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Articles

Synthesis, Characterization, and Reactivity of Cationic Molecular Hydrogen Complexes of Manganese(I)

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Hydride complexes $MnH(CO)_3P_2$ (**1**), $MnH(CO)_2P_3$ (**2**), and $MnH(CO)P_4$ (**3**) ($P = P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**), PPh_2OEt (**c**), $PPh(O^iPr)_2$ (**d**) were prepared by allowing the $MnH(CO)_5$ species to react with an excess of phosphine upon UV irradiation or under reflux conditions. Their formulation and geometry in solution were established by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Protonation reactions with $HBF_4{\cdot}Et_2O$ of the monocarbonyls $MnH(CO)P_4$ (**3**) afford *isolable* dihydrogen derivatives $[Mn(\eta^2\text{-}H_2)(CO)P_4]BPh_4$ (**5**), which were characterized by variable-temperature ^1H and ^{31}P NMR spectra, T_1 measurements, and J_{HD} values. Thermally unstable (above 0 °C) $[Mn(\eta^2\text{-}H_2)(CO)_2P_3]^+$ (**4**) cations were also prepared by protonation of the dicarbonyl hydrides $MnH(CO)_2P_3$ (**2**) and fully characterized in solution. Evolution of H_2 from **4** and **5** results in the formation of the unsaturated complexes $[Mn(CO)_2P_3]BPh_4$ (**6**) and $[Mn(CO)P_4]BPh_4$ (**7**), which are probably stabilized by an agostic interaction between the metal center and a C−H proton of the phosphite. Treatment of the unsaturated complexes **6** and **7** and of the triflate compounds $[Mn(\eta^1\text{-}OSO_2CF_3)(CO)_3P_2]$ (**8**) with $Li^+RC{\equiv}C^-$ gave the new acetylide derivatives $[Mn(C{\equiv}CR)(CO)P_4]$ (**9**), $[Mn(C{\equiv}CR)(CO)_2P_3]$ (**10**), and $[Mn(C{\equiv}CR)(CO)_3P_2]$ (**11**) (R = Ph, *p*-tolyl). The new series of cationic manganese compounds $[Mn(CO)_2(p\text{-tolylCN})P_3]BPh_4$ (**12**), $[Mn(CO)(p\text{-tolylCN})P_4]BPh_4$ (**13**), $[Mn(CO)_2(p\text{-tolylNC})P_3]BPh_4$ (**14**), $[Mn(CO)(p\text{-tolylNC})P_4]BPh_4$ (**15**), $[Mn(CO)_3P_3]BPh_4$ (**16**), and $[Mn(CO)_2P_4]BPh_4$ (**17**) were also obtained by reacting the unsaturated compounds **6** and **7** with the appropriate ligands.

Introduction

Transition-metal dihydrogen complexes are an important class of compounds which have attracted considerable interest in recent years.[1,2] A large number of isolable H_2 complexes have been prepared, and the majority of them contain metals of the second and third row with a d^6 octahedral configuration. In contrast, although the initial focus of work in this field has been the synthesis of new dihydrogen complexes, relatively few examples have been described for the first-row transition metals and only recently have stable dihydrogen complexes of manganese been reported.[2b,3,4] These include the trihydride[3] $MnH_3(R_2PCH_2CH_2PR_2)_2$ (R = Me, Et) which was proposed to contain a η^2-H_2 ligand, the compound $CpMn(CO)_2(\eta^2\text{-}H_2)$,[4] and the very recently reported derivative $[Mn(\eta^2\text{-}H_2)(CO)(dppe)_2]BAr'_4$ (dppe = $Ph_2PCH_2CH_2PPh_2$; $BAr'_4 = B\{C_6H_3(3,5\text{-}CF_3)_2\}_4$).[2b] Furthermore, much work has been addressed to study the structure, the bonding, and the reactivity of these interesting complexes[1] in an attempt to provide insight into the catalytic and stoichiometric activation of H_2 by transition metals and now it seems certain that the stability and the chemical properties of the η^2-H_2 compounds are a function not only of the central metal but also of the nature of the ancillary ligands and of the formal charge on the central metal.

We have previously reported[5] the synthesis and some properties of molecular hydrogen derivatives of the iron

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family of the type $[MH(\eta^2\text{-}H_2)P_4]^+$ containing monodentate phosphite ligands $PPh_2(OR)$, $PPh(OR)_2$, and $P(OR)_3$ as ancillary ligands. As these ligands have shown interesting properties in stabilizing the H_2 complexes, we have extended these studies to include the manganese as a central metal, and in this paper we report the synthesis and characterization of new *isolable* molecular hydrogen complexes of this metal along with some studies on the properties of these derivatives.

Experimental Section

All synthetic work was carried out under an appropriate atmosphere (H_2, Ar) using standard Schlenk techniques or a Vacuum Atmospheres drybox. 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. Triethyl phosphite was an Aldrich product, purified by distillation under nitrogen; the phosphines $PPh(OEt)_2$, PPh_2OEt, and $PPh(O^iPr)_2$ were prepared by the method of Rabinowitz and Pellon.[6] $Mn_2(CO)_{10}$, $HBF_4\cdot Et_2O$ (54% solution), triflic acid, and the alkynes were Aldrich products, used without any further purification. Lithium acetylides $Li^+RC{\equiv}C^-$ (R = Ph, *p*-tolyl) were prepared by reacting a slight excess of the appropriate acetylene (40 mmol) with lithium (35 mmol, 0.24 g) in 10 mL of THF. *p*-Tolyl isocyanide was obtained by the phosgene method of Ugi *et al.*[7] 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. The photolysis was carried out under an argon atmosphere with a standard 400 W medium-pressure mercury arc lamp using a Pyrex Schlenk flask. 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 +30 and −90 °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. Proton T_1 values were measured by the inversion-recovery method between +30 and −90 °C with a standard 180°−τ−90° pulse sequence. 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.[8]

$MnH(CO)_3P_2$ (1) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b), PPh_2OEt (c), $PPh(O^iPr)_2$ (d)). An excess of the appropriate phosphite (80 mmol) was added to a solution of $MnH(CO)_5$ (12.8 mmol, 2.5 g) in 30 mL of toluene and the reaction mixture was refluxed for about 2 h. The solvent was removed under reduced pressure, and the oil obtained was chromatographed on a silica gel column (length 70 cm, diameter 4 cm) using a mixture of petroleum ether (40−70 °C) and diethyl ether in a 10:1 ratio as eluent. The first eluted (300 mL) was evaporated to dryness, leaving an oil which was treated with ethanol (5−10 mL). A white solid slowly separated out from the resulting stirred solution, which was filtered and dried under vacuum; yield from 60 to 70%. Anal. Calcd for $C_{15}H_{31}O_9P_2Mn$ (**1a**): C, 38.15; H, 6.62. Found: C, 38.24; H, 6.58. Mp: 38 °C dec. IR (KBr and ($CH_3C_6H_5$)): 2027 w (2015 w), 1941 s (1938 s), 1915 s (1921 s) ν_{CO} cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C): δ 3.99 (m, 12H, CH_2), 1.15 (t, 18H, CH_3), −8.13 (t, 1H, Mn−H, J_{PH} = 43 Hz). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C): δ 191.0 s. Anal. Calcd for $C_{23}H_{31}O_7P_2Mn$ (**1b**): C, 51.50; H, 5.83. Found: C, 51.67; H, 5.90. Mp: 67 °C dec. IR (KBr and (*n*-hexane)): 2019 w (2017 w), 1941 s (1943 s), 1918 s (1926 s) ν_{CO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 8.00−7.00 (m, 10H, Ph), 3.95, 3.71 (m, 8H, CH_2), 1.06 (t, 12H, CH_3), −7.65 (t, 1H, Mn−H, J_{PH} = 40 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 205.3 s. Anal. Calcd for $C_{31}H_{31}O_5P_2Mn$ (**1c**): C, 62.01; H, 5.20. Found: C, 62.17; H, 5.11. Mp: 138 °C dec. IR (KBr and (*n*-hexane)): 2002 w (2008 w), 1933 s (1933 s), 1919 (s) (1916 s) ν_{CO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 8.00−7.00 (m, 20H, Ph), 3.90 (qi, 4H, CH_2), 1.10 (t, 6H, CH_3), −7.36 (t, 1H, Mn−H, J_{PH} = 33 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 177.7 s. Anal. Calcd for $C_{27}H_{39}O_7P_2Mn$ (**1d**): C, 54.73; H, 6.63. Found: C, 54.58; H, 6.55. Mp: 132 °C. IR (KBr): 2023 m, 1937 s, 1901 s ν_{CO} cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C): δ 8.03−6.97 (m, 10H, Ph), 4.69 (m, 4H, CH), 1.22, 1.13 (d, 24H, CH_3), −7.71 (t, 1H, Mn−H, J_{PH} = 38 Hz). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C): δ 197.1 s.

$MnH(CO)_2P_3$ (2) and $MnH(CO)P_4$ (3) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b), PPh_2OEt (c), $PPh(OiPr)_2$ (d)). A solution of $MnH(CO)_5$ (12.8 mmol, 2.5 g) in 30 mL of toluene was treated under argon with 90 mmol of the appropriate phosphite and the mixture irradiated at room temperature for 48 h in a Pyrex Schlenk flask using a standard 400-W medium-pressure mercury arc lamp. The solvent was then evaporated under reduced pressure to give an oil which was triturated with ethanol until a white solid, containing a mixture of **2** and **3**, separated out. Fractional crystallization from ethanol or chromatographic separation on silica gel using a mixture of petroleum ether (40−70 °C) and diethyl ether in a 10:2 ratio as eluent allowed us to obtain pure samples of both the hydrides **3** (25−35% yield, first eluted) and **2** (40−60% yield). Anal. Calcd for $C_{20}H_{46}O_{11}P_3Mn$ (**2a**): C, 39.35; H, 7.60. Found: C, 39.22; H, 7.67. Mp: 71 °C. IR (KBr): 1934 s, 1872 s ν_{CO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 4.10 (m, 18H, CH_2), 1.23 (t, 27H, CH_3), −8.02 (d of t, 1H, Mn−H, spin system A_2BX (X = H), J_{AX} = 49 Hz, J_{BX} = 61 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): spin system A_2B, δ_A 194.2, δ_B 186.9, J_{AB} = 96 Hz. Anal. Calcd for $C_{32}H_{46}O_8P_3Mn$ (**2b**): C, 54.40; H, 6.56. Found: C, 54.55; H, 6.49. Mp: 78 °C. IR (KBr): 1933 s, 1869 s ν_{CO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 7.90−7.00 (m, 15H, Ph), 4.10−3.70 (m, 12H, CH_2), 1.13, 1.09, 1.05 (t, 18H, CH_3), −7.45 (d of t, 1H, Mn−H, spin system A_2BX (X = H), J_{AX} = 45 Hz, J_{BX} = 61 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): spin system A_2B, δ_A 206.6, δ_B 200.9, J_{AB} = 70 Hz. Anal. Calcd for $C_{44}H_{46}O_5P_3Mn$ (**2c**): C, 65.84; H, 5.78. Found: C, 65.78; H, 5.85. Mp: 137 °C. IR (KBr): 1922 s, 1864 s cm^{-1}. ^1H NMR ($CD_3C_6D_5$, −30 °C): δ 8.10−6.90 (m, 30H, Ph), 3.94, 3.68, 3.42 (br, 6H, CH_2), 1.01 (t, br, 9H, CH_3), −6.64 (d of t, 1H, Mn−H, spin system A_2BX (X = H), J_{AX} = 40 Hz, J_{BX} = 61 Hz). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, −30 °C): spin system A_2B, δ_A = 173.8, δ_B = 169.6, J_{AB} = 60 Hz. Anal. Calcd for $C_{38}H_{58}O_8P_3Mn$ (**2d**): C, 57.72; H, 7.39. Found: C, 57.90; H, 7.45. Mp: 164 °C. IR (KBr): 1933 s, 1875 s cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 8.20−7.00 (m, 15H, Ph), 4.78, 4.52 (m, 6H, CH), 1.33−1.11 (m, 36H, CH_3), −7.17 (q, 1H, Mn−H, spin system A_2BX (X = H), J_{AX} = J_{BX} = 57 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): spin system A_2B, δ_A 202.9, δ_B 196.0, J_{AB} = 70 Hz. Anal. Calcd for $C_{25}H_{61}O_{13}P_4Mn$ (**3a**): C, 40.11; H, 8.21. Found: C, 40.28; H, 8.17. Mp: 135 °C. IR (KBr): 1852 s cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 4.20 (m, 24H, CH_2), 1.28 (t, 36H, CH_3), −8.13 (qi, 1H, Mn−H, J_{PH} = 52 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 194.6 s. Anal. Calcd for $C_{41}H_{61}O_9P_4Mn$ (**3b**): C, 56.17; H, 7.01. Found: C, 56.27; H, 7.15. Mp: 169 °C. IR (KBr): 1853 s ν_{CO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 8.15−7.10 (m, 20H, Ph), 3.72, 3.45 (m, 16H, CH_2), 1.03 (t, 24H, CH_3), −7.07 (qi, 1H, Mn−H, J_{PH} = 52 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 208.0 s, br.

$[Mn(\eta^2\text{-}H_2)(CO)_2P_3]^+BF_4^-$ (4) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b), PPh_2OEt (c)). These complexes were prepared in solution (CD_2Cl_2) at low temperature (−78 °C) by protonation with $HBF_4\cdot Et_2O$ of the hydride compounds $MnH(CO)_2P_3$ (**2**), but they were not isolated as solids owing to the easy loss of hydrogen above 0 °C. A typical preparation involves the addition by microsyringe of $HBF_4\cdot Et_2O$ (0.02 mmol, 2.9 μL) to

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a solution of the appropriate hydride (0.2 mmol) in 0.5 mL of CD_2Cl_2 placed into a 5 mm NMR tube and cooled to −78 °C. The tube was brought to about −20 °C to complete the reaction and then, with the temperature kept below 0 °C, the NMR spectra (^1H and ^{31}P) were measured. The related isotopomer $[Mn(\eta^2\text{-}HD)(CO)_2\{P(OEt)_3\}_3]^+CF_3CO_2^-$ (**4a$_1$**) was prepared in a NMR tube exactly like **4a** using CF_3COOD as the protonating agent. **4a**: ^1H NMR (CD_2Cl_2, −90 °C) δ 4.02 (m, 18H, CH_2), 1.36 (t, 27H, CH_3), −8.5 (br, 2H, η^2-H_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C) spin system A_2B, δ_A 167.3, δ_B 159.3, J_{AB} = 89 Hz **4b**: ^1H NMR (CD_2Cl_2, −90 °C) δ 7.70−7.50 (m, 15H, Ph), 3.92 (br, 12H, CH_2), 1.40 (br, 18H, CH_3), −7.9 (br, 2H, η^2-H_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C) spin system A_2B, δ_A 191.7, δ_B 174.7, J_{AB} = 72 Hz. **4c**: ^1H NMR (CD_2Cl_2, −90 °C) δ 7.51 (m, 30H, Ph), 3.90, 3.41 (m, 6H, CH_2), 1.39, 1.12 (br, 9H, CH_3), −7.1 (br, 2H, η^2-H_2); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C) spin system A_2B, δ_A 160.4, δ_B 154.4, J_{AB} = 52 Hz.

$[Mn(\eta^2\text{-}H_2)(CO)P_4]BPh_4$ (5) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b)). $HBF_4\cdot Et_2O$ (0.2 mmol, 29 μL of a 54% solution in Et_2O) was added to a solution of $MnH(CO)P_4$ (**3**) (0.2 mmol) in 7 mL of ethanol under H_2 (1 atm) cooled to −78 °C. The reaction mixture was brought to about 0 °C and after 20 min, a solution of $NaBPh_4$ (0.2 mmol, 0.068 g) in 3 mL of ethanol was added. A pale yellow solid slowly separated out which was filtered, washed with ethanol, and dried under vacuum: yield 65% (**5a**), 78% (**5b**). Anal. Calcd for $C_{49}H_{82}BO_{13}P_4Mn$ (**5a**): C, 55.06; H, 7.73. Found: C, 54.91; H, 7.81. Λ_M (CH_3NO_2, 25 °C): 55.7 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1926 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.30−6.70 (m, 20H, Ph), 4.10 (m, 24H, CH_2), 1.36 (t, 36H, CH_3), −8.28 (br, 2H, η^2-H_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 175.7 s, br. Anal. Calcd for $C_{65}H_{82}BO_9P_4Mn$ (**5b**): C, 65.22; H, 6.90. Found: C, 65.13; H, 7.06. Λ_M (CH_3NO_2, 25 °C): 53.4 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1926 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.50−6.80 (m, 40H, Ph), 3.56 (m, 16H, CH_2), 1.56 (t, 24H, CH_3), −7.22 (br, 2H, η^2-H_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 195.4 s.

$[Mn(\eta^2\text{-}HD)(CO)P_4]^+CF_3CO_2^-$ (P = $P(OEt)_3$ (5a$_1$), $PPh(OEt)_2$ (5b$_1$)). These isotopomers were prepared in solution (CD_2Cl_2) like the related η^2-H_2 compounds **5** by adding an equimolar amount of CF_3COOD to the appropriate hydrides **3** in an NMR tube.

$[Mn(CO)_2P_3]BPh_4$ (6) and $[Mn(CO)P_4]BPh_4$ (7) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b)). $HBF_4\cdot Et_2O$ (0.2 mmol, 29 μL of a 54% solution in Et_2O) was added to a solution of $MnH(CO)_2P_3$ (**2**) or $MnH(CO)P_4$ (**3**; 0.2 mmol) in 7 mL of ethanol cooled to −78 °C under argon. The reaction mixture was slowly brought to 30 °C and stirred for 2 h. The addition of $NaBPh_4$ (0.2 mmol, 0.068 g) in 3 mL of ethanol caused the precipitation of a yellow solid, which was filtered, washed with ethanol, and dried under vacuum. Yield between 84% and 68%. Anal. Calcd for $C_{44}H_{65}BO_{11}P_3Mn$ (**6a**): C, 56.91; H, 7.06. Found: C, 56.77; H, 7.12. Λ_M (CH_3NO_2, 25 °C): 60.6 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1983 s, 1872 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.30−6.80 (m, 20H, Ph), 4.09 (m, 18H, CH_2), 1.30 (t, 27H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 25 °C, δ 170.7 s, br; −80 °C, δ 169.9 s, br. Anal. Calcd for $C_{56}H_{65}BO_8P_3Mn$ (**6b**): C, 65.63; H, 6.39. Found: C, 65.79; H, 6.26. Λ_M (CH_3NO_2, 25 °C): 57.4 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1970 s, 1894 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2): 25 °C, δ 7.60−6.80 (m, 35H, Ph), 3.93 (qi, 12H, CH_2), 1.35, 1.33, 1.26 (t, 18H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C): spin system A_2B, δ_A 187.9, δ_B 177.3, J_{AB} = 80.0 Hz. Anal. Calcd for $C_{49}H_{80}BO_{13}P_4Mn$ (**7a**): C, 55.17; H, 7.56. Found: C, 55.03; H, 7.50. Λ_M (CH_3NO_2, 25 °C): 56.0 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1872 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2): 25 °C, δ 7.30−6.70 (m, 20H, Ph), 4.09 (m, br, 24H, CH_2), 1.30 (t, br, 36H, CH_3); −80 °C, δ 4.30, 4.09 (br, CH_2), 1.56, 1.30 (br, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 25 °C, δ 170.0 br; −80 °C, δ 170.2 br, 168.7 s, br. Anal. Calcd for $C_{65}H_{80}BO_9P_4Mn$ (**7b**): C, 65.33; H, 6.75. Found: C, 65.52; H, 6.50. Λ_M (CH_3NO_2, 25 °C): 58.3 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1915 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.80−6.80 (m, 40H, Ph), 3.71, 3.59 (m, 16H, CH_2), 1.28, 1.22, 1.18 (m, 24H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 25 °C, δ 185.9 s, br; −80 °C, δ 188.8 s, br.

$Mn(\eta^1\text{-}OSO_2CF_3)(CO)_3[PPh(OEt)_2]_2$ (8). An equivalent amount of CF_3SO_3H (0.75 mmol, 66 μL) was added to a solution of $MnH(CO)_3[PPh(OEt)_2]_2$ (**1b**; 0.75 mmol, 0.5 g) in 5 mL of diethyl ether cooled to −78 °C. The reaction mixture was brought to room temperature, stirred for about 1 h, and then the solvent removed under reduced pressure. The oil obtained was triturated with *n*-hexane (4 mL) until a yellow solid began to separate out (about 1 h). After cooling to −25 °C to complete the precipitation, the solid was filtered and dried under vacuum; yield ≥80%. Anal. Calcd for $C_{24}H_{30}F_3O_{10}P_2SMn$: C, 42.12; H, 4.42. Found: C, 41.96; H, 4.50. IR (KBr): 2066 m, 1975 s, 1932 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.70, 7.50 (m, 10H, Ph), 4.05 (m, 8H, CH_2), 1.36 (t, 12H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 182.8 s.

$[Mn(C{\equiv}CPh)(CO)_3P_2]$ (9) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b), PPh_2OEt (c), $PPh(O^iPr)_2$ (d)) and $[Mn(C{\equiv}C\text{-}p\text{-tolyl})(CO)_3P_2]$ (9) (P = $PPh(OEt)_2$ (b$_1$), PPh_2OEt (c$_1$)). To a solution of the appropriate hydride $MnH(CO)_3P_2$ (**1**; 1.5 mmol) in 8 mL of toluene cooled to −78 °C was added an equivalent amount of CF_3SO_3H (1.5 mmol, 133 μL), and the reaction mixture was then brought to room temperature and stirred for 1 h. An excess of $Li^+[RC{\equiv}C]^-$ (4.5 mmol, 1.8 mL of a 2.5 M solution in THF) was added to the resulting solution, which was then further stirred at room temperature for 2 h. The solvent was removed under reduced pressure, giving an oil which was triturated with ethanol (5 mL) at 0 °C for 2−3 h. In some cases a pale yellow solid separated out after 2−3 h of stirring, but often an oil remained. This oil was chromatographed on a silica gel column (70 × 4 cm) using a mixture of petroleum ether (40-60 °C), diethyl ether, and benzene in a 8:1:1 ratio as eluent. The first eluted band (about 400 mL) was evaporated to dryness, leaving an oil which was triturated with ethanol (5 mL) until a solid separated out (10−30 min). This solid was filtered and dried under vacuum; yield between 30 and 55%. Anal. Calcd for $C_{23}H_{35}O_9P_2Mn$ (**9a**): C, 48.26; H, 6.16. Found: C, 48.41; H, 6.24. IR (KBr): 2096 m $\nu_{C\equiv C}$; 2040 m, 1959 s, 1947 s ν_{CO} cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C): δ 7.42−6.95 (m, 5H, Ph), 4.18 (m, 12H, CH_2), 1.17 (t, 18H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C): δ 173.3 s. Anal. Calcd for $C_{31}H_{35}O_7P_2Mn$ (**9b**): C, 58.50; H, 5.54. Found: C, 58.28; H, 5.65. Mp: 139 °C. IR (KBr and (CH_2Cl_2)): 2100 m (2094 m) $\nu_{C\equiv C}$; 2027 m, 1940 s (2036 m, 1958 s, 1928 s) ν_{CO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 7.95−7.00 (m, 15H, Ph), 4.22, 3.85 (m, 8H, CH_2), 1.10 (t, 12H, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 193.0 s. Anal. Calcd for $C_{39}H_{35}O_5P_2Mn$ (**9c**): C, 66.86; H, 5.04. Found: C, 66.71; H, 5.13. Mp: 179 °C. IR (KBr): 2094 m $\nu_{C\equiv C}$; 2022 m, 1943 s, 1927 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 8.00−6.90 (m, 25H, Ph), 3.85 (m, 4H, CH_2), 1.25 (t, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 161.7 s. Anal. Calcd for $C_{35}H_{43}O_7P_2Mn$ (**9d**): C, 60.70; H, 6.26. Found: C, 60.58; H, 6.39. IR (KBr): 2090 m $\nu_{C\equiv C}$; 2038 m, 1953 s, 1924 s ν_{CO} cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C): δ 8.00−6.95 (m, 15H, Ph), 5.00 (m, 4H, CH), 1.27, 1.20 (d, 24H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 2 °C): δ 188.8 s. Anal. Calcd for $C_{32}H_{37}O_7P_2Mn$ (**9b$_1$**): C, 59.08; H, 5.73. Found: C, 59.24; H, 5.66. Mp: 68 °C. IR (KBr): 2094 m $\nu_{C\equiv C}$; 2038 m, 1958 s, 1929 s ν_{CO} cm^{-1}. ^1H NMR (C_6D_6, 25 °C): δ 8.00−6.90 (m, 14H, Ph), 4.25, 3.86 (m, 8H, CH_2), 2.13 (s, 3H, CH_3 *p*-tolyl), 1.12 (t, 12H, CH_3 phos). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ 192.9 s. Anal. Calcd for $C_{40}H_{37}O_5P_2Mn$ (**9c$_1$**): C, 64.47; H, 4.58. Found: C, 64.64; H, 4.51. Mp: 132 °C. IR (KBr): 2092 m $\nu_{C\equiv C}$; 2032 m, 1945 s, 1924 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.95−6.80 (m, 24H, Ph), 3.86 (m, br, 4H, CH_2), 2.22 (s, 3H, CH_3 *p*-tolyl), 1.24 (t, 6H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 161.7 s.

$[Mn(C{\equiv}CPh)(CO)_2P_3]$ (10) and $[Mn(C{\equiv}CPh)(CO)P_4]$ (11) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b)). An equivalent amount of $HBF_4\cdot Et_2O$ (0.75 mmol, 108 μL of a 54% solution in Et_2O) was added to a cooled (−78 °C) solution of the appropriate hydride $MnH(CO)_2P_3$ (**2**) or $MnH(CO)P_4$ (**3**) in 5 mL of toluene. The reaction mixture was slowly brought to

30 °C and stirred for 2 h. An excess of $Li^+[PhC\equiv C]^-$ (3 mmol, 0.83 mL of a 2.5 M solution in THF) was added to the resulting solution containing the $[Mn(CO)_2P_3]^+$ and $[Mn(CO)P_4]^+$ cations, and the stirring was continued for 2 h. Evaporation of the solvent under reduced pressure gave an oil which was chromatographed on a silica gel column (70 × 4 cm) using as eluent a mixture of petroleum ether (40−60 °C), diethyl ether, and benzene in a 8:1:1 ratio. The first eluted band (about 400 mL) was evaporated under reduced pressure, giving an oil which was triturated with ethanol until a pale yellow solid separated out. After filtration, the solid was dried under vacuum; yield ≥45%. Anal. Calcd for $C_{40}H_{50}O_8P_3Mn$ (**10b**): C, 59.56; H, 6.25. Found: C, 59.71; H, 6.31. IR (KBr): 2083 m $\nu_{C\equiv C}$; 1960 s, 1885 s ν_{CO} cm^{-1}. ^1H NMR ($CD_3C_6D_5$, 25 °C): δ 7.90−6.80 (m, 20H, Ph), 4.30−3.70 (m, 12H, CH_2), 1.14, 1.13, 1.09 (t, 18H, CH_3). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$, 25 °C): spin system A_2B, δ_A 195.2, δ_B 188.7, $J_{AB} = 70.0$ Hz. Anal. Calcd for $C_{33}H_{65}O_{13}P_4Mn$ (**11a**): C, 46.70; H, 7.72. Found: C, 46.88; H, 7.60. Mp: 127 °C. IR (KBr and (CH_2Cl_2)): 2079 m (2075 m) $\nu_{C\equiv C}$; 1852 s (1862 s, 1843 s) ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.07 m, 6.89 br (5H, Ph), 4.20 (m, 24H, CH_2), 1.20 (t, 36H, CH_3). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C): δ 184.5 s.

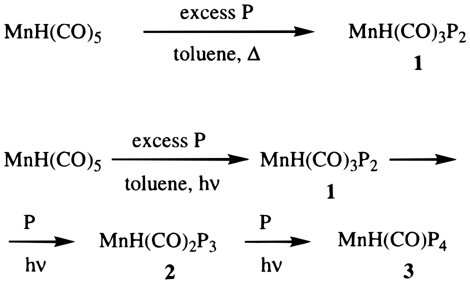
$[Mn(4\text{-}CH_3C_6H_4CN)(CO)_2P_3]BPh_4$ (12) and $[Mn(4\text{-}CH_3C_6H_4CN)(CO)P_4]BPh_4$ (13) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b)). To a suspension of the appropriate hydride $MnH(CO)_2P_3$ (**2**) or $MnH(CO)P_4$ (**3**) (0.4 mmol) in 4 mL of ethanol cooled to −78 °C was added an equivalent amount of $HBF_4\cdot Et_2O$ (0.4 mmol, 58 μL of a 54% solution). The reaction mixture was slowly brought to about 30 °C and stirred for 2 h, and then a slight excess of *p*-toluonitrile (0.6 mmol, 70 μL) was added. After 1 h of stirring an excess of $NaBPh_4$ (0.8 mmol, 0.27 g) in 3 mL of ethanol was added and the reaction mixture stirred until a yellow solid separated out. The compound was filtered and crystallized from CH_2Cl_2 (2 mL) and ethanol (6 mL); yield ≥80%. Anal. Calcd for $C_{52}H_{72}NBO_{11}P_3Mn$ (**12a**): C, 59.72; H, 6.94; N, 1.34. Found: C, 59.88; H, 7.03; N, 1.29. Mp: 94 °C. Λ_M (CH_3NO_2, 25 °C): 53.6 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2261 w ν_{CN}; 1976 s, 1916 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.80−6.70 (m, 24H, Ph), 4.23 (m, 18H, CH_2), 2.45 (s, 3H, CH_3 *p*-tolyl), 1.35, 1.31 (t, 27H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): spin system A_2B, δ_A 167.7, δ_B 157.4, $J_{AB} = 99$ Hz. Anal. Calcd for $C_{64}H_{72}NBO_8P_3Mn$ (**12b**): C, 67.32; H, 6.36; N, 1.23. Found: C, 67.15; H, 6.23; N, 1.18. Mp: 157 °C. Λ_M (CH_3NO_2, 25 °C): 49.7 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2250 w ν_{CN}; 1979 s, 1917 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.70−6.70 (m, 39H, Ph), 4.05 (m, 12H, CH_2), 2.36 (s, 3H, CH_3 *p*-tolyl), 1.40, 1.37 (t, 18H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): spin system A_2B, δ_A 197.1, δ_B 181.0, $J_{AB} = 62$ Hz. Anal. Calcd for $C_{57}H_{87}NBO_{13}P_4Mn$ (**13a**): C, 57.83; H, 7.41; N, 1.18. Found: C, 57.80; H, 7.57; N, 1.10. Mp: 145 °C. Λ_M (CH_3NO_2, 25 °C): 55.3 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2239 w ν_{CN}; 1894 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.70−6.70 (m, 24H, Ph), 4.20 (m, 24H, CH_2), 2.43 (s, 3H, CH_3 *p*-tolyl), 1.31 (t, 36H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): δ 173.9 s. Anal. Calcd for $C_{73}H_{87}NBO_9P_4Mn$ (**13b**): C, 66.82; H, 6.68; N, 1.07. Found: C, 66.70; H, 6.57; N, 1.11. Mp: 147 °C. Λ_M (CH_3NO_2, 25 °C): 57.2 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1886 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 20 °C): δ 7.80−6.70 (m, 44H, Ph), 3.75 (m, 16H, CH_2), 2.44 (s, 3H, CH_3 *p*-tolyl), 1.23 (t, 24H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): δ 199.9 s.

$[Mn(4\text{-}CH_3C_6H_4NC)(CO)_2P_3]BPh_4$ (14) and $[Mn(4\text{-}CH_3C_6H_4NC)(CO)P_4]BPh_4$ (15) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b)). These complexes were prepared exactly like the related nitrile compounds **12** and **13** by adding a slight excess of *p*-tolyl isocyanide to a solution containing $[Mn(CO)_2P_3]^+$ and $[Mn(CO)P_4]^+$ cations in ethanol; yield ≥80%. Anal. Calcd for $C_{52}H_{72}NBO_{11}P_3Mn$ (**14a**): C, 59.72; H, 6.94; N, 1.34. Found: C, 59.58; H, 6.82; N, 1.36. Λ_M (CH_3NO_2, 25 °C): 52.9 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2141 s ν_{CN}; 1993 s, 1947 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.45−6.70 (m, 24H, Ph), 4.23 (m, 18H, CH_2), 2.40 (s, 3H, CH_3 *p*-tolyl), 1.35 (t, br, 27H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C): spin system A_2B, δ_A 168.7, δ_B 159.9, $J_{AB} = 87$ Hz. Anal. Calcd for $C_{64}H_{72}NBO_8P_3Mn$ (**14b**): C, 67.32; H, 6.36; N, 1.23. Found: C, 67.50; H, 6.42; N, 1.19. Mp: 189 °C. Λ_M (CH_3NO_2, 25 °C): 61.7 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2137 s ν_{CN}; 1981 s, 1931 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.70−6.60 (m, 39H, Ph), 4.01 (m, 12H, CH_2), 2.33 (s, 3H, CH_3 *p*-tolyl), 1.37, 1.34 (t, 18H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C): spin system A_2B, δ_A 192.6, δ_B 183.6, $J_{AB} = 61$ Hz. Anal. Calcd for $C_{57}H_{87}NBO_{13}P_4Mn$ (**15a**): C, 57.83; H, 7.41; N, 1.18. Found: C, 57.55; H, 7.30; N, 1.20. Mp: 183 °C. Λ_M (CH_3NO_2, 25 °C): 53.2 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2116 s ν_{CN}; 1922 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.33−6.70 (m, 24H, Ph), 4.19 (m, 24H, CH_2), 2.36 (s, 3H, CH_3 *p*-tolyl), 1.31 (t, 36H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): δ 175.2 s. Anal. Calcd for $C_{73}H_{87}NBO_9P_4Mn$ (**15b**): C, 66.82; H, 6.68; N, 1.07. Found: C, 66.75; H, 6.59; N, 1.07. Mp: 167 °C. Λ_M (CH_3NO_2, 25 °C): 54.3 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2109 s ν_{CN}; 1915 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.75−6.70 (m, 44H, Ph), 3.68 (m, 16H, CH_2), 2.37 (s, 3H, CH_3 *p*-tolyl), 1.21 (t, 24H, CH_3 phos). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C): δ 204.7 s.

$[Mn(CO)_3P_3]BPh_4$ (16) and $[Mn(CO)_2P_4]BPh_4$ (17) (P = $P(OEt)_3$ (a), $PPh(OEt)_2$ (b)). An equivalent amount of $HBF_4\cdot Et_2O$ (0.4 mmol, 58 μL of a 54% solution) was added to a suspension of the appropriate hydride $MnH(CO)_2P_3$ (**2**) and $MnH(CO)P_4$ (**3**) (0.4 mmol) in 4 mL of ethanol cooled to −78 °C. The reaction mixture was slowly brought to +30 °C, stirred for 2 h, and then placed under a CO atmosphere (1 atm) for 1 h. The addition of an excess of $NaBPh_4$ (0.8 mmol, 0.27 g) in 3 mL of ethanol caused the precipitation of a pale yellow solid, which was filtered and crystallized from CH_2Cl_2 (2 mL) and ethanol (5 mL); yield ≥70%. Anal. Calcd for $C_{45}H_{65}BO_{12}P_3Mn$ (**16a**): C, 56.50; H, 6.85. Found: C, 56.43; H, 6.88. Mp: 136 °C. Λ_M (CH_3NO_2, 25 °C): 51.7 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2062 m, 1980 s, 1972 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.35−6.00 (m, 20H, Ph), 4.25 (m, br, 18H, CH_2), 1.37 (t, br, 27H, CH_3). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): δ 160 br. Anal. Calcd for $C_{57}H_{65}BO_9P_3Mn$ (**16b**): C, 65.03; H, 6.22. Found: C, 64.98; H, 6.25. Mp: 202 °C. Λ_M (CH_3NO_2, 25 °C): 56.9 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2051 m, 1980 s, 1968 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.61−6.70 (m, 35H, Ph), 4.01, 3.90 (m, 12H, CH_2), 1.36, 1.35 (t, 18H, CH_3). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): δ 186, 180 br. Anal. Calcd for $C_{50}H_{80}BO_{14}P_4Mn$ (**17a**): C, 54.85; H, 7.37. Found: C, 54.81; H, 7.39. Mp: 193 °C. Λ_M (CH_3NO_2, 25 °C): 50.7 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1991 s, 1932 s ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.30−6.70 (m, 20H, Ph), 4.18 (m, 24H, CH_2), 1.34 (t, br, 36H, CH_3). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): δ 170.1 s; 167.8, 160.3 t (spin system A_2B_2, δ_A 167.8, δ_B 160.3, $J_{AB} = 84$ Hz). Anal. Calcd for $C_{66}H_{80}BO_{10}P_4Mn$ (**17b**): C, 64.82; H, 6.59. Found: C, 64.76; H, 6.57. Mp: 190 °C. Λ_M (CH_3NO_2, 25 °C): 52.5 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1985 s, 1922 s, br ν_{CO} cm^{-1}. ^1H NMR ($(CD_3)_2CO$, 25 °C): δ 7.90−6.70 (m, 40H, Ph), 3.87, 3.68 (m, 16H, CH_2), 1.35, 1.24 (t, 24H, CH_3). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$, −90 °C): δ 194.9 s, 192 m, br.

$[Mn(OH_2)(CO)_3P_2]BF_4$ (18) (P = $PPh(OEt)_2$ (b), PPh_2OEt (c)). To a suspension of the appropriate hydride $MnH(CO)_3P_2$ (**1**) (0.4 mmol) in 3 mL of ethanol cooled to −78 °C was added an equivalent amount of aqueous HBF_4 (0.4 mmol, 52 μL of a 48% solution in water), and the reaction mixture was brought to room temperature. After 1 h of stirring the solvent was removed under reduced pressure, giving a yellow oil which was triturated with diethyl ether (5 mL). A yellow solid began to separate out after 1−2 h, which was filtered and crystallized from ethanol (2 mL) and diethyl ether (7 mL): yield ≥70%. Anal. Calcd for $C_{23}H_{32}BF_4O_8P_2Mn$ (**18b**): C, 43.15; H, 5.04. Found: C, 43.12; H, 6.09. Mp: 120 °C. Λ_M (CH_3NO_2, 25 °C): 87.6 Ω^{-1} mol^{-1} cm^2. IR (KBr): 2064 m, 1978 s, 1936 s ν_{CO} cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ 7.80−7.50 (m, 10H, Ph), 4.10 (m, 8H, CH_2), 2.53 (t, 2H, OH_2, $J_{PH} = 2.1$ Hz), 1.40 (t, 12H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 25 °C, δ 182.1 s, br; −90 °C, δ 183.5 s. Anal. Calcd for $C_{31}H_{32}BF_4O_6P_2Mn$ (**18c**): C,

Scheme 1[a]



[a] P = P(OEt)$_3$ (**a**), PPh(OEt)$_2$ (**b**), PPh$_2$OEt (**c**), PPh(O^{i}Pr)$_2$ (**d**).

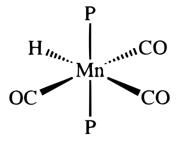
52.87; H, 4.58. Found: C, 52.93; H, 4.50. Λ_M (CH_3NO_2, 25 °C): 90.2 Ω^{-1} mol^{-1} cm^2. IR (Nujol): 2051 m, 1971 s, 1925 s ν_{CO} cm^{-1}. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.80−7.70 (m, 20H, Ph), 3.66 (m, 4H, CH_2), 2.48 (t, 2H, OH_2), 1.22 (t, 6H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): 25 °C, δ 158.4 s; −90 °C, 156.9 s.

Results and Discussion

Preparation and Characterization of Hydride Species. The manganese complexes $MnH(CO)_3P_2$ (**1**), $MnH(CO)_2P_3$ (**2**), and $MnH(CO)P_4$ (**3**) were prepared by substituting carbonyl ligands in the hydride pentacarbonyl complex $MnH(CO)_5$ with the appropriate phosphite, as shown in Scheme 1.

The reaction of $MnH(CO)_5$ with an excess of phosphine proceeds in refluxing toluene to give exclusively the tricarbonyl complexes **1**, which were isolated as white solids in high yield. Irradiation of $MnH(CO)_5$ solutions containing an excess of P, instead, gives rise to the sequential substitution of the carbonyl ligands affording the $MnH(CO)_3P_2$ (**1**), $MnH(CO)_2P_3$ (**2**), and $MnH(CO)P_4$ (**3**) derivatives, which were isolated after chromatographic separation and characterized. Also, the formation of the first substitution product, the tetracarbonyl $MnH(CO)_4P$ species was detected (IR) by working in a low phosphite to pentacarbonyl *ratio*, but the compound was not separated. Furthermore, the substitution of all the carbonyl groups in $MnH(CO)_5$ to give $MnHP_5$ species was not observed, and the protracted irradiation led only to decomposition products. Finally, the monocarbonyls $MnH(CO)P_4$ with PPh$_2$OEt (**3c**) and with PPh(O^{i}Pr)$_2$ (**3d**) were formed in small amounts owing to the low substitution rates and were not isolated.

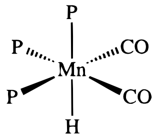
Good analytical data were obtained for all the hydride complexes, which are white or pale yellow solids, air-stable both as solids and in solution of polar and nonpolar organic solvents, where they behave as non-electrolytes. The infrared spectra of tricarbonyl compounds $MnH(CO)_3P_2$ (**1**) show in the ν_{CO} region three bands (one weak and two of strong intensity), suggesting a *mer* arrangement[9] of the three carbonyl ligands. In the temperature range between +20 and −90 °C the ^{31}P{^{1}H} NMR spectra consist of only one sharp singlet at 205.3−173.3 ppm, indicating the magnetic equivalent of the two phosphorus *nuclei*. In the ^{1}H NMR spectra the hydride appears as a sharp triplet between −8.13 and −7.36 ppm. On these bases a *mer-trans* geometry of type **I** can be proposed in solution for complexes **1**.



I

mer-trans

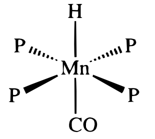
Two ν_{CO} bands at 1934-1864 cm^{-1} are instead present in the spectra of the compounds $MnH(CO)_2P_3$ (**2**), in agreement with two carbonyl ligands in mutually *cis* positions. The ^{31}P{^{1}H} NMR spectra appear as an A_2B spin system (one doublet and one triplet), indicating that two phosphorus *nuclei* are magnetically equivalent and are different from the third. In the ^{1}H NMR spectra the hydride signal appears as a multiplet which can be easily simulated as the X part of a A_2BX spin system with the parameters reported in the Experimental Section. Finally, the ^{13}C{^{1}H} NMR spectra of complex **2b** (Table 1) show only one multiplet, formed by a doublet of triplets, at 225.5 ppm for the carbonyl carbon atom, suggesting the magnetic equivalence of the two CO ligands as in *fac-cis* structure **II**.



II

cis-fac

The two monocarbonyls complexes $MnH(CO)P_4$ (**3a**,**b**) show similar IR spectra, with only one ν_{CO} band at 1852 (**3a**) and 1853 (**3b**) cm^{-1}, but slightly different ^{1}H and ^{31}P NMR spectra. In the temperature range between +30 and −90 °C the ^{31}P{^{1}H} spectrum of MnH(CO)[P(OEt)$_3$]$_4$ (**3a**) consists of only one sharp singlet at 194.6 ppm, in agreement with a *trans* geometry (**III**). In the ^{1}H NMR spectrum the hydride signal appears as a quintet at −8.13 ppm with a coupling constant J_{HP} of 52 Hz.



III

trans

The ^{1}H and ^{31}P NMR spectra of the related complex MnH(CO)[PPh(OEt)$_2$]$_4$ (**3b**), in contrast, are temperature dependent and the broad singlet at 208.5 ppm that appears at room temperature in the phosphorus spectra changes as the temperature is lowered and resolves into a complicated multiplet at −80 °C. Also, the hydride signal changes from a quintet (at −7.07 ppm) at room temperature to a slightly broad multiplet at −80 °C.

These results implicate the presence of inequivalent phosphorus *nuclei* and may suggest the presence of a geometry with the hydride and the CO ligands in *cis* positions. However, the ^{31}P spectra may also be interpreted on the basis of the presence of a *trans* geometry (**III**), in which the four PPh(OEt)$_2$ phosphite ligands are

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[9] Adams, D. M. *Metal-Ligand and Related Vibrations*; St. Martin's Press: New York, 1968.

Table 1. $^{13}C\{^1H\}$ NMR Data for Selected Manganese Compounds

compd	$\delta^{a,b}$	assignt
$MnH(CO)_2[PPh(OEt)_2]_3$ (**2b**)	225.5 d of t ($^2J_{CP}$ = 20 Hz)	CO
	61.4, 61.2 s, br	CH_2
	16.5 s, br	CH_3
$Mn(C{\equiv}CPh)(CO)_3[P(OEt)_3]_2$ (**9a**)	216.3 m	CO
	117.0 s, br	C_β
	111.7 t ($^2J_{CP}$ = 37 Hz)	C_α
	61.9 s	CH_2
	16.3 s	CH_3
$Mn(C{\equiv}CPh)(CO)_3[PPh(OEt)_2]_2$ (**9b**)	217.0 t ($^2J_{CP}$ = 26 Hz)	CO
	140−124 m	Ph
	116.8 s, br	C_β
	113.7 t ($^2J_{CP}$ = 32 Hz)	C_α
	62.8 t	CH_2
	16.5 t	CH_3
$Mn(C{\equiv}CPh)(CO)_3(PPh_2OEt)_2$ (**9c**)	217.8 t ($^2J_{CP}$ = 22 Hz), 217.3 t ($^2J_{CP}$ = 16 Hz)	CO
	121.8 t, br	C_β
	116.4 t ($^2J_{CP}$ = 32 Hz)	C_α
	62.6 t	CH_2
	16.5 t	CH_3
$Mn(C{\equiv}C\text{-}p\text{-tolyl})(CO)_3[PPh(OEt)_2]_2$ (**9b$_1$**)	217.0 t ($^2J_{CP}$ = 25 Hz)	CO
	116.6 s, br	C_β
	111.4 t ($^2J_{CP}$ = 32 Hz)	C_α
	62.8 t	CH_2
	21.4 s	CH_3 *p*-tolyl
	16.5 t	CH_3 phos
$Mn(C{\equiv}C\text{-}p\text{-tolyl})(CO)_3(PPh_2OEt)_2$ (**9c$_1$**)	217.8 t ($^2J_{CP}$ = 22 Hz)	CO
	121.7 s, br	C_β
	114.1 t ($^2J_{CP}$ = 32 Hz)	C_α
	62.6 s, br	CH_2
	21.4 s	CH_3 *p*-tolyl
	16.5 s, br	CH_3 phos
$Mn(C{\equiv}CPh)(CO)_2[PPh(OEt)_2]_3$ (**10b**)	222.9 d of t ($^2J_{CP}$ = 24 Hz), 220.8 d of t ($^2J_{CP}$ = 24 Hz)	CO
	119.6 qi, br	C_β
	62.4, 62.2 t	CH_2
	16.7, 16.5 t	CH_3
$Mn(C{\equiv}CPh)(CO)[P(OEt)_3]_4$ (**11a**)	221.1 qi ($^2J_{CP}$ = 28 Hz)	CO
	119.4 qi, br	C_β
	61.0 s, br	CH_2
	16.4 s, br	CH_3
$[Mn(4\text{-}CH_3C_6H_4NC)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**14b**)	218.1 m, br	CO
	66.7, 64.1 t	CH_2
	21.4 s	CH_3 *p*-tolyl
	16.5, 16.3 t	CH_3 phos
$Mn(OH_2)(CO)_3(PPh_2OEt)_2]BF_4$ (**18c**)	219.9 t ($^2J_{CP}$ = 18 Hz), 213.4 t ($^2J_{CP}$ = 22 Hz)	CO
	65.3 t	CH_2
	15.9 t	CH_3

[a] At 25 °C in CD_2Cl_2; coupling constants in Hz. [b] Phenyl group signals are omitted.

made inequivalent by the different arrangement of the phenyl and ethoxy groups of one phosphite with respect to the other. Examples of inequivalent phosphorus *nuclei* in octahedral complexes containing four $PPhMe_2$ or $PPh(OEt)_2$ ligands in a plane have recently been reported for $[IrCl_2(PPhMe_2)_4]ClO_4$[10] and $FeHCl[PPh(OEt)_2]_4$[11] derivatives. Taking into account these precedents and the fact that the related $MnH(CO)[P(OEt)_3]_4$ (**3a**) complex containing the $P(OEt)_3$ ligands shows, in solution, a *trans* geometry, we find that a similar *trans* octahedral geometry can also be proposed for the $MnH(CO)[PPh(OEt)_2]_4$ (**3b**) species.

Hydrido-carbonyl complexes of manganese have been reported[12−14]in the past years, and the majority are tricarbonyls of the type $MnH(CO)_3P_2$ containing tertiary phosphine as coligands.[12]

Relatively few dicarbonyls $MnH(CO)_2P_3$ have been described,[12d,13] and only one example,[14] $MnH(CO)[P(OMe)_3]_4$, to our knowledge, has been reported of monocarbonyl derivatives. Furthermore, the use of phosphite ligands to stabilize these manganese−hydride compounds has been restricted to $P(OR)_3$ and $P(OCH_2)_3CR$, and there are no examples of phosphonite $PPh(OEt)_2$ or phosphinite PPh_2OEt as ancillary ligands. The photochemical substitution of CO groups in $MnH(CO)_5$ allows the synthesis of a rare example of manganese hydride such as the monocarbonyl $MnH(CO)P_4$ com-

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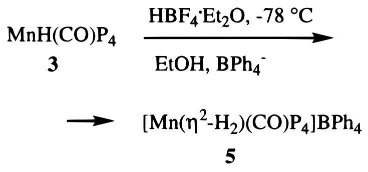
Table 2. ^{1}H NMR Data (200 MHz) in the Hydride Region for Selected Manganese Complexes

compd	*T*, K	δ(M−H$_2$)[a]	δ(M−H)[a]	T_1(min), ms	J_{HD}, Hz	*r*(H−H), Å[b]
$MnH(CO)_2[PPh(OEt)_2]_3$ (**2b**)	195		−7.91 d of t	85		
$MnH(CO)[PPh(OEt)_2]_4$ (**3b**)	202		−7.34 m, br	68		
	293		−7.36 qi			
$[Mn(\eta^2\text{-}H_2)(CO)_2\{P(OEt)_3\}_3]^+$ (**4a**)	205	−8.5 br		5		0.79
$[Mn(\eta^2\text{-}HD)(CO)_2\{P(OEt)_3\}_3]^+$ (**4a$_1$**)	223	−8.56 t			33	
$[Mn(\eta^2\text{-}H_2)(CO)_2\{PPh(OEt)_2\}_3]^+$ (**4b**)	198	−7.9 br		5.5		0.80
$[Mn(\eta^2\text{-}H_2)(CO)_2(PPh_2OEt)_3]^+$ (**4c**)	210	−7.0 br		5		0.79
$[Mn(\eta^2\text{-}H_2)(CO)\{P(OEt)_3\}_4]^+$ (**5a**)	195	−8.3 br		7		0.83
	293	−8.3 br				
$[Mn(\eta^2\text{-}HD)(CO)\{P(OEt)_3\}_4]^+$ (**5a$_1$**)	224	−8.41 t			32.0	
$[Mn(\eta^2\text{-}H_2)(CO)\{PPh(OEt)_2\}_4]^+$ (**5b**)	204	−7.4 br		6		0.81
	293	−7.22 br				
$[Mn(\eta^2\text{-}HD)(CO)\{PPh(OEt)_2\}_4]^+$ (**5b$_1$**)	234	−7.41 t			32.5	

[a] In CD_2Cl_2. [b] Fast rotation; for calculations see refs 15c and 16.

Scheme 2[a]



[a] P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**).

pounds together with a systematic investigation using $P(OEt)_3$, $PPh(OR)_2$, or PPh_2OR as a ligand.

Preparation and Characterization of Dihydrogen Complexes. The new hydrides *trans*-MnH(CO)P$_4$ (**3**) (P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**)) react under an hydrogen atmosphere at −78 °C with $HBF_4{\cdot}Et_2O$ to give the $[Mn(\eta^2\text{-}H_2)(CO)P_4]^+$ (**5a,b**) derivatives which can be isolated as BPh_4^- salts and characterized (Scheme 2).

The compounds are pale yellow solids, diamagnetic and 1:1 electrolytes. Under an argon atmosphere they are relatively stable as solids, whereas in solutions of polar organic solvents the loss of H_2 at room temperature is easy for **5a**, but slow for **5b**, whose solution can be handled unchanged for 1−2 h.

Spectroscopic data (Table 2) confirm the formulation of **5** as a dihydrogen complex. The ^{1}H NMR spectrum of each compound shows, in fact, a broad resonance in the hydride region at δ −8.3 (**5a**) and at δ −7.22 (**5b**) ppm. Variable-temperature T_1 measurements carried out at 200 MHz on this signal give a T_1(min) value of 7 ms at 195 K for **5a** and 6 ms at 204 K for **5b**, in agreement with the presence of an η^2-H_2 ligand.[15] The hydride precursor **3b** gives a T_1(min) value of 68 ms at 202 K.

In order to further support these assignments, we prepared the isotopomers $[Mn(\eta^2\text{-}HD)(CO)P_4]^+$ (**5a$_1$**, **5b$_1$**) by protonation of **3** with an equivalent amount of CF_3COOD in CD_2Cl_2 and found by ^{1}H NMR spectra a $^1J_{HD}$ value of 32.0 Hz for **5a$_1$** and of 32.5 Hz for **5b$_1$** (Figure 1). These results strongly suggest for **5** the presence of a true η^2-H_2 ligand with an estimated H−H distance of about 0.83 (**5a**) and 0.81 (**5b**) Å as can be calculated[15c,16] from the T_1(min) value.

The infrared spectra of both **5a** and **5b** show only one ν_{CO} band at 1926 cm^{-1}. In the temperature range between +20 and −90 °C the $^{31}P\{^1H\}$ NMR spectra of **5a** appear as only one singlet, suggesting the presence in solution of a *trans* geometry (**IV**) with the H_2 ligand *trans* to the CO moiety.

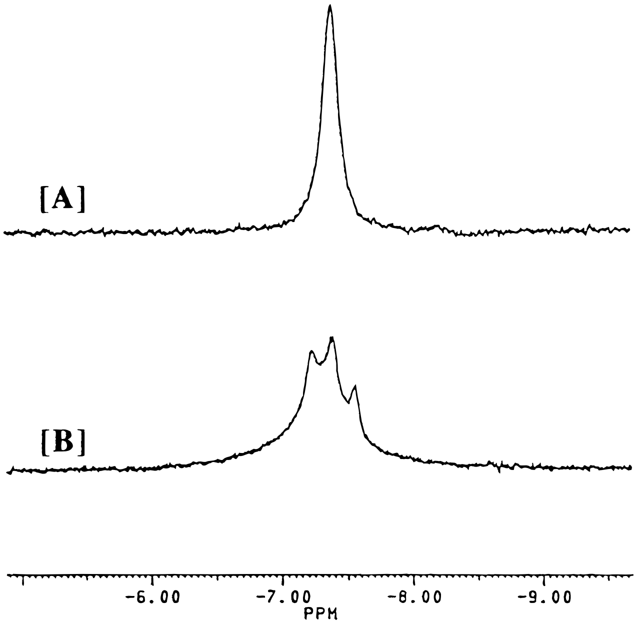
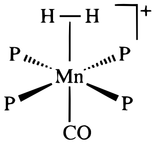


Figure 1. ^{1}H NMR spectra of the cations (**A**) $[Mn(\eta^2\text{-}H_2)(CO)\{PPh(OEt)_2\}_4]^+$ (**5b**) and (**B**) $[Mn(\eta^2\text{-}HD)(CO)\{PPh(OEt)_2\}_4]^+$ (**5b$_1$**) in CD_2Cl_2 at 234 K in the high-field region.



IV

The related $[Mn(\eta^2\text{-}H_2)(CO)\{PPh(OEt)_2\}_4]BPh_4$ (**5b**) derivative, instead, shows a broad multiplet at −90 °C in the ^{31}P spectra, indicating the magnetic inequivalence of the phosphorus *nuclei*. However, a *trans* geometry (**IV**) can also be proposed for this compound, as we have proposed for the parent hydride $MnH(CO)[PPh(OEt)_2]_4$ (**3b**) and observed in the related **3a**, attributing the magnetic inequivalence of the P *nuclei* to a different arrangement of the Ph and the OEt groups of each of the $PPh(OEt)_2$ ligands. A similar geometry, with the CO and the H_2 ligands in *trans* positions, has previously been observed in the related $[Mn(\eta^2\text{-}H_2)(CO)(dppe)_2]$-

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(15) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988,** *110*, 7031. (c) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

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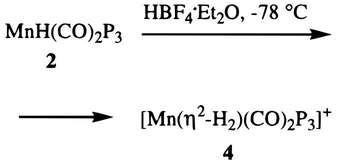
Scheme 3[a]



[a] P = P(OEt)$_3$ (**a**) PPh(OEt)$_2$ (**b**), PPh$_2$OEt (**c**).

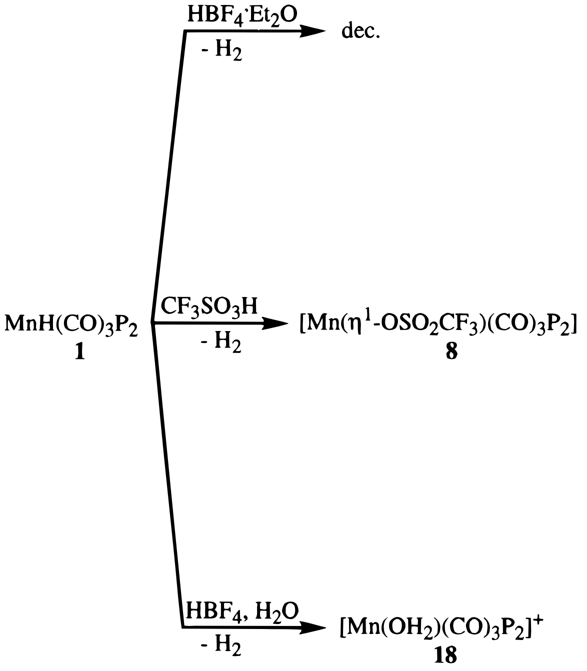
BAr′$_4$ complexes,[2b] while for the comparable [Re(η^2-H$_2$)(CO){P(Me)$_3$}$_4$]$^+$ cation[17] a *cis* geometry was proposed.

A comparison of the spectroscopic data of our η^2-H$_2$ complexes with the recently reported manganese analogues[2b] [Mn(η^2-H$_2$)(CO)(dppe)$_2$]BAr′$_4$ shows an identical value for the HD coupling constant of 32 Hz. However, a shorter H−H distance of 0.83 or 0.81 Å was estimated in our case from solution NMR T_1 data as compared to the 0.89(2) Å value determined by solid-state NMR measurements in [Mn(η^2-H$_2$)(CO)(dppe)$_2$]BAr′$_4$, and these results may be attributed to the greater π-acceptor properties of our P(OEt)$_3$ and PPh(OEt)$_2$ ligands as compared to that of dppe; the former ligands in complexes **5** lower the donation of electron density to the σ^* H$_2$ orbital. Accordingly, in the neutral MnH$_3$(R$_2$PCH$_2$CH$_2$PR$_2$)$_2$ compound a H−H distance of 0.90 Å (fast H$_2$ rotation) was calculated from T_1 values.

Protonation reactions with HBF$_4$·Et$_2$O at −78 °C of the dicarbonyls *fac,cis*-MnH(CO)$_2$P$_3$ (**2**) also afforded dihydrogen cations [Mn(η^2-H$_2$)(CO)$_2$P$_3$]$^+$ (**4**) (Scheme 3), which were fairly stable below 0 °C in solution but were not isolated as solids owing to the easy loss of hydrogen. However, the ^{1}H NMR spectra of solutions containing **4** exhibit a single broad resonance in the hydride region at δ −8.5 (**4a**), −7.9 (**4b**), and −7.0 (**4c**) ppm with T_1(min) values of 5 ms for **4a** and **4c** and 5.5 ms for **4b** (Table 2), in agreement with the proposed formulation, which is further confirmed by the $^1J_{HD}$ value of 33 Hz found in the isotopomer **4a$_1$**.

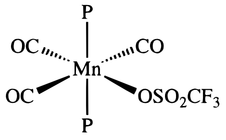
The protonation reaction with HBF$_4$·Et$_2$O at low temperature (−78 °C) of the tricarbonyl MnH(CO)$_3$P$_2$ (**1**) complexes (Scheme 4) proceeds with the evolution of H$_2$ (by ^{1}H NMR) and formation of a yellow solution from which no stable compound was isolated. The progress of the reaction was also studied by ^{1}H NMR spectra, but the presence of an η^2-H$_2$ complex was never observed. However, using triflic acid (CF$_3$SO$_3$H) instead of HBF$_4$·Et$_2$O, the protonation of **1** proceeds with evolution of H$_2$ and formation of the triflate complexes [Mn(η^1-OSO$_2$CF$_3$)(CO)$_3$P$_2$], which, in the case P = PPh(OEt)$_2$ (**8**), was isolated as a solid and characterized. Furthermore, the water complex [Mn(OH$_2$)(CO)$_3$P$_2$]BF$_4$ (**18**) (P = PPh(OEt)$_2$ (**b**), PPh$_2$OEt (**c**)) can also be obtained as a yellow solid by the protonation reaction of **1** with aqueous HBF$_4$ (Scheme 4).

Scheme 4[a]



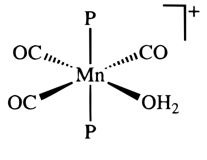
[a] P = P(OEt)$_3$ (**a**), PPh(OEt)$_2$ (**b**), PPh$_2$OEt (**c**).

The analytical and spectroscopic data of the triflate (**8**) and the water (**18**) complexes confirm their formulation. In particular, the IR spectra of the triflate complexes [Mn(η^1-OSO$_2$CF$_3$)(CO)$_3${PPh(OEt)$_2$}$_2$] (**8**) show three ν_{CO} bands, two of which are strong at 1975 and 1932 cm^{-1} and one is of medium intensity at 2066 cm^{-1}, suggesting a *mer* arrangement of the CO ligands. At 1323 cm^{-1} the diagnostic band[18] of the η^1-(O)-coordination of the triflate ion is also observed. Furthermore, in the temperature range from +30 to −90 °C the ^{31}P NMR spectrum appears as a sharp singlet near 182 ppm, in agreement with a *mer-cis* geometry of type **V** for the compound.



V

A *mer* arrangement of the CO groups in the water complexes [Mn(OH$_2$)(CO)$_3$P$_2$]BF$_4$ (**18**) is also suggested by the three characteristic ν_{CO} bands observed in the IR spectra. Furthermore, the presence of coordinated H$_2$O in **18** is confirmed by its ^{1}H NMR resonance observed as a triplet with J_{PH} = 2.1 Hz at 2.53 ppm (**18b**) and at 2.48 ppm (**18c**). Finally, a *mer-trans* geometry (**VI**) is confirmed by the ^{31}P spectra, which always show, between +30 and −90 °C, a sharp singlet.



VI

A comparison of the protonation reactions on the three hydrides MnH(CO)$_3$P$_2$ (**1**), MnH(CO)$_2$P$_3$ (**2**), and MnH(CO)P$_4$ (**3**) shows that only the dicarbonyls **2** and monocarbonyls **3** give stable dihydrogen complexes (**4, 5**). Furthermore, a comparison among these η^2-H$_2$ complexes **4** and **5** shows that, although the spectroscopic properties (T_1(min) and $^1J_{HD}$) are very similar, the stability to the loss of H$_2$ changes widely, according to the carbonyl−phosphine ratio in the complexes and to the nature of the phosphite ligands. Only the

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(17) Gusev, D. G.; Nietlispach, D.; Eremenko, I. L.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3628.

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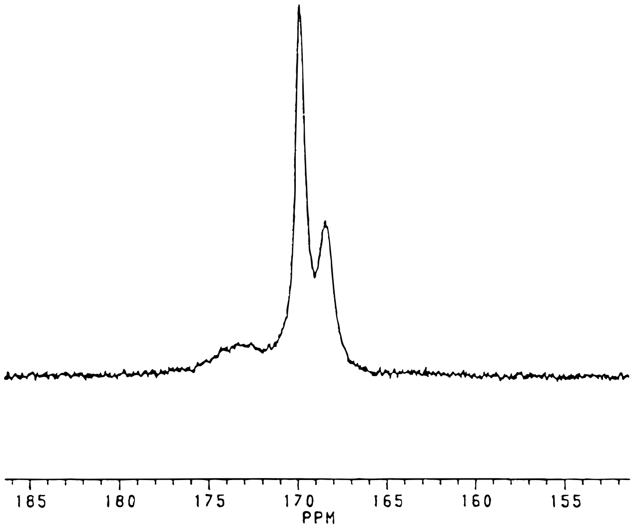


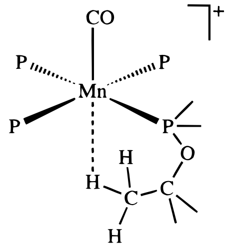
Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum (200 MHz) of the [Mn(CO){P(OEt)$_3$}$_4$]$^+$ (**7a**) cation in CD_2Cl_2 at 183 K.

monocarbonyl fragment [Mn(CO)P_4] can in fact bind the H_2 molecule to give *isolable* complexes, and between them, the PPh(OEt)$_2$ derivative (**5b**) is the most stable both in the solid state and in solution, thereby confirming the known properties of the phosphonite PPh(OEt)$_2$ in stabilizing dihydrogen complexes.[5a,b,d]

It is worth noting that all the η^2-H_2 derivatives **4** and **5** can be deprotonated with triethylamine to give the MnH(CO)P_4 (**3**) and MnH(CO)$_2P_3$ (**2**) hydride precursors.

Evolution of H_2 from **4** and **5** results in the disappearance of the η^2-H_2 resonance at δ −8.5 to −7.22 ppm in the ^1H NMR spectra and formation of the formally 16-electron complexes [Mn(CO)$_2P_3$]BPh_4 (**6**) and [Mn(CO)P_4]BPh_4 (**7**). The compounds are yellow solids moderately stable in air, diamagnetic, and 1:1 electrolytes. The diamagnetism and the reluctance of Mn(I) to give unsaturated compounds[19] seem to exclude a pentacoordinate complex for **6** and **7** and suggest the existence of an octahedral geometry in which an agostic interaction[20] between the electron-deficient manganese center and a C−H bond of the ethyl (or phenyl) group of one P(OEt)$_3$ or PPh(OEt)$_2$ ligand provides electronic stabilization of the complexes.

Support for the existence of an agostic bond in **6** and **7** comes from the $^{31}P\{^{1}H\}$ NMR spectra of [Mn(CO){P(OEt)$_3$}$_4$]BPh_4 (**7a**), which show the broad resonance that appears at room temperature (at 170 ppm) to resolve, at −90 °C, into two signals at δ 170.2 and 168.7 ppm and one hump as shown in Figure 2. Although even at this temperature the spectrum is too broad to give a fine structure, the inequivalence of the four phosphite ligands is clear and the profile of the spectra at −90 °C suggests that the low-exchange spectrum is approaching an AB_2C spin system. On this basis an agostic interaction of the type shown in **VII**, in which the agostic C−H interaction is interchanged from one of the P(OEt)$_3$ ligands to the other, may be reasonably proposed.



VII

In the related dicarbonyl cations [Mn(CO)$_2P_3$]$^+$ (**6**) this dynamic process, in which the agostic hydrogen exchanges with the other methyl (or phenyl) protons of the other phosphines, seems still very fast also at −90 °C, resulting in the ^{31}P spectra at −90 °C being unchanged with respect to those observed at room temperature.

An example of an agostic bond in manganese complexes has recently been demonstrated, by X-ray crystallography, in the strictly comparable [Mn(CO)(dppe)]-BAr′$_4$ complex,[2b] which contains two agostic interactions from H atoms of separate phenyl rings. Other examples of such an interaction have been reported in related Mo(CO)(dppe),[21] Cr(CO)$_3$(PCy$_3$)$_2$,[22] [Re(PR$_3$)$_2$(CO)$_3$]BAr′$_4$,[23] and [{MeC(CH$_2$PPh$_2$)$_3$}Re(CO)$_2$]BF$_4$[24] unsaturated complexes and these precedents give further support for the presence of an agostic interaction in our unsaturated complexes **6** and **7**.

Reactivity: New Manganese Complexes. The unsaturated complexes **6** and **7** and the triflate compounds [Mn(η^1-OSO$_2$CF$_3$)(CO)$_3P_2$] (**8**) react quickly with a variety of ligands to give a large series of new manganese complexes which can be isolated and characterized (Scheme 5).

The acetylide derivatives **9**−**11** are air-stable yellow or orange solids that are diamagnetic and nonelectrolytes. The presence of the acetylide ligand is confirmed by the IR spectra, which show the characteristic medium-intensity ν(C≡C) band at 2100−2079 cm^{-1}, and by the ^{13}C NMR spectra (Table 2), which exhibit the C_α of the acetylide as a well-resolved multiplet with an appreciable $^2J_{CP}$ value and C_β as a rather broad signal due to the low value of $^3J_{CP}$. The infrared and the NMR spectra also allow us to assign a geometry in solution for the complexes **9**−**11** as reported for the related hydrides **1**−**3**.

The infrared spectra of the tricarbonyls Mn(C≡CR)(CO)$_3P_2$ (**9**) show, in fact, two strong bands and one band of medium intensity for ν_{CO}, while the ^{31}P spectra, between +30 and −90 °C, appear as a sharp singlet, in agreement with a *mer,trans* geometry (**VIII**). The ^{13}C NMR spectra confirm such a structure, showing, for the carbonyl carbon atom, two triplets of intensity ratio 2:1 with a $^2J_{CP}$ value of about 25 Hz due to the coupling of the CO carbon atoms with the two equivalent phosphorus *nuclei* of the phosphite.

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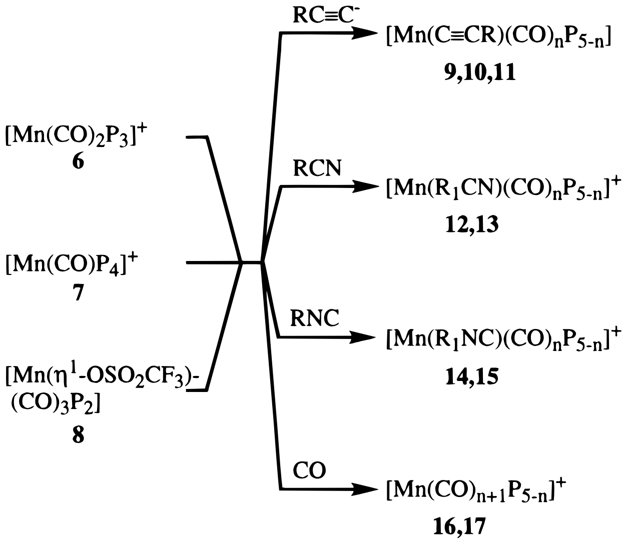
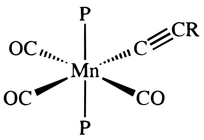
[24] Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R.; Vacca, A. *Organometallics* **1995**, *14*, 3203.

Scheme 5[a]

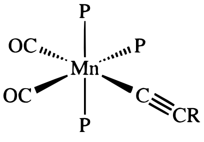


[a] $n = 3$ (**9**), 2 (**10, 12, 14, 16**), 1 (**11, 13, 15, 17**). P = $P(OEt)_3$ (**a**), $PPh(OEt)_2$ (**b**), PPh_2OEt (**c**), $PPh(O^iPr)_2$ (**d**), R = Ph (**a**–**d**), *p*-tolyl (**b$_1$, c$_1$**). R_1 = *p*-tolyl.

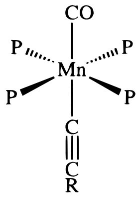


VIII

In the temperature range between +30 and −90 °C the ^{31}P spectrum of the dicarbonyl $Mn(C{\equiv}CPh)(CO)_2[PPh(OEt)_2]_3$ (**10b**) is an A_2B multiplet, while the IR spectra show two ν_{CO} bands at 1960 s and 1885 s cm^{-1} beside the $\nu_{C\equiv C}$ band at 2083 cm^{-1}, indicating the *cis* positions of the CO ligands. Furthermore, in the carbonyl carbon region the ^{13}C NMR spectra display two doublets of triplets at 220.8 and 222.9 ppm (Table 2), respectively. The presence of the two multiplets seems to indicate the magnetic inequivalence of the two CO groups, as in a *cis-mer* structure of the type **IX**. Finally, the $^{13}C\{^1H\}$ NMR spectra of the monocarbonyl compound $Mn(C{\equiv}CPh)(CO)\{P(OEt)_3\}_4$ (**11a**) show only one well-resolved quintet for the carbonyl carbon atoms at 221.1 ppm due to the coupling with four equivalent P nuclei. The magnetic equivalence of the four phosphite ligands is confirmed by the sharp singlet observed in the ^{31}P spectra, as expected for the *trans* geometry **X**.



IX

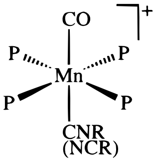


X

Relatively few manganese−alkynyl complexes have been reported[25] in comparison to other transition-metal centers, and the use of the unsaturated complexes **6** and **7** or of the triflate **8** allows the easy synthesis of new series of acetylide derivatives.

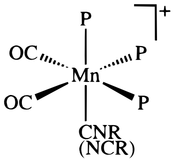
The alkynyl complexes **9**−**11** were treated with $HBF_4{\cdot}Et_2O$ or CF_3SO_3H in an attempt to prepare vinylidene $Mn{=}C{=}C(H)R$ or η^2-alkyne $Mn(\eta^2\text{-}HC{\equiv}CR)$ complexes through protonation reactions of the $C{\equiv}CR$ moiety.[26] Unfortunately, no stable complexes could be isolated, only intractable oils or mixtures of products whose ^1H and ^{13}C NMR spectra did not reveal the presence of any vinylidene or η^2-alkyne derivative. Studies on the progress of the reaction by IR and NMR spectra showed that, although the protonation reaction proceeds easily at room temperature, no evidence of a $={C}{=}C(H)R$ or a $\eta^2\text{-}HC{\equiv}CR$ complex was detected. However, the presence of free alkyne in the reaction mixture may suggest that the protonation reaction takes place at the $C{\equiv}CR$ group, probably affording a vinylidene[27] complex, which is unstable, preventing the isolation of stable derivatives.

New mononitrile (**12, 13**) and monoisocyanide (**14,-15**) complexes were also prepared from the unsaturated complexes which were isolated as air-stable pale yellow solids that are diamagnetic and 1:1 electrolytes. The infrared spectra show only one ν_{CN} band at 2261−2239 cm^{-1} for the nitrile and at 2141−2109 cm^{-1} for the isocyanide. Furthermore, in the carbonyl stretching region only one strong ν_{CO} band is present in the case of the monocarbonyl compounds $[MnL(CO)P_4]BPh_4$ (**13, 15**; L = *p*-tolylCN, *p*-tolylNC), whose ^{31}P spectra appear as a sharp singlet, suggesting the magnetic equivalence of the four phosphite ligands as in the *trans* geometry **XI**.



XI

The infrared spectra of the dicarbonyl cations $[MnL(CO)_2P_3]^+$ (**12, 14**; L = *p*-tolylCN, *p*-tolylNC) show two ν_{CO} bands, in agreement with a mutually *cis* arrangement of the two CO groups. The $^{31}P\{^1H\}$ NMR spectra are A_2B multiplets, while the ^{13}C spectrum of $[Mn(p\text{-}tolylNC)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**14b**) shows, in the carbonyl carbon region, only one broad multiplet at 218.1 ppm, which seems to indicate the magnetic equivalence of the two CO ligands. On this basis a *fac-cis* geometry of type **XII** can be reasonably proposed for the dicarbonyl compounds **12** and **14**.



XII

The carbonyl complexes $[Mn(CO)_3P_3]BPh_4$ (**16**) and $[Mn(CO)_2P_4]BPh_4$ (**17**) are air-stable pale yellow solids whose formulation is confirmed by the elemental analy-

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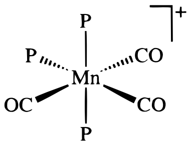
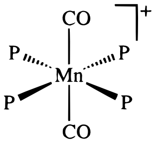
ses and IR and NMR spectra. In the ν_{CO} region the tricarbonyls **16** show three bands between 2062 and 1968 cm^{-1}, two of which are strong and the third of which has medium intensity, in agreement with a *mer* arrangement of the three CO ligands as in a type **XIII** geometry. The ^{1}H and ^{31}P NMR spectra indicate that the complexes are fluxional and also at −90 °C the spectra are still rather broad and result of difficult simulation. However, the presence of two broad signals of intensity ratio 2:1 seem to suggest that two phosphites are magnetically equivalent and are different from the third, in agreement with the *mer* geometry **XIII**.

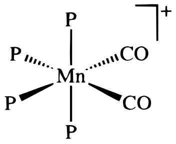


XIII

The IR spectra of the dicarbonyl derivatives [Mn(CO)$_2$P$_4$]BPh$_4$ (**17**) show two ν_{CO} bands at 1991−1922 cm^{-1} of different intensity, *i.e.* one medium and sharp and the other strong and rather broad. At room temperature the ^{31}P spectra show a broad signal, which resolves at −90 °C into a sharp singlet and an A$_2$B$_2$ multiplet. These results may be interpreted on the basis of the presence of both the *trans* (**XIV**) (singlet in the ^{31}P spectra) and the *cis* (**XV**) (A$_2$B$_2$ in the ^{31}P spectra) isomers, whose ν_{CO} bands are in part overlapping in the IR spectra.



XIV



XV

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