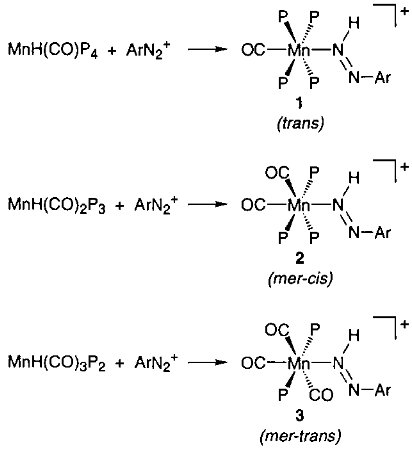
Anal. Calc. for $C_{55}H_{88}BMnN_2O_{13}P_4$ (**14b**): C, 56.2; H, 7.6; N, 2.4. Found: C, 56.0; H, 7.5; N, 2.5%.

Anal. Calc. for $C_{39}H_{46}BMnN_2O_9P_2$ (**15a**): C, 57.5; H, 5.7; N, 3.4. Found: C, 57.2; H, 5.8; N, 3.4%.

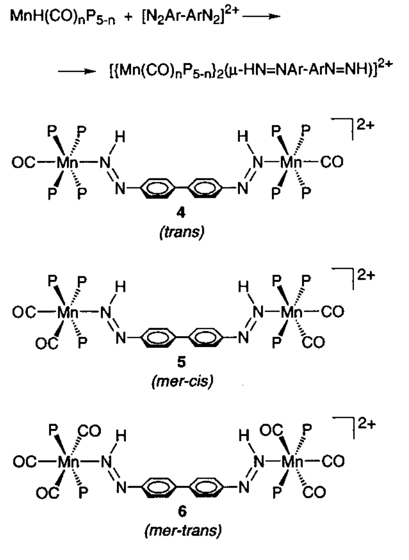
2.2.16. [{Mn(CO)$_3$[P(OEt)$_3$]$_2$}$_2$(μ-NH$_2$NH$_2$)](BPh$_4$)$_2$ (**16b**)

To a solution of MnH(CO)$_3$[P(OEt)$_3$]$_2$ (0.39 g, 0.83 mmol) in 10 cm^3 of CH$_2$Cl$_2$ cooled to -196°C was added an equimolar amount of HBF$_4$·Et$_2$O (119 μl of a 54%° solution in Et$_2$O, 0.83 mmol). The reaction mixture was brought to r.t., stirred for 90 min and then again cooled to -196°C. Hydrazine (13.0 μl, 0.415 mmol) was added, and the solution, brought to r.t., was stirred (at this temperature) for 24 h. The solvent was removed under reduced pressure, giving an oil which was treated with ethanol (3 cm^3) containing an excess of NaBPh$_4$ (0.68 g, 2 mmol). By slow cooling of the resulting solution to -25°C, white microcrystals separated out, which were filtered and dried under vacuum; yield $\geq 55\%$; Λ_M/S cm^2 mol^{-1} = 118.6.

Anal. Calc. for C$_{78}$H$_{104}$B$_2$Mn$_2$N$_2$O$_{18}$P$_4$: C, 58.1; H, 6.5; N, 1.7. Found: C, 57.9; H, 6.7; N, 1.6%.



Scheme 1. P = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**) or P(OPh)$_3$ (**c**); Ar = C$_6$H$_5$ or 4-CH$_3$C$_6$H$_4$.



Scheme 2. P = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**) or P(OPh)$_3$ (**c**); Ar–Ar = 4,4′-C$_6$H$_4$–C$_6$H$_4$ or 4,4′-C$_6$H$_4$–CH$_2$–C$_6$H$_4$.

2.2.17. [Mn(CH$_3$N=NH)(CO){P(OMe)$_3$}$_4$]BPh$_4$ (**17a**)

A sample of [Mn(CH$_3$NHNH$_2$)(CO){P(OMe)$_3$}$_4$]-BPh$_4$ (**12a**) (0.472 g, 0.5 mmol) was placed in a three-necked 25 cm^3 round-bottomed flask fitted with a solid-addition sidearm containing an equimolar amount of Pb(OAc)$_4$ (0.222 g, 0.5 mmol). Dichloromethane (10 cm^3) was added, the solution cooled to -40°C, and Pb(OAc)$_4$ added portionwise over 20–30 min to the cold stirred solution. The reaction mixture was then brought to r.t. and filtered, and the solvent was removed under reduced pressure, giving an oil. The addition of ethanol containing an excess of NaBPh$_4$ (0.34 g, 1 mmol) caused the separation of a yellow–orange solid which was filtered and crystallised from CH$_2$Cl$_2$ and ethanol; yield $\geq 70\%$; Λ_M/S cm^2 mol^{-1} = 56.2.

Anal. Calc. for C$_{38}$H$_{60}$BMnN$_2$O$_{13}$P$_4$: C, 48.4; H, 6.4; N, 3.0. Found: C, 48.6; H, 6.3; N, 3.1%.

3. Results and discussion

3.1. Aryldiazene and aryldiazenido derivatives

All the hydride complexes MnH(CO)$_n$P$_{5-n}$,where $n = 1$, 2 or 3, react with both mono and bis(aryldiazonium) cations to give mono [Mn(ArN=NH)(CO)$_n$-P$_{5-n}$]$^+$ (**1**–**3**) and binuclear [{Mn(CO)$_n$P$_{5-n}$}$_2$(μ-HN=NAr–ArN=NH)]$^{2+}$ (**4**–**6**) derivatives, which were isolated as BPh$_4^-$ salts and characterised (Schemes 1 and 2).

An exact stoichiometric ratio between the reagents and the start of the reaction at low temperature seems to be crucial for successful synthesis of the aryldiazene derivatives. Otherwise, some decomposition products or oily substances are found in the final reaction products.

The formation of stable aryldiazene species for all carbonyl:phosphite ratios of [Mn(ArN=NH)(CO)$_n$-P$_{5-n}$]$^+$ is rather surprising, because with substituted phosphites of the type PPh(OEt)$_2$ or PPh$_2$OEt only the tricarbonyl fragment Mn(CO)$_3$P$_2$ has been reported [5] to stabilise aryldiazene [Mn(ArN=NH)(CO)$_3$P$_2$]$^+$ derivatives. The use of P(OR)$_3$ phosphite as ancillary ligand allows stable aryldiazene species to be obtained for every CO:P ratio, and shows the important influence of the phosphine ligand in the synthesis of 'diazo' complexes. The P(OR)$_3$ groups are in fact good π-acceptor ligands, certainly better than PPh(OR)$_2$ or PPh$_2$(OR) ones [11], and this probably allows the substitution of CO with phosphite in the Mn(CO)$_5$ group without extensively altering the electronic properties of the manganese fragment Mn(CO)$_n$P$_{5-n}$, so that the related aryldiazene complexes **1**–**4** are stable with all the CO:P ratios of the Mn(CO)$_n$P$_{5-n}$ group.

Aryldiazene complexes **1**–**6** are orange or red solids, stable in air and in solution of polar organic solvents, in which they behave as 1:1 (**1**–**3**) or 2:1 (**4**–**6**) electrolytes [12]. Analytical and spectroscopic data (IR and NMR, Tables 1 and 2) support the proposed formulation and also allow a geometry in solution of the type reported in Schemes 1 and 2 to be established.

The ^{1}H-NMR spectra are consistent with the presence of the diazene ligand, showing the characteristic, slightly broad NH signal in the high frequency region at 14.82–14.14 ppm. In the related labelled $[Mn(C_6H_5N{=}^{15}NH)(CO)_n\{P(OEt)_3\}_{5-n}]BPh_4$ **1b**$_1$, **2b**$_1$, **3b**$_1$ and $[\{Mn(CO)[P(OEt)_3]_4\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4\text{–}C_6H_4N{=}^{15}NH)](BPh_4)_2$ **4b**$_1$ complexes, this broad signal is split into a doublet of multiplets with $^1J_{15_{NH}}$ of 62 or 65 Hz, in agreement with the proposed formulation. Proton-coupled ^{15}N-NMR spectra (Table 2) also support the presence of the diazene ligand, showing a doublet of multiplets between 43.6 and 22.6 ppm for the resonances of the labelled derivatives.

At room temperature, the $^{31}P\{^1H\}$-NMR spectra of monocarbonyl complexes **1** and **4** show a slightly broad signal which resolves into a sharp singlet at -90°C, indicating the presence of four equivalent phosphite ligands. The IR spectra only show one ν(CO) band, and a mutually *trans* position of the diazene and CO ligands may therefore be proposed for these derivatives.

The presence of a broad $^{31}P\{^1H\}$ signal at room temperature for **1** and **4** indicates a fluxional process, which may involve the aryldiazene ligand or a simple interchange of the positions of the phosphine groups. Since the ^{1}H-NMR spectra of ^{15}N-labelled **1b**$_1$ and **4b**$_1$ are sharp between $+30$ and -90°C, a fluxional process related to the aryldiazene ligand may be excluded. Therefore, it is plausible to assume that this fluxional process simply results in the interchange of the position of the P ligands at room temperature and, as temperature is lowered, this change is slowed giving, at -90°C, a static structure with four equivalent phophorus nuclei.

The infrared spectra of dicarbonyl complexes **2** and **5** show two strong ν(CO) bands, in agreement with the presence of two carbonyls in a mutually *cis* position. These two CO ligands are magnetically inequivalent, as shown by the $^{13}C\{^1H\}$-NMR spectra of **5b**, which display two well-separated multiplets at 222.4 and 217.5 ppm, attributed to two inequivalent carbonyl carbon atoms. Furthermore, the $^{31}P\{^1H\}$-NMR spectra of **2** and **5** appear as A_2B multiplets, suggesting a *mer–cis* geometry for the dicarbonyl derivatives.

The IR spectra of complexes **3** and **6** containing the tricarbonyl fragment $Mn(CO)_3P_2$ show three ν(CO) bands (one medium, and two of strong intensity) indicating a *mer* arrangement of the three carbonyl ligands. At room temperature, the $^{31}P\{^1H\}$-NMR spectra appear as a broad signal, which resolves into a sharp singlet at -90°C, in agreement with the presence of two magnetically equivalent phosphite ligands. On this basis, a *mer–trans* geometry can be proposed in solution for tricarbonyl aryldiazene complexes **3** and **6**.

The chemical properties of aryldiazene complexes **1**–**6** were studied and the results are summarised in Scheme 3.

Both mono and binuclear tricarbonyl complexes **3** and **6** quickly react with triethylamine to give pentacoordinate aryldiazenido $Mn(ArN_2)(CO)_2P_2$ (**7**) and $[Mn(CO)_2P_2]_2(\mu\text{-}N_2Ar\text{–}ArN_2)$ (**8**) derivatives in almost quantitative yield ($\geq 90\%$); they were isolated in the solid state and characterised. Evolution of CO was observed during the reaction course, which also proceeds with the formation of the ammonium cation $[NHEt_3]^+$. Its separation as BPh_4 salt in an equivalent amount supports the stoichiometry reported in Scheme 3 (Eqs. (1) and (2)).

Surprisingly, treatment of dicarbonyl complexes **2** and **5** with NEt_3 changes the colour of the solution, with the formation of the same aryldiazenido complexes **7** and **8** obtained starting from tricarbonyls **3** and **6**. Free phosphite was liberated during the reaction course, in agreement with the stoichiometry reported in Scheme 3 (Eqs. (3) and (4)).

Instead, monocarbonyls $[Mn(ArN{=}NH)(CO)P_4]^+$ (**1**) and the related binuclear derivatives **4** do not react with neither NEt_3 nor stronger bases ($NaOC_2H_5$), and the starting diazene complexes can be recovered unchanged after 24 h of reaction in the presence of an excess of base (Scheme 3, Eqs. (5) and (6)).

Aryldiazenido complexes **7** and **8** are orange solids stable in air and in solution of organic solvents, where they behave as non-electrolytes. The infrared spectra of both mono- and binuclear compounds show two strong bands in the ν(CO) region, indicating that the two carbonyls are in a mutually *cis* position. The spectra also have two medium-intensity bands at 1650–1561 cm^{-1}, which are both shifted at a lower frequency in the corresponding labelled **7c**$_1$ and may be attributed to the $\nu(N_2)$ of the aryldiazenido ligand. The presence of two or more $\nu(N_2)$ bands for complexes containing only one ArN_2 group is not surprising, having already been observed in several derivatives [1,5]. It has been reported [13] that these bands result from resonance interaction of $\nu(N{\equiv}N)$ with the weak vibrational mode of the attached phenyl group, and this probably also applies to our derivatives. The values of the imperturbated $\nu'(N_2)$ were also calculated and fall in the range 1618–1591 cm^{-1}, suggesting, by comparison with other aryldiazenido complexes [5,14–16], a singly-bent aryldiazenido ligand.

The ^{15}N-NMR spectra also fit the presence of a singly bent ArN_2 ligand [17], showing a broad triplet at 62.8 ppm, due to the coupling with two magnetically equivalent phosphorus nuclei for the $[Mn(C_6H_5N{\equiv}^{15}N)(CO)_2[P(OEt)_3]_2$ derivative.

In the temperature range between $+30$ and -90°C the $^{31}P\{^1H\}$-NMR spectra of aryldiazenido complexes **7** and **8** consist of a sharp singlet, indicating the magnetic equivalence of the two phosphorus nuclei. On the basis of these data, we cannot distinguish between the two geometries **I** and **II** reported in Scheme 4.

However, taking into account the fact that previously reported X-ray structures of pentacoordinate aryldiazenido complexes [15,16] contain the singly-bent ArN_2^+ ligand in the equatorial position of a trigonal bipyramidal geometry, we tentatively propose structure **I** for our derivatives **7** and **8**.

The presence of a singly-bent ArN_2^+ group in $Mn(ArN_2)(CO)_2P_2$ complexes containing a formal $Mn(-1)$ central metal suggests [4e,5,16b] that deprotonation of the aryldiazene ArN=NH in precursors **1**–**6** is followed by rearrangement of the ArN_2^- ligand to ArN_2^+, with formal two e^- reduction of the central metal to $Mn(-1)$. The concurrent dissociation of one ligand gives the final pentacoordinate 18-electron complexes (Scheme 5).

The formation exclusively of dicarbonyl aryldiazenido $Mn(ArN_2)(CO)_2P_2$ derivatives by deprotonation of both tricarbonyl $[Mn(ArN{=}NH)(CO)_3P_2]^+$ and dicarbonyl $[Mn(ArN{=}NH)(CO)_2P_3]^+$ precursors indicates that the final product does determine the nature of the ligand liberated in the reaction course. In other words, the dissociation of one carbonyl in one case and one phosphite in the other is dictated by the need to reach the most stable stoichiometry in the final $Mn(ArN_2)(CO)_2P_2$ derivative. Aryldiazenido compounds not containing the dicarbonyl fragment $Mn(CO)_2P_2$ are probably not stable and cannot be isolated.

The instability of aryldiazenido complexes with a CO:P ratio different from 2:2 may also explain the unreactivity toward base of both monocarbonyls $[Mn(ArN{=}NH)(CO)P_4]^+$ (**1**) and $[\{Mn(CO)P_4\}_2(\mu\text{-}HN{=}NAr\text{–}ArN{=}NH)]^{2+}$ (**3**). Deprotonation and concurrent dissociation of one ligand (CO or P) should give aryldiazenido species containing MnP_4 or $Mn(CO)P_3$ fragments, the probable instability of which prevents the deprotonation reaction. However, the unreactivity toward base of aryldiazene monocarbonyl complexes **1** and **3** may also be due to other factors, such as reluctance to dissociate a ligand or low acidity of the diazene proton, although the stability of final aryldiazenido complexes and/or their stoichiometry cannot be underestimated in determining the total reaction course.

Preliminary studies on the reactivity of aryldiazenido complexes **7** and **8** show that they are unreactive towards HCl or other Brønsted acids, HX, and the starting complex can be recovered unchanged after several hours of reaction with a 20-fold excess of acid. This unreactivity is rather surprising, since related $Mn(ArN_2)(CO)_2P_2$ complexes [5] containing $PPh(OEt)_2$ or PPh_2OEt phosphine ligands quickly react with HCl to give aryldiazene derivatives $MnCl(ArN{=}NH)(CO)_2P_2$ through protonation of the N1 nitrogen atom of the aryldiazenido group. The unreactivity of our $Mn(ArN_2)(CO)_2P_2$ species towards acids may be attributed to the properties of phosphites $P(OR)_3$, which are better π-acceptor ligands [11] than $PPh(OEt)_2$ or PPh_2OEt, and probably make the ArN_2 group less reactive toward protonation. In fact, the reaction with Brønsted acid of a singly-bent aryldiazenido complex giving an aryldiazene should result in a two e^- oxidation of the central metal [4a,5], from $Mn(-1)$ to $Mn(+1)$, and the presence in $Mn(ArN_2)(CO)_2P_2$ **7**, **8** derivatives of four good π-acceptor ligands [two CO and two $P(OR)_3$] may make oxidation rather difficult, as complexes **7**, **8** are unreactive towards acids. Also in this case, therefore, the nature of the ancillary ligands seems to play an important role in determining the properties of the 'diazo' derivatives.

3.2. Hydrazine complexes

A series of hydrazine complexes $[Mn(RNHNH_2)(CO)_nP_{5-n}]BPh_4$ (**9**–**15**) were prepared by reacting hydride $MnH(CO)_nP_{5-n}$ first with $HBF_4{\cdot}Et_2O$ or CF_3SO_3H and then with an excess of the appropriate hydrazine, as shown in Scheme 6.

Protonation of $MnH(CO)_nP_{5-n}$ with $HBF_4{\cdot}Et_2O$ or CF_3SO_3H proceeds with the formation of dihydrogen complexes [10] $[Mn(\eta^2\text{-}H_2)(CO)_nP_{5-n}]^+$, which in some cases are thermally unstable and, after loss of H_2, give coordinatively unsaturated cations $[Mn(CO)_nP_{5-n}]^+$ or triflate complexes $Mn(\eta^1\text{-}OSO_2CF_3)(CO)_nP_{5-n}$. Treatment of solutions containing $\eta^2\text{-}H_2$ complexes or species forming by loss of H_2 with an excess of $RNHNH_2$ affords hydrazine derivatives **9**–**15**, which were isolated as BPh_4 salts and characterised.

Good analytical data were obtained for all hydrazine complexes **9**–**15**, which are white or pale yellow stable solids, and soluble in polar organic solvents, in which they behave as 1:1 electrolytes [12].

Diagnostic for the presence of the hydrazine ligand (Table 1) were both IR spectra, showing the characteristic ν(NH) at 3371–3216 cm^{-1}, and ^1H-NMR ones, which display two broad signals at 4.67–2.69 and 6.23–2.22 ppm attributed to $MnNH_2$ and NH_2 or NH of the $RNHNH_2$ ligand. The IR and NMR data also allow us to propose the geometries of Scheme 6 for hydrazine complexes **9**–**15**. Thus, the sharp singlet observed in the $^{31}P\{^1H\}$-NMR spectra of monocarbonyls **9**, **12**, **14** supports a *trans* geometry, while a *mer–cis* one may be proposed for dicarbonyls **10**, **13**, on the basis of the AB_2-type $^{31}P\{^1H\}$-NMR spectra and of the presence of two ν(CO) strong bands observed in the IR spectra. The inequivalence of the two carbonyls is confirmed by the $^{13}C\{^1H\}$ spectra.

In the temperature range between +20 and −80°C, the $^{31}P\{^1H\}$ spectra of tricarbonyls **11**, **15** are sharp

Table 1
Infrared and NMR data for the manganese complexes

	Compound	IR [a]		^{1}H-NMR [b,c]		Spin system	$^{31}P\{^1H\}$-NMR [d,e]
		$\bar{\nu}$ (cm^{-1})	Assignment	δ (J Hz)	Assignment		δ (J Hz)
1a	$[Mn(C_6H_5N{=}NH)(CO)\{P(OMe)_3\}_4]BPh_4$	1899s	ν(CO)	14.36 (s, br)	NH	A_4	175.4 (s)
				3.80 (br)	CH_3		
1b	$[Mn(C_6H_5N{=}NH)(CO)\{P(OEt)_3\}_4]BPh_4$	1895s	ν(CO)	14.50 (qnt)	NH	A_4	171.0 (s)
				$J_{PH} = 5$			
				4.18 (m)	CH_2		
				1.30 (t)	CH_3		
1b$_1$	$[Mn(C_6H_5N{=}^{15}NH)(CO)\{P(OEt)_3\}_4]BPh_4$	1904s	ν(CO)	14.50 (dqnt)	NH	A_4	171.0 (s)
				$J_{^{15}NH} = 62$			
				$J_{PH} = 5$			
				4.18 (q)	CH_2		
				1.30 (t)	CH_3		
1*b	$[Mn(4\text{-}CH_3C_6H_4N{=}NH)(CO)\{P(OEt)_3\}_4]BPh_4$	1894s	ν(CO)	14.37 (s, br)	NH	A_4	171.3 (s)
				4.19 (br)	CH_2		
				2.40 (s)	$C\mathit{H}_3C_6H_4$		
				1.30 (br)	$POCH_2C\mathit{H}_3$		
2b	$[Mn(C_6H_5N{=}NH)(CO)_2\{P(OEt)_3\}_3]BPh_4$	1991s	ν(CO)	14.15 (d, br)	NH	A_2B [f]	δ_A 163.6
		1923s		$J_{PH} = 10$			δ_B 155.4
				4.35 (qnt)	CH_2		$J_{AB} = 101$
				4.15 (m)			
				1.41 (t)	CH_3		
				1.28 (t)			
2b$_1$	$[Mn(C_6H_5N{=}^{15}NH)(CO)_2\{P(OEt)_3\}_3]BPh_4$	1991s	ν(CO)	14.14 (dd)	NH	A_2BX [f]	δ_A 163.7
		1923s		$J_{^{15}NH} = 62$			δ_B 155.4
				$J_{PH} = 10$			$J_{AB} = 101$
				4.37 (qnt)	CH_2		J_{AX}, $J_{BX} < 1$
				4.15 (m)			
				1.41 (t)	CH_3		
				1.28 (t)			
2c	$[Mn(C_6H_5N{=}NH)(CO)_2\{P(OPh)_3\}_3]BPh_4$	2017s	ν(CO)	14.28 (d, br)	NH	A_2B	165–155 (m, br)
		1960s					
3a	$[Mn(C_6H_5N{=}NH)(CO)_3\{P(OMe)_3\}_2]BPh_4$	2066m	ν(CO)	14.69 (s)	NH	A_2 [f]	164.0 (s, br)
		1984s		3.85 (t)	CH_3		
		1974s					
3b	$[Mn(C_6H_5N{=}NH)(CO)_3\{P(OEt)_3\}_2]BPh_4$	2063m	ν(CO)	14.73 (s, br)	NH	A_2	159.3 (s)
		1986s		4.24 (m)	CH_2		
		1971s		1.29 (t)	CH_3		
3b$_1$	$[Mn(C_6H_5N{=}^{15}NH)(CO)_3\{P(OEt)_3\}_2]BPh_4$	2064m	ν(CO)	14.74 (d)	NH	A_2X	159.3 (s, br)
		1986s		$J_{^{15}NH} = 65$			$J_{AX} < 1$
		1972s		4.23 (m)	CH_2		
				1.29 (t)	CH_3		
3c	$[Mn(C_6H_5N{=}NH)(CO)_3\{P(OPh)_3\}_2]BF_4$	2090m	ν(CO)	14.41 (s)	NH	A_2	157.8 (s)
		2019s					
		1982s					
4a	$[\{Mn(CO)[P(OMe)_3]_4\}_2$	1905s	ν(CO)	14.44 (s, br)	NH	A_4	175.2 (s)
	$(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)]\text{–}(BPh_4)_2$			3.83 (t, br)	CH_3		
4b	$[\{Mn(CO)[P(OEt)_3]_4\}_2$	1900s	ν(CO)	14.56 (s, br)	NH	A_4	170.9 (s)
	$(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)]\text{–}(BPh_4)_2$			4.18 (br)	CH_2		
				1.31 (br)	CH_3		
4b$_1$	$[\{Mn(CO)[P(OEt)_3]_4\}_2$	1900s	ν(CO)	14.58 (dqnt) [g]	NH	A_4 [g]	170.8 (s, br)
	$(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4\text{–}C_6H_4N{=}^{15}NH)](BPh_4)_2$			$J_{^{15}NH} = 62$			
				$^3J_{PH} = 5$			
				4.19 (m)	CH_2		
				1.32 (t)	CH_3		
4*b	$[\{Mn(CO)[P(OEt)_3]_4\}_2$	1908s	ν(CO)	14.41 (qnt)	NH	A_4	171.0 (s)
	$(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}CH_2\text{–}C_6H_4N{=}NH)](BPh_4)_2$			$J_{PH} = 5$			
				4.15 (m)	CH_2		
				1.28 (t)	CH_3		

Table 1 (*Continued*)

	Compound	IR [a]		^{1}H-NMR [b,c]		Spin system	$^{31}P\{^1H\}$-NMR [d,e]
		$\bar{\nu}$ (cm^{-1})	Assignment	δ (J Hz)	Assignment		δ (J Hz)
5b	$[\{Mn(CO)_2[P(OEt)_3]_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$ [h]	1987s	ν(CO)	14.23 (d, br)	NH	A_2B [f]	δ_A 163.7
		1926s		$J_{PH} = 10$			δ_B 155.4
				4.38 (qnt)	CH_2		$J_{AB} = 101$
				4.18 (m)			
				1.43 (t)	CH_3		
				1.29 (t)			
5c	$[\{Mn(CO)_2[P(OPh)_3]_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$	2017s	ν(CO)	14.33 (s, br)	NH	A_2B	160–147 (m, br)
		1961s					
6a	$[\{Mn(CO)_3[P(OMe)_3]_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$	2070m	ν(CO)	14.76 (s, br)	NH	A_4	165.0 (s)
		1991s		3.87 (t, br)	CH_3		
		1968s					
6b	$[\{Mn(CO)_3[P(OEt)_3]_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$	2065m	ν(CO)	14.82 (s, br)	NH	A_4	159.3 (s)
		1985s		4.24 (m, br)	CH_2		
		1969s		1.31 (br)	CH_3		
7c	$Mn(C_6H_5N_2)(CO)_2[P(OPh)_3]_2$	1949s	ν(CO)			A_2 [f]	179.9 (s)
		1875s					
		1650m					
		1589m	$\nu(N_2)$				
		1618	$\nu'(N_2)$				
7c$_1$	$Mn(C_6H_5N{\equiv}^{15}N)(CO)_2[P(OPh)_3]_2$	1949s	ν(CO)			A_2X	180.8 (s) $J_{AX} < 1$
		1877s					
		1630m	$\nu(N+^{15}N)$				
		1561m					
		1594	$\nu'(N+^{15}N)$				
8a	$[Mn(CO)_2\{P(OMe)_3\}_2]_2(\mu\text{-}4,4'\text{-}N_2C_6H_4\text{–}C_6H_4N_2)$	1957s	ν(CO)	3.68 (t)	CH_3	A_2 [f]	191.4 (s, br)
		1870s					
		1617m	$\nu(N_2)$				
		1570m					
		1593	$\nu'(N_2)$				
8b	$[Mn(CO)_2\{P(OEt)_3\}_2]_2(\mu\text{-}4,4'\text{-}N_2C_6H_4\text{–}C_6H_4N_2)$	1952s	ν(CO)	4.05 (m)	CH_2	A_2 [f]	186.0 (s, br)
		1870s		1.23 (t)	CH_3		
		1616m	$\nu(N_2)$				
		1568m					
		1591	$\nu'(N_2)$				
8c	$[Mn(CO)_2\{P(OPh)_3\}_2]_2(\mu\text{-}4,4'\text{-}N_2C_6H_4\text{–}C_6H_4N_2)$	1963s	ν(CO)			A_2 [f]	179.8 (s)
		1886s					
		1637m	$\nu(N_2)$				
		1587m					
		1609	$\nu'(N_2)$				
9a	$[Mn(NH_2NH_2)(CO)\{P(OMe)_3\}_4]BPh_4$	3371w	ν(NH)	4.47 (m, br) [g]	NH_2	A_4 [g]	175.2 (s, br)
		3320w		3.27 (br)	$MnNH_2$		
		3269w		3.70 (t, br)	CH_3		
		3216w					
		1873s	ν(CO)				
9b	$[Mn(NH_2NH_2)(CO)\{P(OEt)_3\}_4]BPh_4$	3368m	ν(NH)	3.20 (br) [g]	NH_2	A_4 [f,g]	173.8 (s, br)
		3319w		4.08 (m)	CH_2		
		3279w		1.30 (t)	CH_3		
		1880s	ν(CO)				
10b	$[Mn(NH_2NH_2)(CO)_2\{P(OEt)_3\}_3]BPh_4$	3361w	ν(NH)	3.86 (m, br)	NH_2	A_2B [f]	δ_A 164.3
		3320m		3.16 (m, br)	$MnNH_2$		δ_B 157.1
		3270w		4.12 (m)	CH_2		$J_{AB} = 104$
		1976s	ν(CO)	1.37 (t)	CH_3		
		1895s		1.34 (t)			
11a	$[Mn(NH_2NH_2)(CO)_3\{P(OMe)_3\}_2]BPh_4$	3312w	ν(NH)	2.22 (br) [i]	NH_2	A_2 [i]	164.5 (s)
		3288w		2.69 (br)	$MnNH_2$		
		3260w		3.82 (t, br)	CH_3		
		3229w					
		2069w	ν(CO)				
		1979s					
		1948s					

Table 1 (*Continued*)

	Compound	IR [a]		^{1}H-NMR [b,c]		Spin system	^{31}P{^{1}H}-NMR [d,e]
		$\bar{\nu}$ (cm^{-1})	Assignment	δ (*J* Hz)	Assignment		δ (*J* Hz)
11b	$[Mn(NH_2NH_2)(CO)_3\{P(OEt)_3\}_2]BPh_4$	3280w	ν(NH)	2.51 (br) [g]	NH_2	A_2 [g]	160.3 (s)
		3262m		3.00 (br)	$MnNH_2$		
		3235w		4.17 (m, br)	CH_2		
		2059w	ν(CO)	1.40 (t, br)	CH_3		
		1973s					
		1947s					
12a	$[Mn(CH_3NHNH_2)(CO)\{P(OMe)_3\}_4]BPh_4$	3343w	ν(NH)	3.35 (m, br) [g]	$MnNH_2$	A_4 [g]	175.7 (s)
		3301w		2.52 (d)	$NHCH_3$		
		1880s	ν(CO)	3.74 (br)	$POCH_3$		
12b	$[Mn(CH_3NHNH_2)(CO)\{P(OEt)_3\}_4]BPh_4$	3349w	ν(NH)	3.71 (m, br) [g]	$MnNH_2$	A_4 [g]	174.0 (s, br)
		3298w		3.99 (m)	CH_2		
		1880s	ν(CO)	2.41 (d)	$NHCH_3$		
				1.21 (t)	$POCH_2CH_3$		
13b	$[Mn(CH_3NHNH_2)(CO)_2\{P(OEt)_3\}_3]BPh_4$	3342w	ν(NH)	3.10 (m) [g]	NH	A_2B [f,g]	δ_A 163.9
		3309m		3.79 (br)	$MnNH_2$		δ_B 157.0
		1993s	ν(CO)	4.13 (m)	CH_2		$J_{AB} = 100$
		1900s		2.57 (d)	$NHCH_3$		
				1.35 (t)	$POCH_2CH_3$		
				1.31 (t)			
14a	$[Mn(C_6H_5NHNH_2)(CO)\{P(OMe)_3\}_4]BPh_4$	3350w	ν(NH)	4.15 (br)	$MnNH_2$	A_4	179.3 (s)
		3279w		3.78 (br)	CH_3		
		1867s	ν(CO)				
14b	$[Mn(C_6H_5NHNH_2)(CO)\{P(OEt)_3\}_4]BPh_4$	3354m	ν(NH)	6.23 (t, br) [g]	NH	A_4 [f,g]	171.8 (s, br)
		3305w		4.67 (m, br)	$MnNH_2$		
		3249w		4.10 (m)	CH_2		
		1890s	ν(CO)	1.30 (t)	CH_3		
		1603m	$\delta(NH_2)$				
15a	$[Mn(C_6H_5NHNH_2)(CO)_3\{P(OMe)_3\}_2]BPh_4$	3335m	ν(NH)	5.08 (t, br)	NH	A_2	162.6 (s)
		3302m		4.51 (m)	$MnNH_2$		
		3230w		3.88 (t)	CH_3		
		2067m	ν(CO)				
		1986s					
		1953s					
		1600m	$\delta(NH_2)$				
16b	$[\{Mn(CO)_3[P(OEt)_3]_2\}_2(\mu\text{-}NH_2NH_2)](BPh_4)_2$	3285w	ν(NH)	4.49 (br) [g]	$MnNH_2$	A_2 [f,g]	156.5 (s)
		3250w		4.26 (m, br)	CH_2		
		2065m	ν(CO)	1.46 (t)	CH_3		
		1983s					
		1960s					
17a	$[Mn(CH_3N{=}NH)(CO)\{P(OMe)_3\}_4]BPh_4$	1894s	ν(CO)	13.8 (s, br) [g]	NH	A_4 [f,g]	174.0 (s, br)
				4.15 (s)	$CH_3N{=}NH$		
				3.72 (br)	$POCH_3$		

[a] In KBr pellets.

[b] In $(CD_3)_2CO$ at 25°C, unless otherwise noted.

[c] Phenyl proton resonances are omitted.

[d] In $(CD_3)_2CO$ at −90°C, unless otherwise noted.

[e] Positive shift downfield from 85% H_3PO_4.

[f] At 25°C.

[g] In CD_2Cl_2.

[h] ^{13}C{^{1}H}-NMR, δ_C: 222.4, 217.5 (4 C, m, CO), 165–120 (60 C, m, Ph), 63.32 (d), 62.76 (t) (18 C, CH_2), 16.4 (18 C, s, br, CH_3).

[i] In $ClCD_2CD_2Cl$.

singlets, indicating the magnetic equivalence of the two phosphorus nuclei. The IR spectra show three ν(CO) bands (one medium, and two of strong intensity) in agreement with a *mer* arrangement of the carbonyl ligands. On this basis, a *mer–trans* geometry may be proposed for the $[Mn(NH_2NHR)(CO)_3P_2]^+$ **11**, **15** derivatives.

We also attempted to prepare binuclear complexes with a hydrazine bridging ligand and, in the case of the tricarbonyl species containing $P(OEt)_3$ ligand, compound $[\{Mn(CO)_3P_2\}_2(\mu\text{-}NH_2NH_2)](BPh_4)_2$ (**16b**) was prepared by treating $MnH(CO)_3P_2$ first with $HBF_4{\cdot}Et_2O$ and then with NH_2NH_2, as reported in Scheme 7.

The IR spectra of binuclear complex **16b** show one medium-intensity and two strong bands in the ν(CO) region, in agreement with a *mer* arrangement of the three carbonyl ligands. The spectrum also contains only two ν(NH) bands at 3285 and 3250 cm^{-1} of the NH_2NH_2 ligand. Furthermore, only one broad signal at 4.49 ppm appears in the ^{1}H-NMR spectrum of compound **16b**, attributable to the NH_2 protons. The presence of only one signal for the NH_2 protons and of only two ν(NH) absorptions in the IR spectra strongly suggest the presence of a binuclear complex with the NH_2NH_2 bridging ligand of the geometry **V** type (Scheme 8).

Support for this *mer–trans* geometry **V** comes from the $^{31}P\{^1H\}$-NMR spectra, which display a sharp singlet between +20 and −80°C, indicating the magnetic equivalence of the phosphorus nuclei. Furthermore, analytical data agree with the binuclear formulation of the complex, and comparisons between the spectroscopic data of **16b** and the related mononuclear complex $[Mn(NH_2NH_2)(CO)_3\{P(OEt)_3\}_2]BPh_4$ (**11b**) (Table 1) strongly support the presence of a bridging NH_2NH_2 ligand in a binuclear species with geometry **V**.

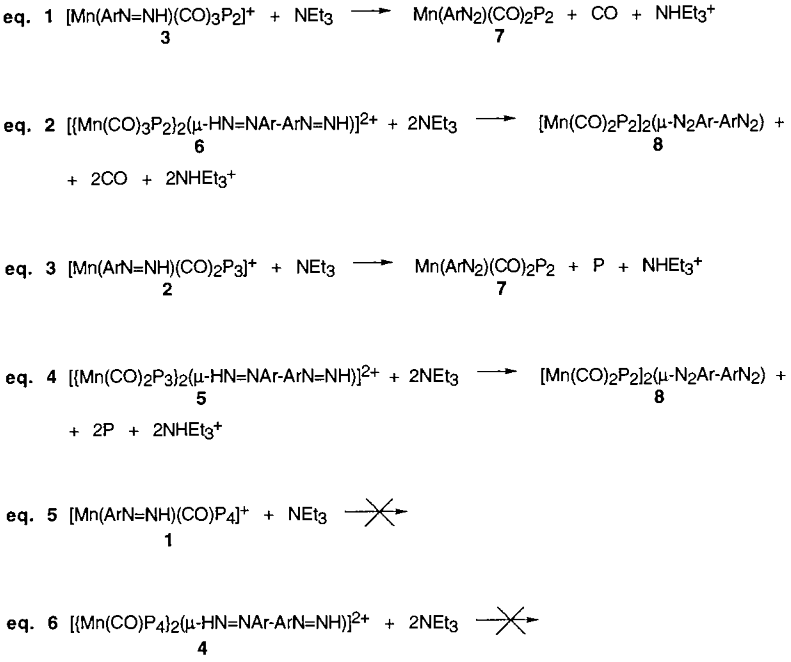
Oxidation of the hydrazine complexes with $Pb(OAc)_4$ was studied extensively and, although the reaction proceeds with all the hydrazine complexes prepared (**9**–**15**),

Table 2
^{15}N-NMR data for selected labelled compounds [a,b]

	Compound	δ (*J* Hz)	Assignment
1b$_1$	$[Mn(C_6H_5N{=}^{15}NH)(CO)\{P(OEt)_3\}_4]BPh_4$	43.6 (d, br) $^1J_{^{15}NH} = 62$	^{15}NH
2b$_1$	$[Mn(C_6H_5N{=}^{15}NH)(CO)_2\{P(OEt)_3\}_3]BPh_4$	33.1 (dq) $^1J_{^{15}NH} = 62$ $^2J_{^{15}NPcis} = 8$ $^2J_{^{15}NPtrans} = 8$	^{15}NH
3b$_1$	$[Mn(C_6H_5N{=}^{15}NH)(CO)_3\{P(OEt)_3\}_2]BPh_4$	22.6 (d, br) $^1J_{^{15}NH} = 65$	^{15}NH
4b$_1$	$[\{Mn(CO)[P(OEt)_3]_4\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4\text{–}C_6H_4N{=}^{15}NH)](BPh_4)_2$	42.9 (dqnt) $^1J_{^{15}NH} = 62$ $^2J_{^{15}NP} = 8$	^{15}NH
7c$_1$	$Mn(C_6H_5N{\equiv}^{15}N)(CO)_2[P(OPh)_3]_2$	62.8 (t, br)	$\equiv^{15}$N

[a] In CD_2Cl_2 at 25°C.

[b] Positive shift downfield from $CH_3^{15}NO_2$.



eq. 1 $[\mathrm{Mn(ArN{=}NH)(CO)_3P_2}]^+_{\mathbf{3}} + \mathrm{NEt_3} \longrightarrow \mathrm{Mn(ArN_2)(CO)_2P_2}_{\mathbf{7}} + \mathrm{CO} + \mathrm{NHEt_3^+}$

eq. 2 $[\{\mathrm{Mn(CO)_3P_2}\}_2(\mu\text{-}\mathrm{HN{=}NAr\text{-}ArN{=}NH})]^{2+}_{\mathbf{6}} + 2\mathrm{NEt_3} \longrightarrow [\mathrm{Mn(CO)_2P_2}]_2(\mu\text{-}\mathrm{N_2Ar\text{-}ArN_2})_{\mathbf{8}} + 2\mathrm{CO} + 2\mathrm{NHEt_3^+}$

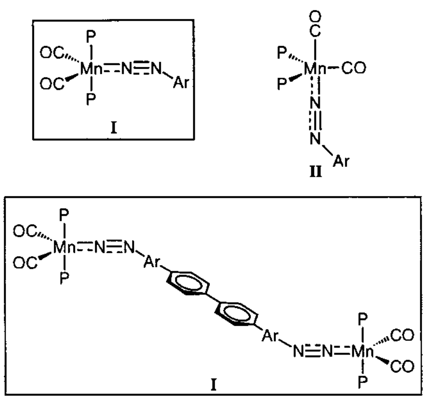
eq. 3 $[\mathrm{Mn(ArN{=}NH)(CO)_2P_3}]^+_{\mathbf{2}} + \mathrm{NEt_3} \longrightarrow \mathrm{Mn(ArN_2)(CO)_2P_2}_{\mathbf{7}} + \mathrm{P} + \mathrm{NHEt_3^+}$

eq. 4 $[\{\mathrm{Mn(CO)_2P_3}\}_2(\mu\text{-}\mathrm{HN{=}NAr\text{-}ArN{=}NH})]^{2+}_{\mathbf{5}} + 2\mathrm{NEt_3} \longrightarrow [\mathrm{Mn(CO)_2P_2}]_2(\mu\text{-}\mathrm{N_2Ar\text{-}ArN_2})_{\mathbf{8}} + 2\mathrm{P} + 2\mathrm{NHEt_3^+}$

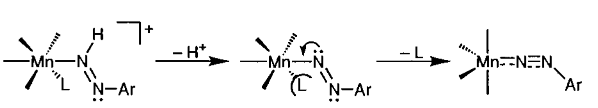
eq. 5 $[\mathrm{Mn(ArN{=}NH)(CO)P_4}]^+_{\mathbf{1}} + \mathrm{NEt_3} \not\longrightarrow$

eq. 6 $[\{\mathrm{Mn(CO)P_4}\}_2(\mu\text{-}\mathrm{HN{=}NAr\text{-}ArN{=}NH})]^{2+}_{\mathbf{4}} + 2\mathrm{NEt_3} \not\longrightarrow$

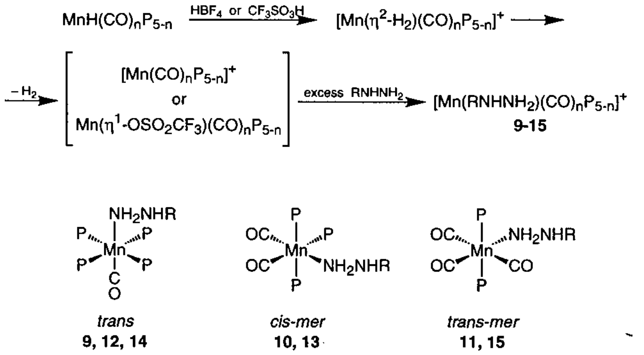
Scheme 3. P = $P(OMe)_3$ (**a**), $P(OEt)_3$ (**b**) or $P(OPh)_3$ (**c**); Ar = C_6H_5; Ar–Ar = 4,4'-C_6H_4–C_6H_4.



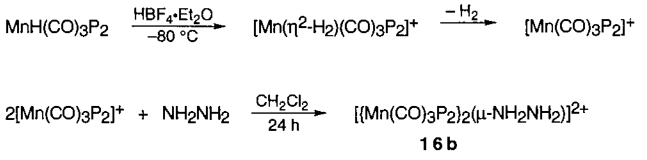
Scheme 4.



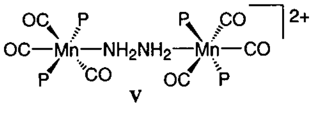
Scheme 5.



Scheme 6. P = P(OMe)$_3$ (**a**), P(OEt)$_3$ (**b**) or P(OPh)$_3$ (**c**); $n = 1$, R = H (**9a**–**b**); $n = 1$, R = CH$_3$ (**12a**–**b**); $n = 1$, R = C$_6$H$_5$ (**14a**–**b**); $n = 2$, R = H (**10b**); $n = 2$, R = CH$_3$ (**13b**); $n = 3$, R = H (**11a**–**b**); $n = 3$, R = C$_6$H$_5$ (**15a**).



Scheme 7. P = P(OEt)$_3$.



Scheme 8.

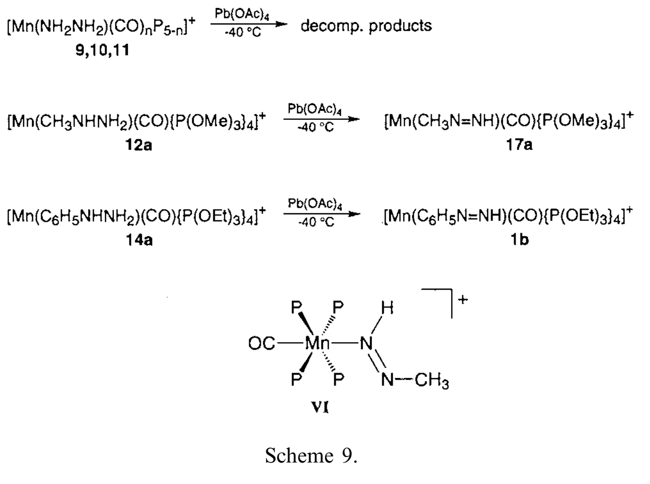
only in two cases were the related diazene derivatives isolated in pure form and characterised (Scheme 9).

Hydrazine complexes **9**, **10**, **11** react at −30°C with Pb(OAc)$_4$ to give a yellow solution from which only decomposition products were obtained. Instead, the reaction of related methylhydrazine complexes **12**, **13** proceeds with selective oxidation of the CH$_3$NHNH$_2$ ligand, to give the corresponding methyldiazene [Mn(CH$_3$N=NH)(CO)$_n$P$_{5-n}$]$^+$ which, in the case of the P(OMe)$_3$ derivative [Mn(CH$_3$N=NH)(CO){P(OMe)$_3$}$_4$]BPh$_4$ (**17a**), was isolated in the solid state and characterised. In the other cases, instead, the complexes were rather unstable and decomposed during crystallisation.

Methyldiazene complexes are rare [4a,18], and the use of the Mn(CO)[P(OMe)$_3$]$_4$ fragment allows the preparation of the unprecedented manganese derivative.

Phenylhydrazine complexes **14**, **15** were also oxidised by Pb(OAc)$_4$ to give the corresponding aryldiazene [Mn(C$_6$H$_5$N=NH)(CO)$_n$P$_{5-n}$]$^+$ cations which, however, were isolated in the solid state as a mixture of products. Since the same complexes (**1**–**3**) were obtained from the reaction of hydrides MnH(CO)$_n$P$_{5-n}$ with phenyldiazonium cations and were rather stable both as solids and in solution, the mixture obtained from oxidation cannot be formed by decomposition of the aryldiazene complex, but rather by oxidation byproducts of the hydrazine complexes. However, compound [Mn(C$_6$H$_5$N=NH)(CO){P(OEt)$_3$}$_4$]BPh$_4$ (**1b**) was isolated in pure form, and its spectroscopic properties are identical to those of a sample prepared by reacting hydride MnH(CO)[P(OEt)$_3$]$_4$ with C$_6$H$_5$N$_2^+$BF$_4^-$ and this feature, together with the analytical data, confirms its formulation.

In the high field region, the ^{1}H-NMR spectrum of methyldiazene complex **17a** shows one slightly broad signal at 13.8 ppm, characteristic of a diazene ligand. In the temperature range between +30 and −80°C, the ^{31}P{^{1}H}-NMR spectrum shows a sharp singlet, in agreement with the presence of four equivalent phosphite ligands. The IR spectrum shows only one ν(CO)



Scheme 9.

band at 1894 cm^{-1}. On these bases, a *trans* geometry (**VI**) of the type reported in Scheme 9 can be proposed for our methyldiazene derivative.

4. Conclusions

This contribution highlights the influence of phosphine ligands in the chemistry of 'diazo' complexes of manganese. In particular, the use of phosphite $P(OR)_3$ allows a large series of mono $[Mn(ArN{=}NH)(CO)_n P_{5-n}]^+$ and binuclear $[\{Mn(CO)_n P_{5-n}\}_2(\mu\text{-}HN{=}NAr\text{–}ArN{=}NH)]^{2+}$ aryldiazene complexes to be prepared. However, in contrast with previous reports [5] on phosphonite, $PPh(OEt)_2$, and phosphinite, PPh_2OEt, ligands, all the $Mn(CO)_n P_{5-n}$ fragments with CO:P ratios ranging from 3:2 to 1:4 stabilise the ArN=NH ligand. Phosphite also stabilises pentacoordinate aryldiazenido complexes containing bis(carbonyl)bis(phosphite) ligands of the type $Mn(ArN_2)(CO)_2P_2$ and $[Mn(CO)_2P_2]_2(\mu\text{-}N_2Ar\text{–}ArN_2)$. Lastly, new hydrazine complexes $[Mn(RNHNH_2)(CO)_n P_{5-n}]BPh_4$ were prepared and their oxidation with $Pb(OAc)_4$ led to the corresponding substituted-diazene $[Mn(RN{=}NH)(CO)_n P_{5-n}]^+$ cations, including the first example of a methyldiazene $[Mn(CH_3N{=}NH)(CO)\{P(OMe)_3\}_4]^+$ derivative for this metal.

Acknowledgements

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