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$[(CO)_3(dppe)Mn(OH_2)]BF_4$ (1). A synthetically versatile compound and its use as a probe for determining the preferred site of coordination on ambident ligands

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Abstract

Previous work in this laboratory has shown that the Mn(I) octahedral complex, $[(CO)_3(dppe)Mn(OH_2)]BF_4$ (**1**), may be used for the synthesis of many related complexes by the ready replacement of the aqua ligand by neutral and anionic ligands, leading to new complexes having a variety of functional groups sigma (η^1) bonded to the Mn atom. This procedure has now been extended to ligands possessing phenolic and carboxylic acid groups, including amino acids. Compound **1** is used as a probe to compare the relative coordinating ability of different heteroatoms on ambident ligands. The ^1H NMR spectra of the resulting complexes show two signals at room temperature for the four protons (each 2H m) of the dppe-Mn metallacyle whose position depends on the specific atom of the ligand that is attached to the metal. The spectrum of **1**, however, shows only one signal (4H m). On cooling to −53 °C this signal is split in two (both 2H, m) owing to a slowing of the rapid reversible dissociation of the aqua ligand.

Keywords: Manganese complexes; Ambident ligands; Competitive coordination; Infrared and NMR spectra; Metallacycles

1. Introduction

Although the ionic octahedral Mn(I) aqua complex, $[(CO)_3(dppe)Mn(OH_2)]BF_4$ (**1**) is an air-stable crystalline [1,3] complex, which is thermally stable to about 150 °C [2], the aqua ligand of the complex is extremely labile in solution; it exchanges rapidly with D_2O [3], and is readily replaced by a large variety of other neutral or anionic ligands [4]. The preparation of **1** [2,3] involves the synthesis of the hydride, $(CO)_3(dppe)MnH$, followed by its reaction with HBF_4. Although weak acids such as carboxylic acids and phenols do not react with the hydride, they do react as anions in water or aqueous NaOH, to give neutral $K^1(O)$ complexes. When a ligand possessing two equivalent coordinating sites, such as dibasic acids, reacts with two moles of **1**, dinuclear Mn complexes are formed, and tricarboxylic acids give K^1, K^1, K^1 (O, O, O) complexes. Polymeric sodium poylacrylate (av. mol. wt. 2100) reacts to give a novel polymer in which a manganese atom is attached to each unit of the polymer. When a ligand possesses two non-equivalent coordination sites (ambident ligands) **1** is used to evaluate their relative ligating ability. Differential coordination at the bonding sites of ambident ligands has important implications for the design of chelating catalysts. Compound **1** may also be used for screening potential imaging agents related to its widely used congener ^{99m}Tc [5].

Table 1 shows the various compounds that we have used as ligands and identifies the atoms attached to the Mn atom in their complexes.

2. Experimental

All reactions were conducted under an argon atmosphere in a 50-mL round-bottom flask fitted with

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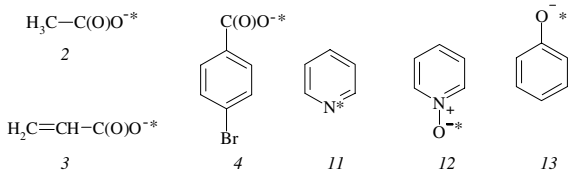
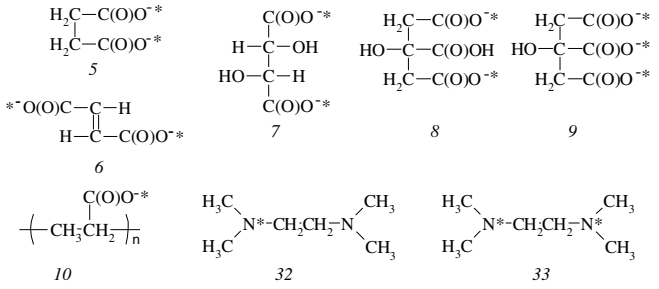
Table 1
Ligands substituted for H_2O in $(CO)_3(dppe)Mn(OH_2)$ (* indicates atom(s) attached to Mn)

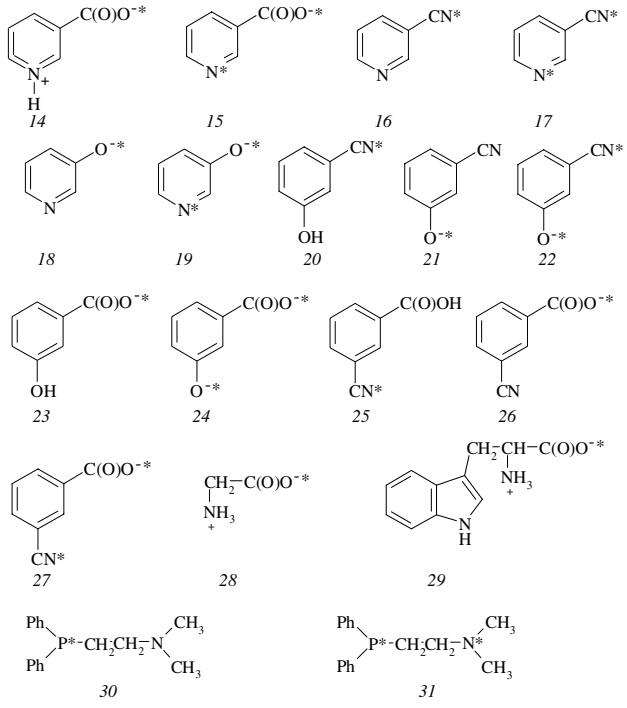
A. Monodentate ligands



B. Polydentate ligands



C. Ambident ligands



a magnetic stirrer and all involved the simple replacement of the aqua ligand of **1** by a new ligand. If the new ligand is neutral, it is used as a solution in $CHCl_3$, and if acidic, it is dissolved either in a few milliliters of water or in aqueous alkali. The general procedure was as follows: To a $CHCl_3$ solution of about 40–100 mg of **1** in about 20 mL $CHCl_3$, a solution of an equimolar quantity of the new ligand is added drop-wise. The order of addition is reversed when ambident ligands are used. After addition, stirring is continued for 10–20 min, the $CHCl_3$ solution is separated, washed with water, dried and evaporated. The resulting yellow to brown solids are thoroughly washed with hexane, dried in vacuo, collected and weighed. The yield of recovered product is 80–90%; the loss of material is incurred in handling the very small quantities involved. Only deviations form the general procedure are included in the experimental details. Our characterization of the new complexes, after ascertaining purity by TLC, relies very heavily on three techniques: high-resolution mass spectra (identification of the exact mass of the molecular ion and some significant daughter ions); close inspection of infrared spectra (carbonyl and nitrile stretching frequencies); and ^1H NMR spectra (particularly the chemical shifts of the dppe methylene protons). High-resolution mass spectra were obtained using a Kratos MS-25 high performance mass spectrometer fitted with an electrospray ionization (ESI) attachment. IR spectra were recorded on a P-E spectrum One FT-IR employing a 5-mm CaF_2 liquid cell. ^1H NMR data were obtained with $CDCl_3$ solutions using a Bruker AC-400 MHz spectrometer with the chemical shifts recorded relative to TMS $[Si(CH_3)_4]$. Ultimate analyses were not routinely determined, because, in addition to being less definitive for the characterization of pure compounds than exact mass spectra, such analyses are frequently unreliable and are further complicated by the tendency of many of these types of complexes to crystallize with non-integral molecules of solvent, which resist efforts to remove, and whose reported content must be adjusted in order to conform with results of ultimate analysis.

2.1. Reaction of *1* with monocarboxylic acids

2.1.1. Acetic acid complex, $[(CO)_3(dppe)MnOC(O)CH_3]$ (*2*)

Data ***2***: m.p.: softens at about 172 °C and decomposes above 178 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2026, 1959 and 1910; ^1H NMR (δ, $CDCl_3$): 7.8–7.3 (m, 20H, Ph), 2.92 (m, 2H) and 2.74 (m, 2H) both from dppe, 2.18 (s, 3H, CH_3); High-resolution MS (m/z): 597.084, calc. for $[(CO)_3(dppe)MnOC(O)CH_3 + H]^+$, $C_{31}H_{28}O_5P_2Mn$, 597.079; 537.060, calc. for $[(CO)_3(dppe)Mn]^+$, $C_{29}H_{24}O_3P_2Mn$, 537.058.

The reversibility of the reaction was demonstrated by the following experiment. One drop of HBF_4 was added to the acetic acid complex **2**, dissolved in $CHCl_3$ and then stirred for 1 min. The IR of the solution showed the spectrum characteristic of the aqua complex **1**.

2.1.2. Acrylic acid complex, $[(CO)_3(dppe)MnOC(O)CH{=}CH_2]$ (*3*)

Data ***3***: m.p.: the color of the solid product changes from pale yellow at room temperature to white at 276–280 °C and decomposes at 372–378 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2026, 1960 and 1911; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 20H, Ph), 5.65 (t, 1H, CH), 4.97 (d, 2H, CH_2 attached to double bond), 2.91 (m, 2H), and 2.82 (m, 2H) both from

dppe; High-resolution MS (*m*/*z*): 609.0764, calc. for $[(CO)_3(dppe)MnOC(O)CH{=}CH_2 + H]^+$, $C_{32}H_{28}O_5P_2Mn$, 609.0792, 537.0335, calc. for $[(CO)_3(dppe)Mn]^+$, $C_{29}H_{24}O_3P_2Mn$, 537.058.

2.1.3. p-Bromobenzoic acid complex, [(CO)$_3$(dppe)MnOC(O)C$_6$H$_4$Br] (4)

The reaction was carried out using an aqueous solution of *p*-bromobenzoic acid.

Data **4**: m.p.: softens at about 192 °C and decomposes at above 225 °C; IR (cm^{-1}, $CHCl_3$): *v*(CO) 2027, 1959 and 1913; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 24H, Ph), 2.99 (m, 2H) and 2.89 (m, 2H) both from dppe; High-resolution MS (*m*/*z*): 772.9814, calc. for $[(CO)_3(dppe)Mn{-}OC(O)C_6H_4Br\text{-}p + Cl]^-$, $C_{36}H_{28}O_5P_2BrClMn$, 772.9646 (Cl^- originated from the chloroform solvent used in the electrospray).

2.2. Reaction of 1 with dicarboxylic acids

Unless otherwise noted, aqueous solutions of the sodium salts of the acids were used.

2.2.1. Succinic acid complex, [(CO)$_3$(dppe)MnOC(O)CH$_2$CH$_2$C(O)OMn(dppe)(CO)$_3$] (5)

Data **5**: m.p.: softens at about 268 °C and decomposes above 298 °C; IR (cm^{-1}, $CHCl_3$): *v*(CO) 2025, 1958 and 1907; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 40H, Ph), 2.86 (m, 4H, from dppe), 2.68 (m, 4H, from dppe), 2.52 (m, 2H, from succinic acid), 2.27 (m, 2H, from succinic acid); High-resolution MS (*m*/*z*): 1191.1299, calc. for $[(CO)_3(dppe)Mn{-}OC(O)CH_2CH_2C(O)O{-}Mn(dppe)(CO)_3 + H]^+$, $C_{62}H_{53}O_{10}P_4Mn_2$, 1191.135.

2.2.2. Fumaric acid complex, [(CO)$_3$(dppe)MnOC(O)CH=CHC(O)OMn(dppe)(CO)$_3$] (6)

Data **6**: m.p.: softens at about 145 °C and decomposes above 160 °C; IR (cm^{-1}, $CHCl_3$) *v*(CO) 2027, 1959 and 1914; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 40H, Ph), 6.5 (s, 2H, from two CHs of fumaric acid moiety), 3.05 (m, 4H, from dppe), 2.84 (m, 4H, from dppe); High-resolution MS (*m*/*z*): 1189.200, calc. for $[(CO)_3(dppe)MnOC(O)CH{=}CHC(O)OMn(dppe)(CO)_3 + H]^+$, $C_{62}H_{51}O_{10}P_2Mn_2$, 1189.1188.

2.2.3. D-Tartaric acid complex, [(CO)$_3$(dppe)MnOC(O)(CHOH)$_2$C(O)OMn(dppe)(CO)$_3$] (7)

Data **7**: m.p.: softens at about 131 °C and decomposes above 154 °C; IR (cm^{-1}, $CHCl_3$) *v*(CO) 2029, 1962 and 1916; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 40H, Ph), 2.95 (m, 4H, from dppe), 2.84 (m, 4H, from dppe); High-resolution MS (*m*/*z*): 1223.1241, calc. for $[(CO)_3(dppe)Mn{-}OC(O)(CHOH)_2C(O)O{-}Mn(dppe)(CO)_3 + H]^+$, $C_{62}H_{53}O_{12}P_2Mn_2$, 1223.1248.

2.3. Reaction of 1 with polycarboxylic acids

2.3.1. Preparation of citric acid complex, K^1(O),K^1(O)[(CO)$_3$(dppe)MnOC(O)CH$_2$–C(OH)(COOH)CH$_2$C(O)OMn(dppe)(CO)$_3$] (8)

8.2 mg (0.039 mM) of citric acid (99%, Aldrich) was suspended in a solution of **1** (75 mg, 0.117 mM) in 25 mL $CHCl_3$. After stirring for approximately 45 min, the solvent was removed by rotary evaporator. The residue was chromatographed on a column of neutral alumina gel with hexane and ethyl acetate as gradient eluents to give **8** as a yellow solid.

Data **8**: m.p.: softens at 205 °C and decomposes above 220 °C; IR (cm^{-1}, $CHCl_3$) *v*(CO) 2027, 1959 and 1916; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 40H, Ph), 2.92 (m, 4H, from dppe), 2.72 (m, 4H, from dppe), 2.51 (s, 4H, CH_2); High-resolution MS (*m*/*z*): 1265.1896, calc. for $[(CO)_3(dppe)MnOC(O)CH_2C(OH)(COOH)CH_2C(O)OMn(dppe)(CO)_3 + H]^+$, $C_{64}H_{55}O_{13}P_4Mn_2$, 1265.19. *Anal.* Calc. for $C_{64}H_{54}O_{13}P_4Mn_2 \cdot 2H_2O \cdot C_6H_{14}$: C, 60.61; H, 5.23. Found: C, 59.34; H, 5.28% (NMR showed both water and hexane; the stoichiometry of the associated solvents is adjusted to conform with the hydrogen analysis). It is assumed that the manganese coordinates at the terminal carboxylic groups.

2.3.2. Preparation of citric acid complex, K^1(O),K^1(O),K^1(O)[(CO)$_3$(dppe)Mn–OC(O)CH$_2$C(OH)C(O)OMn(CO)$_3$(dppe)CH$_2$C(O)OMn(dppe)(CO)$_3$] (9)

A solution of **1** (75 mg, 0.117 mM) in 25 mL of $CHCl_3$ was added drop-wise to 3.9 mL of an aqueous solution containing 8.2 mg of citric acid (0.039 mM) and 4.68 mg of NaOH (0.117 mM). After stirring the mixture for approximately 75 min, the product was isolated in the usual manner.

Data **9**: m.p.: softens at 176 °C and decomposes above 200 °C; IR (cm^{-1}, $CHCl_3$) *v*(CO) 2026, 1955 and 1909; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 40H, Ph), 2.96 (m, 6H, from dppe), 2.71 (m, 6H, from dppe), 2.51 (s, 4H, CH_2); High-resolution MS (*m*/*z*): 1802.2294 calc. for $[(CO)_3(dppe)MnOC(O)CH_2C(OH)C(O)OMn(CO)_3(dppe)CH_2C(O)OMn(dppe)(CO)_3 + H]^+$, $C_{93}H_{78}O_{16}P_6Mn_3$, 1802.19.

2.3.3. Na-polyacrlyate polymer complex, –[–CH$_2$–CH–[C(O)OMn(CO)$_3$(dppe)]]$_n$– (10)

A solution of the aqua complex, **1** (67.2 mg, 0.105 mM) in 25 mL of MeOH was placed in a round-bottom flask. A solution of sodium polyacrylate (10 mg, 0.005 mM) in 10 mL water was added drop-wise to the solution of **1** and the resulting solution was stirred for 2 h. During this time, the original clear solution became turbid. Stirring was continued overnight. The reaction mixture was evaporated to dryness with a rotary evaporator. The resulting solid was washed with 20 mL of $CHCl_3$ and 10 mL of CH_3OH leaving an orange solid, which was dried in vacuum. Yield 67%.

*Data **10***: m.p.: decomposes without melting at about 350 °C; IR (cm^{-1}, KBr): ν(CO) 2025, 1953 and 1910; *Anal*. Calc. for one unit of polymer, $C_{31}H_{27}O_5P_2Mn$: C, 62.42; H, 4.56; P, 10.38. Found: C, 60.25; H, 5.12; P, 9.86%. The calculated atomic C/P for one unit of polymer is 15.8; Found: 16.0, indicating that approximately each unit of the polyacrylate polymer is bonded to an Mn atom.

2.4. Reaction of **1** with pyridine and pyridine-N-oxide

2.4.1. Pyridine complex, $K^1(N)[(CO)_3(dppe)MnNC_5H_5]^+BF_4^-$ (**11**)

*Data **11***: m.p.: softens at about 103 °C and decomposes above 116 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2030, 1957 and 1944; ^{1}H NMR (δ, $CDCl_3$): 7.90–6.65 (m, 20H, from Ph, 5H, from pyridine), 3.65 (m, 2H) and 3.25 (m, 2H) both from dppe; Low temperature (−53 °C) ^{1}H NMR gave the same two signals with the same intensity. High-resolution MS (*m*/*z*): 616.0856, calc. for $[(CO)_3(dppe)MnNC_5H_5]^+$, $C_{34}H_{29}NO_3P_2Mn$, 616.0921.

2.4.2. Pyridine-N-oxide complex, $K^1(O)[(CO)_3(dppe)MnONC_5H_4]^+BF_4^-$ (**12**)

*Data **12***: m.p.: softens at about 82 °C and decomposes above 90 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2025, 1950 and 1925; ^{1}H NMR (δ, $CDCl_3$): 7.8–6.8 (m, 20H, from dppe Ph, 5H, from pyridine-*N*-oxide), 3.41 (m, 2H), 2.88 (m, 2H) both from dppe CH_2; High-resolution MS (*m*/*z*): 632.0970, calc. for $[(CO)_3(dppe)MnONC_5H_5]^+$, $C_{34}H_{29}NO_4P_2Mn$, 632.0952, 537.0581, calc. for $[Mn(dppe)(CO)_3]$, $C_{29}H_{24}O_3P_2Mn$, 537.0581.

2.4.3. Reaction of **1** with 1:1 mixture of pyridine and pyridine-N-oxide

Data: ^{1}H NMR (δ, $CDCl_3$): 7.8–6.8 (m, 40H, from dppe Ph, 5H, from pyridine and 5H, from py-*N*-oxide), 3.62 (m, 2H, from pyridine complex), 3.41 (m, 2H, from pyridine-*N*-oxide complex), 3.25 (m, 2H, from pyridine complex), 2.89 (m, 2H, from pyridine-*N*-oxide complex) These data (Table 2) for the dppe CH_2 indicate that both ligand complexes were present; from the relative intensities it was estimated that they were present in approximately equal quantities.

2.5. Reaction of **1** with phenolate anion

2.5.1. Preparation of phenol complex, $[(CO)_3(dppe)MnOC_6H_5]$ (**13**)

The reaction was carried out either by using pure phenol, or more rapidly, by adding complex **1** in $CHCl_3$ to an aqueous NaOH solution of phenol.

*Data **13***: m.p.: softens at about 128 °C and decomposes above 142 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2017, 1942 and 1906; ^{1}H NMR (δ, $CDCl_3$): 7.8–7.1 (m, 25H, Ph), 2.97 (m, 2H) and 2.83 (m, 2H) both from dppe; High-resolution MS (*m*/*z*): 630.19, calc. for $[(CO)_3(dppe)Mn–OC_6H_5 + H]^+$, $C_{35}H_{30}O_4P_2Mn$, 630.20; 537.028, calc. for $[Mn(CO)_3\text{-}(dppe)]^+$, $C_{29}H_{24}O_3P_2Mn$, 537.058.

2.6. Reaction of **1** with ambident ligands

2.6.1. Derivatives of pyridine

2.6.1.1. $K^1(O)$ complex with pyridine-3-carboxylic acid, (nicotinic acid), $[(CO)_3(dppe)MnOC(O)C_5H_4N]$ (**14**).

*Data **14***: m.p.: softens at about 108 °C and decomposes above 135 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2027, 1960 and 1914; ^{1}H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 24H, Ph), 3.02 (m, 2H) and 2.87 (m, 2H) both from dppe; High-resolution MS (*m*/*z*): 660.105, calc. for $[(CO)_3(dppe)MnNC_5H_4\text{-}C(O)OH]^+$, $C_{35}H_{29}NO_5P_2Mn$, 660.112.

2.6.1.2. $K^1(N),K^1(O)$ dinuclear Mn complex with pyridine-3-carboxylic acid, (nicotinic acid), $[(CO)_3(dppe)MnN\text{-}C_5H_4C(O)OMn(dppe)(CO)_3]^+BF_4^-$ (**15**).

Pure **15** was obtained by column chromatography on neutral alumina using hexane and ethyl acetate as gradient eluents.

*Data **15***: m.p.: softens at 110 °C and decomposes above 150 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2027 (broad), 1960 (broad) and 1939 (shoulder) and 1913; ^{1}H NMR (δ, $CDCl_3$): 8.73 (m), 8.35 (m, H) and 7.98 (m, H) all from nicotinic acid moiety, 7.9–7.2 (m, 40H, from Ph) 6.97 (m, H, from nicotinic acid), 3.63 (m, 2H, from dppe bonded to the Mn attached to N), 3.20 (m, 2H, from dppe bonded to the Mn attached to N), 3.01 (m, 2H, from dppe bonded to the Mn attached to the acid group), 2.85 (m, 2H, from dppe bonded to the Mn attached to the acid group); High-resolution MS (*m*/*z*): 1196.1440, calc. for $[(CO)_3\text{-}(dppe)Mn–NC_5H_4C(O)O–Mn(dppe)(CO)_3]$ $C_{64}H_{52}NO_8\text{-}P_4Mn_2$, 1196.1404; 537.0581, calc. for $[Mn(dppe)(CO)_3]$, $C_{29}H_{24}O_3P_2Mn$, 537.0581. This complex was also prepared by adding 2 molar equivalents of aqua complex to 1 mol of nicotinic acid.

2.6.1.3. $K^1(NC)$ complex with 4-cyanopyridine, $[(CO)_3\text{-}(dppe)MnNCC_5H_4N]^+BF_4^-$ (**16**).

The product was chromatographed on a column of neutral alumina with hexane and ethyl acetate as gradient eluents to give pure **16**.

*Data **16***: m.p.: softens at about 85 °C and decomposes above 108 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2039, 1971 and 1961: ^{1}H NMR (δ, $CDCl_3$): 7.8–6.8 (m, 20H, from dppe Ph, 4H, from 4-cyanopyridine), 3.48 (m, 2H), 3.05 (m, 2H) both from dppe CH_2; High-resolution MS (*m*/*z*): 641.0930, calc. for $[(CO)_3(dppe)MnNCC_5H_4N]^+$, $C_{35}H_{28}\text{-}N_2O_3P_2Mn$, 641.0956, 537.0316, calc. for $[Mn(dppe)(CO)_3]$, $C_{29}H_{24}O_3P_2Mn$, 537.0581.

2.6.1.4. Preparation of $K^1(NC),K^1(N)$ dinuclear Mn complex with 4-cyanopyridine, $[(CO)_3(dppe)MnNCC_5H_4\text{-}N–Mn(dppe)(CO)_3]^{2+}2BF_4^-$ (**17**).

The crude product was chromatographed on neutral alumina with hexane and ethyl acetate as gradient eluents to give pure **17**.

*Data **17***: m.p.: softens at about 105 °C and decomposes above 128 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2039, 2027

Table 2
Chemical shift of dppe CH_2 protons (ppm) and IR spectra (cm^{-1}, in $CHCl_3$) of $(CO)_3$(dppe)MnZ

Complex No.	Attached to Mn		DPPE methylene protons (δ) ppm			Stretching frequencies			
						CO			CN
	Z	Atom of	CH_2[a]	CH_2[b]	Diff.	A′	A″	A′	
1	H_2O (−53 °C)	O	3.04	2.65	0.39				
1	H_2O (25 °C)	O	2.97	2.97	0.00	2035	1965	1934	
2	Acetic acid	O	2.92	2.74	0.18	2026	1959	1910	
3	Acrylic acid	O	2.91	2.82	0.09	2026	1960	1911	
4	*p*-Bromobenzoic acid	O	2.99	2.89	0.10	2027	1959	1913	
5	Succinic acid[c]	O, O	2.86[d]	2.68[d]	0.18	2025	1958	1907	
6	Fumaric acid[c]	O, O	3.05[d]	2.84[d]	0.21	2027	1959	1914	
7	D-Tartaric Acid[c]	O, O	2.95[d]	2.84[d]	0.11	2029	1962	1916	
8	Citric acid[c]	O, O	2.92[d]	2.72[d]	0.20	2027	1959	1916	
9	Citric acid[c]	O, O, O	2.96[e]	2.71[e]	0.15	2026	1955	1909	
10	Na-Polyacrylate[c,f]					2025	1953	1910	
11	Pyridine (25 °C)	N	3.65	3.25	0.40	2030	1957	1944	
11	Pyridine (−50 °C)	N	3.53	3.20	0.33				
12[g]	Pyridine-*N*-oxide	O	3.41	2.88	0.53	2025	1950	1925	
13	Phenol	O	2.97	2.83	0.14	2017	1942	1906	
14	Nicotinic acid	O	3.02	2.87	0.15	2027	1960	1914	
15	Nicotinic acid	N	3.63	3.20	0.43	2027	1960	1939	
15	Nicotinic acid	O	3.01	2.85	0.16	2027	1960	1913	
16	4-Cyanopyridine	CN	3.48	3.05	0.43	2039	1971	1961	2259
17	4-Cyanopyridine (2)	N	3.50	3.11	0.39	2027	1961	1939	2240
		CN	3.50	3.11	0.39	2039	1971	1961	2259
18	3-Hydroxypyridine	O	3.07	2.92	0.15	2025	1948	1922	
19	3-Hydroxypyridine (2)	O	3.05	2.89	0.16	2028	1955	1918	
		N	3.59	3.23	0.36	2028	1955	1940	
20	3-Cyanophenol	N	3.39	3.04	0.35	2038	1971	1959	2257
21	3-Cyanophenol	O	2.99	2.83	0.16	2019	1945	1911	2223
22	3-Cyanophenol (2)	N	3.36	3.04	0.32	2038	1971	1958	2257
		O	3.01	2.85	0.16	2021	1947	1912	
23	3-Hydroxybenzoic acid	C(O)O	3.00	2.85	0.15	2027	1960	1911	
24	3-Hydroxybenzoic acid[c]	C(O)O, O	3.03[d]	2.85[d]	0.18	2027	1959	1916	
25	3-Cyanobenzoic acid	N	3.27	2.86	0.41	2038	1969	1960	2259
26	3-Cyanobenzoic acid	O	3.00	2.83	0.17	2028	1961	1914	2231
27	3-Cyanobenzoic acid (2)	N	3.26	2.86	0.40	2038	1969	1960	2259
		O	3.00	2.74	0.16	2027	1960	1916	
28	Glycine	O	3.03	2.87	0.16	2026	1953	1908	
29	Tryptophan	O	3.15	2.95	0.20	2026	1955	1910	
30	$Ph_2PCH_2CH_2N(CH_3)_2$	P	3.34	3.09	0.25	2027	1958	1917	
31	$Ph_2PCH_2CH_2N(CH_3)_2$ (2)	P	3.34	3.09	0.25	1931	1957	1916	
		N	2.97	2.80	0.17	1931	1957	1934	
32	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	N	3.05	2.87	0.18	2025	1952	1908	
33	$(CH_3)_2NCH_2CH_2N(CH_3)_2$[c]	N, N	3.05	2.87	0.18	2025	1951	1906	
34[h]	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	N	2.7	2.58	0.12	2015	1919	1895	
35	Hydride (at 25 and 100 °C)	H	2.51	2.23	0.28	1995	1915	1910	
36	Nitrato (at 25 and 100 °C)	O	2.97	2.80	0.17	2034	1968	1925	

[a] Assumed to be "*trans*" to apical CO.
[b] Assumed to be "*cis*" to apical CO.
[c] CO stretching frequencies essentially the same for each set of carbonyls.
[d] Integrates for four protons for each signal.
[e] Integrates for six protons for each signal.
[f] IR spectra of Na-polyacrylate complex was taken by using Kbr pellet.
[g] This complex is excluded from the generalizations discussed below.
[h] K^2(N) complex.

(shoulder) 1971, 1961 (broad) and 1939 shoulder; ^{1}H NMR (δ, $CDCl_3$): 7.8–6.8 (m, 40H, from dppe Ph, 4H, from 4-cyanopyridine), 3.50 (broad, m, 4H), 3.11 (broad, m, 4H) both from dppe CH_2; High-resolution MS (*m*/*z*): 1178.1601, calc. for $[(CO)_3(dppe)MnNCC_5H_4N–Mn(dppe)(CO)_3]^{2+}$, $C_{64}H_{62}N_2O_6P_4Mn_2$, 1178.1537. This complex was also prepared by adding one mole of **1** to a solution of **17**.

*2.6.1.5. Preparation of $K^1(O)$ complex with 3-hydroxypyridine, $[(CO)_3(dppe)Mn–OC_5H_4N]$ (**18**).* A solution of **1** was added drop-wise to a solution containing an equimolar

quantity of 3-hydroxypyridine dissolved in aqueous NaOH.

*Data **18***: m.p.: softens at about 75 °C and decomposes above 88 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2025, 1948 and 1922: ^1H NMR (δ, $CDCl_3$): 7.8–6.8 (m, 20H, from dppe Ph, 4H, from 3-hydroxypyridine), 3.07 (m, 2H), 2.92 (m, 2H) both from dppe CH_2; High-resolution MS (*m*/*z*): 632.1005, calc. for $[(CO)_3(dppe)MnOC_5H_4N + H]^+$, $C_{34}H_{29}NO_4P_2Mn$, 632.0952, 537.0556, calc. for $[Mn(dppe)(CO)_3]$, $C_{29}H_{24}O_3P_2Mn$, 537.0581.

*2.6.1.6. $K^1(O),K^1(N)$ dinuclear Mn complex with 3-hydroxypyridine, $[(CO)_3(dppe)MnOC_5H_4NMn(dppe)(CO)_3]^+BF_4^-$ (**19**).* The reaction was carried out in $CHCl_3$ using an equimolar solution of **1** and **18**.

*Data **19***: m.p.: softens at about 89 °C and decomposes above 112 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2028 (broad), 1955 (broad), 1940 (shoulder) and 1918; ^1H NMR (δ, $CDCl_3$): 7.8–6.8 (m, 40H, from dppe Ph, 4H, from 3-hydroxypyridine), 3.59 (m, 2H, from dppe bonded to the Mn attached to N), 3.23 (m, 2H, from dppe bonded to the Mn attached to N), 3.05 (m, 2H, from dppe bonded to the Mn attached to O), 2.89 (m, 2H, from dppe bonded to the Mn attached to O); High-resolution MS (*m*/*z*): 1168.1505, calc. for $[(CO)_3(dppe)MnOC_5H_4N–Mn(dppe)(CO)_3]^+$, $C_{63}H_{62}NO_7P_4Mn_2$, 1168.1454, 537.0567, calc. for $[Mn(dppe)(CO)_3]$, $C_{29}H_{24}O_3P_2Mn$, 537.0581. This complex was also prepared by using 2 molar equivalents of **1** to one of 3-hydroxypyridine.

2.6.2. Derivatives of phenol

*2.6.2.1. Preparation of $K^1(N)$ complex with 3-cyanophenol, $[(CO)_3(dppe)Mn–NCC_6H_4OH]^+BF_4^-$ (**20**).* The reaction was carried out in $CHCl_3$ using equimolar amounts of **1** and ligand.

*Data **20***: m.p.: softens at about 155 °C and decomposes above 163 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2038, 1971 and 1959: ^1H NMR (δ, $CDCl_3$): 7.8–6.2 (m, 20H, from dppe Ph, 5H, from 3-cyanophenol), 3.39 (m, 2H), 3.04 (m, 2H) both from dppe CH_2; High-resolution MS (*m*/*z*): 656.0961, calc. for $[(CO)_3(dppe)MnNCC_6H_4OH]^+$, $C_{36}H_{29}NO_4P_2Mn$, 656.0952, 537.0461, calc. for $[Mn(dppe)(CO)_3]$, $C_{29}H_{24}O_3P_2Mn$, 537.0581.

*2.6.2.2. Preparation of $K^1(O)$ complex with 3-cyanophenol, $[(CO)_3(dppe)MnOC_6H_4CN]$ (**21**).* The reaction was carried out using a $CHCl_3$ solution of **1** and a molar equivalent of 3-cyanophenol in aqueous NaOH.

*Data **21***: m.p.: softens at about 167 °C and decomposes above 181 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2019, 1945 and 1911; ^1H NMR (δ, $CDCl_3$): 7.8–6.2 (m, 20H, from dppe Ph, 5H, from 3-cyanophenol), 2.99 (m, 2H), 2.83 (m, 2H) both from dppe CH_2; High-resolution MS (*m*/*z*): 656.0991, calc. for $[(CO)_3(dppe)MnOC_6H_4CN + H]$, $C_{36}H_{29}$-NO_4P_2Mn, 656.0952, 537.0603, calc. for $[Mn(dppe)(CO)_3]$, $C_{29}H_{24}O_3P_2Mn$, 537.0581. In the absence of alkali but in the presence of water, **20**, and an almost equal quantity of **21** were formed.

*2.6.2.3. Preparation of $K^1(N),K^1(O)$ dinuclear Mn complex with 3-cyanophenol, $[(CO)_3(dppe)MnNCC_6H_4OMn(dpp)(CO)_3]^+BF_4^-$ (**22**).* A $CHCl_3$ solution of two molar equivalents of **1** is added to an aqueous NaOH solution of one molar equivalent of 3-cyanophenol. Compound **22** was also prepared by adding molar equivalents of **1** to either **20** or **21**.

*Data **22***: m.p.: softens at about 162 °C and decomposes above 178 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2038, 2021, 1971, broad 1957 (1959 due to CN, and 1956 due to OH merged) and 1912; ^1H NMR (δ, $CDCl_3$): 7.8–6.2 (m, 40H, from dppe Ph, 4H, from 3-cyanophenol), 3.36 (m, 2H), 3.04 (m, 2 H) both from dppe CH_2 Mn attached to N; 3.01 (m, 2H), 2.85 (m, 2H) both from dppe CH_2 of Mn attached to O; High-resolution MS (*m*/*z*): 1192.1501, calc. for $[(CO)_3(dppe)MnNC$-$C_6H_4OMn(dppe)(CO)_3]^+$, $C_{65}H_{52}O_5P_2Mn_2$, 1192.1454, 656.0961, calc. for $[(CO)_3(dppe)MnNCC_6H_4OH]^+$, $C_{36}H_{29}NO_4P_2Mn$, 656.0952; 537.0461, calc. for $[Mn(dppe)$-$(CO)_3]$, $C_{29}H_{24}O_3P_2Mn$, 537.0581.

2.6.3. Derivatives of benzoic acid

*2.6.3.1. Preparation of $K^1(OCO)$ complex with 3-hydroxybenzoic acid, $[(CO)_3(dppe)Mn–OC(O)C_6H_4OH]$ (**23**).* The reaction was carried out by adding a $CHCl_3$ solution of **1** to an equimolar quantity of 3-hydroxybenzoic acid in aqueous $NaHCO_3$.

*Data **23***: m.p.: softens at about 114 °C and decomposes at above 124 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2027, 1960 and 1911; ^1H NMR (δ, $CDCl_3$): 7.9–6.8 (m, 20H, from dppe Ph, 4H, from 3-hydroxybenzoic acid), 3.00 (m, 2H) and 2.85 (m, 2H) both from dppe CH_2; High-resolution MS (*m*/*z*): 673.0842, calc. for $[(CO)_3(dppe)Mn–OC_6H_4$-$COOH + H]$, $C_{37}H_{30}O_6P_2Mn$, 674.0820.

*2.6.3.2. Preparation of $K^1(OCO),K^1(O)$ complex of 3-hydroxybenzoic acid, $[(CO)_3(dppe)Mn–OC(O)C_6H_4$-$O–Mn(dppe)(CO)_3]$ (**24**).* A $CHCl_3$ solution of two molar equivalents of **1** is added to one molar equivalent of an aqueous NaOH solution of 3-hydroxybenzoic acid.

*Data **24***: m.p.: softens at about 118 °C and decomposes above 133 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2027, 1959 and 1916; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 40H, from dppe Ph, 4H, from 3-hydroxybenzoic acid), 3.03 (broad, m, 4H) and 2.85 (broad, m, 4H) both from dppe CH_2; High-resolution MS (*m*/*z*): 1211.1406, calc. for $[(CO)_3(dppe)$-$Mn–OC(O)C_6H_4O–Mn(dppe)(CO)_3 + H]^+$, $C_{65}H_{53}O_9P_4Mn_2$, 1211.1401.

*2.6.3.3. Preparation of $K^1(N)$ complex with 3-cyanobenzoic acid, $[(CO)_3(dppe)Mn–NCC_6H_4COOH]^+BF_4^-$ (**25**).* The reaction is carried out in carefully dried MeOH. The yellow solid consisted of two complexes, which were separated by chromatography on a neutral alumina column. Based on spectroscopic data, the composition of the

mixture was estimated to consist of about 85% of **25** and 15% of **26**.

*Data **25***: m.p.: softens at about 106 °C and decomposes at above 112 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2038, 1969 and 1960; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 20H, from dppe Ph, 4H, from 3-cyanobenzoic acid), 3.27 (m, 2H) and 2.86 (m, 2H) both from dppe; High-resolution MS (*m*/*z*): 684.0953, calc. for $[(CO)_3(dppe)Mn–NCC_6H_4COOH]^+$, $C_{37}H_{29}O_5P_2NMn$: 684.0901.

*2.6.3.4. Preparation of $K^1(O)$ complex with 3-cyanobenzoic acid, $[(CO)_3(dppe)Mn–O(O)CC_6H_4CN]$ (**26**).* A $CHCl_3$ solution of **1** is added to an equimolar quantity of 3-cyanobenzoic acid in aqueous NaOH.

*Data **26***: m.p.: softens at about 112 °C and decomposes at above 120 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2028, 1961 and 1914; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 20H, from dppe, 4H, from 3-cyanobenzoic acid), 3.00 (m, 2H) and 2.83 (m, 2H) both from dppe; High-resolution MS (*m*/*z*): 684.0961, calc. for $[(CO)_3(dppe)Mn–O(O)CC_6H_4CN + H]^+$, $C_{37}H_{29}O_5P_2NMn$, 684.0901.

*2.6.3.5. Preparation of $K^1(O),K^1(N)$ dinuclear Mn complex with 3-cyanobenzoic acid, $[(CO)_3(dppe)Mn–O(O)-CC_6H_4CN–Mn(dppe)(CO)_3]^+BF_4^-$ (**27**).* A $CHCl_3$ solution of two molar equivalents of **1** is added to one molar equivalent of 3-cyanobenzoic acid in aqueous NaOH solution.

*Data **27***: m.p.: softens at about 118 °C and decomposes above 124 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2038, 2027 and 1969, cyanobenzoic acid, 3.26 (m, 2H), 2.86 (m, 2H) both from dppe CH_2 Mn attached to N; 3.00 (m, 2H), 2.74 (m, 2H) both from dppe CH_2 Mn attached to O; High-resolution MS (*m*/*z*): 3.36 (m, 2H), 3.04 (m, 2H); 3.01 (m, 2H), 2.85 (m, 2H) both from dppe CH_2 of Mn attached to O; High-resolution MS (*m*/*z*): 1220.1394, calc. for $[(CO)_3(dppe)Mn-OC(O)C_6H_4CN–Mn(dppe)(CO)_3]^+$, $C_{65}H_{62}O_8P_4NMn_2$, 1220.140.

*2.6.4. Reaction of **1** with amino acids*

*2.6.4.1. Preparation of $K^1(O)$ complex with glycine, $[(CO)_3(dppe)MnOC(O)CH_2NH_2]$ (**28**).* A $CHCl_3$ solution of **1** is added to an equimolar aqueous solution of glycine.

*Data **28***: m.p.: softens at about 130 °C and decomposes above 138 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2026, 1953.7 and 1908; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 20H, from dppe, 4H, from 3-cyanobenzoic acid), 3.03 (m, 2H) and 2.87 (m, 2H) both from dppe; High-resolution MS (*m*/*z*): 612.0921, calc. for $[(CO)_3(dppe)Mn–OC(O)CH_2NH_2 + H]^+$, $C_{31}H_{29}O_5P_2NMn$, 6121.0903.

*2.6.4.2. $K^1(O)$ complex with tryptophan, $[(CO)_3(dppe)-Mn–OC(O)CHCH_2(NH_2)C_8H_5N]$, (**29**).* The reaction is carried out in MeOH.

*Data **29***: m.p: softens at about 138 °C and decomposes above 160 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2026, 1955 and 1910; ^1H NMR (δ, $CDCl_3$): 7.9–7.2 (m, 20H, from dppe, 4H, from 3-cyanobenzoic acid), 5.1 (broad peak due to NH_3^+ zwitter ion), 3.15 (m, 2H), and 2.95 (m, 2H) both from dppe; 2.5 (m, 2H) from CH_2 of tryptophan, 2.25 (t, H) from CH of tryptophan; High-resolution MS (*m*/*z*): 726.138, calc. for $[(CO)_3(dppe)Mn–OC(O)CHCH_2(NH_2)-C_8H_5N + H]^+$, $C_{40}H_{35}O_5P_2NMn$, 726.1372.

*2.6.5. Reaction of **1** with $Ph_2PCH_2CH_2N(CH_3)_2(pn)$*

*2.6.5.1. Preparation of $K^1(P)[(CO)_3(dppe)MnP(Ph)_2-CH_2CH_2N(CH_3)_2]^+BF_4^-$ (**30**).* The reaction is carried out by adding a $CHCl_3$ solution of **1** to a $CHCl_3$ solution of half the molar equivalent of pn.

*Data **30***: m.p.: softens at about 87 °C, decomposes above 104 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2027, 1958 and 1917; ^1H NMR (δ, $CDCl_3$): 8.0–7.0 (m, 30H, Ph), 3.34 (m, 2H), 3.09 (m, 2H), 3.02 (m, 2H attached to P of pn), 2.72 (2H, CH_2 attached to N), 2.27 (s, 6H, CH_3 attached to N); High-resolution MS (*m*/*z*): 794.1915, calc. for $[(CO)_3Mn(dppe)P(Ph)_2CH_2CH_2\ N(CH_3)_2]$, $C_{45}H_{44}NO_3P_3Mn$, 794.1910; 537.023, calc. for $[(CO)_3Mn(dppe)]$, $C_{29}H_{24}O_3P_2Mn$, 537.058.

*2.6.5.2. $K^1(P),K^1(N)[(dppe)(CO)_3MnP(Ph)_2(CH_2)_2N-(CH_3)Mn(CO)_3(dppe)]^{2+}2BF_4^-$ (**31**).* A $CHCl_3$ solution of equimolar quantities of **1** and **30** was used.

*Data **31***: m.p.: softens at 144 °C, decomposes above 210 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2031(broad), 1957(broad), 1913 (broad) and 1916; ^1H NMR (δ, $CDCl_3$): 8.00–7.00 (m, 50H, Ph), 3.39 (m, 2H, from dppe bonded to the Mn attached to N), 3.10 (m, 2H, from dppe, bonded to the Mn attached to P of pn), 3.01 (m, 4H, CH_2 attached to P of pn), 2.97 (m, 2H, from dppe bonded to the Mn attached to N), 2.80 (m, 2H, from dppe bonded to the Mn attached to N), 2.79 (m, 2H, CH_2 attached to N), 2.60 (s, 6H, $2CH_3$ attached to N); High-resolution MS (*m*/*z*): 1418.2647, calc. for $[(dppe)(CO)_3Mn–P(Ph)_2(CH_2)_2N(CH_3)_2–Mn(CO)_3(dppe)]^{2+}BF_4^-$, 1418.2530; 822.2166, calc. for $[(dppe)(CO)_3Mn–P(Ph)_2(CH_2)_2N-(CH_3)_2H]^{2+}BF_4$, 882.2029, 794.1882, calc. for $[(CO)_3-Mn(dppe)P(Ph)_2CH_2CH_2N(CH_3)_2]$, $C_{45}H_{44}NO_3P_3Mn$, 794.1915, 537.047, calc. for $[(CO)_3Mn(dppe)]$, $C_{29}H_{24}O_3-P_2Mn$, 537.058.

*2.7. Reaction of **1** with $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (**TMED**)*

*2.7.1. $K^1(N)[(CO)_3(dppe)Mn–N(CH_3)_2CH_2CH_2N-(CH_3)_2]^+BF_4^-$ (**32**)*

A $CHCl_3$ solution of **1** is added drop-wise to a half molar equivalent of TMED in $CHCl_3$.

*Data **32***: m.p.: softened at 107 °C, decomposes at above 116 °C; IR (cm^{-1}, $CHCl_3$): ν(CO) 2025, 1952 and 1908. ^1H NMR (δ, $CDCl_3$): 7.80–7.20 (m, 20H, Ph), 3.05 (m, 2H, CH_2) and 2.87 (m, 2H, CH_2) both from dppe, 2.78 (s, 3H, CH_3 attached to quaternary N), 2.75 (s, 3H, CH_3 attached to quaternary N), 2.52 (m, 2H, CH_2 attached to quaternary N), 2.39 (m, 2H, CH_2 attached to tertiary N),

2.24 (s, 6H, CH_3 attached to tertiary N); High-resolution MS (*m/z*): 643.234, calc. for [$(CO)_3$(dppe)Mn–N$(CH_3)_2$ $CH_2CH_2N(CH_3)_2$], $C_{35}H_{38}N_2O_3P_2Mn$, 643.268, 537.042, calc. for [$(CO)_3$Mn(dppe)], $C_{29}H_{24}O_3P_2Mn$, 537.058.

2.7.2. $K^1(N)$, $K1(N)[(CO)_3(dppe)MnN(CH_3)_2$-$CH_2CH_2N(CH_3)_2Mn(CO)_3(dppe)]^{2+}2BF_4^-$ (**33**)

A $CHCl_3$ solution of TMED is added to an equimolar $CHCl_3$ solution of **1** and the product recrystallized from $CHCl_3$/hexane.

Data ***33***: m.p.: softens at about 120 °C and decomposes above 142 °C; IR (cm^{-1}, $CHCl_3$): *ν*(CO) 2025, 1951 and 1906; ^1H NMR (*δ*, $CDCl_3$): 8.00–7.00 (m, 40H, Ph), 3.07 (m, 4H, from dppe), 2.91 (m, 4H, from dppe) 2.79 (s, 6H, $2CH_3$ attached to N), 2.73 (s, 6H, $2CH_3$ attached to N), 2.52 (m, 2H, attached to N), 2.51 (s, 2H, attached to N); High-resolution MS (*m/z*): 1277.1953; calc. for [$(CO)_3$(dppe)MnN$(CH_3)_2CH_2CH_2N(CH_3)_2Mn(CO)_3$(dppe)]$^+$ BF_4^-, $C_{64}H_{64}N_2O_6P_4Mn_2BF_4$, 1277.2505, 1191.1655, calc. for [$(CO)_3$(dppe)Mn–N$(CH_3)_2CH_2CH_2N(CH_3)_2$–Mn$(CO)_3$(dppe) + H]$^+$, $C_{64}H_{65}N_2O_6P_4Mn_2$, 1191.2554.

2.7.3. $[K^2(N,N\text{-}TMED)]Mn(CO)_3Br$ (**34**)

To a solution of $Mn(CO)_5Br$ [6] (0.274 g, 1.0 mmol), in 20 mL of toluene in a round-bottom flask equipped with a condenser, 0.150 mL (1.0 mmol) of TMED dissolved in 20 mL of toluene is added drop-wise. The solution is refluxed for 3 h and the toluene is removed via rotary evaporator to give a brown solid, which is dissolved in benzene, stirred for 5 min and filtered. The filtrate is evaporated via rotary evaporator. The brown solid is recrystallized from 1:1 CH_2Cl_2/hexane, giving orange crystals of **34**. Yield 75%.

Data ***34***: m.p.: 154–158 °C, IR (cm^{-1}, CH_2Cl_2): *ν*(CO) 2015, 1919, 1893 and 1895 as a doublet; ^1H NMR (*δ*, $CDCl_3$): 2.98 (s, 6H, CH_3), 2.92 (s, 6H, CH_3), 2.7 (m, 2H), 2.58 (m, 2H); High-resolution MS (*m/z*): 333.9628, calc. for $Mn(CO)_3$(TMED)Br, 334.0189; 249.9882, calc. for [Mn(TMED)Br], 249.9877; 171.07, calc. for [Mn(TMED)], 171.0694. *Anal.* Calc. for [$Mn(CO)_3$(TMED)Br]: C, 32.26: H, 4.81. Found: C, 32.6; H, 4.85%.

3. Results and discussion

The octahedral Mn(I) complex *fac*-[$(CO)_3$(dppe)-$MnOH_2]^+BF_4^-$ (**1**) central to this study, is easily prepared in high yield by a two-step process from readily available starting materials [2,3]. Replacement of the aqua ligand is achieved by simply stirring a solution of **1** with the desired ligand, Z. Thus derivatives of **1** have been reported, where Z represents the following anions: CN; OMe; NO_3; OC(O)-CH_3; OTf; N_3 [4]; and F [6]. (In the case of the azide, further reaction of the coordinated N_3 by 1,3-dipolar addition, either to acetylenic compounds or to nitriles, gave new manganese-bonded triazoles and tetrazoles, respectively [3]). With neutral ligands [4], the corresponding ionic complexes [$(CO)_3$(dppe)MnZ]BF_4 were prepared, where Z = PhCN, CH_3CN, CH_2=CHCN, *m*-xylylNC, PPh_3 and CO [7].

We have reported [2], that the hydride, $(CO)_3$(dppe)-MnH, precursor to the corresponding aqua complex, reacts not only with HBF_4 but also with a variety of other strong acids. These reactions result in the liberation of dihydrogen and the direct formation of the neutral complex containing the anion of the acid as a new ligand. However, weaker acids such as acetic acid and phenol do not react in this fashion. We now report that such weaker acids do react with the aqua complex resulting in the replacement of the aqua ligand by the anion (conjugate base) of the weak acid thus making available a new route to the corresponding neutral complexes. Water-soluble carboxylic acids can be used in a two-phase system without added alkali, but others require the presence of base to speed the reaction. Amino acid ligands in methanol solution react in their zwitter ion form. Complexes have been prepared from both aliphatic and aromatic carboxylic acids, as well as from phenol. The reaction with succinic and fumaric acids leads to complexes containing two Mn atoms. The reaction with citric acid gives either the 2:1 complex, presumably involving the two terminal carboxyl groups, or when alkali is present, a 3:1 complex. Stirring an excess of the aqua complex with sodium acrylate polymer (Aldrich, av. mol wt. 2100) gives a product that is insoluble in all common solvents and thus resists conventional methods of characterization. The ultimate analysis of the polymer and the calculated C/P ratio from that analysis, (see supra) indicates that almost every –[–CH_2–CH–(CO_2^-)–]– unit of the acrylate polymer is attached to a separate Mn atom, giving a new polymer, **10**, of the approximate formula: –[–CH_2–CH–[C(O)OMn$(CO)_3$(dppe)]]$_n^-$. This appears to be a unique type of polymer, one highly loaded with a transition metal, and it merits further investigation. Attempts to prepare a similar polymer by initiating polymerization of [$(CO)_3$(dppe)Mn(NCCH=CH_2)]BF_4 with benzoyl peroxide or AIBN were unsuccessful.

3.1. ^1H NMR studies

3.1.1. Aqua complex *1*

The signals associated with the protons of the dppe-Mn metallacycle are of particular interest. Unlike the other related dppe complexes, which all show two signals, **1** in $CDCl_3$ at room temperature shows a single signal (*δ* 2.95, m, 4H) for these four protons. The crystal structure [3] of **1** shows a puckered metallacycle, similar to that of other dppe complexes. Apparently the rapid reversible dissociation of the aqua ligand of **1**, which may involve a concomitant rearrangement to an intermediate 5-coordinate trigonal bipyramidal structure, results in all the protons appearing equivalent on the NMR timescale. However, at −53 °C, this signal is split into two distinct methylene signals (m, *δ* 2.67, 2H; m, *δ* 3.1, 2H) owing to the slowing of dissociation of the aqua ligand at low temperature. However, even at this low temperature it appears that

axial–equatorial interconversions of the puckered structure continue, leading, on average, to an essentially planar, 5-membered ring (see Graphical Abstract). Such a planar C_s structure results in a pair of equivalent protons on adjacent carbon *cis* to the apical CO and a pair that is *trans* to this CO, giving rise to the two signals characteristic of the ^{1}H NMR of the dppe-metallacyle.

3.1.2. Hydrido and nitrato derivatives of *1*

In an attempt to obtain evidence for ligand dissociation, the ^{1}H NMR of the hydrido (the smallest ligand) and nitrato (with a long Mn–O bond) complexes [2,4] was examined in the temperature range 100 to 120 °C. However, the chemical shifts remained unchanged (m, 2H, 2.51 and m, 2H, 2.23 for hydrido, m, 2.97, 2H and m, 2.80, 2H for nitrato) indicating no dissociation under these conditions.

3.1.3. The dppe-Mn metallacycle

The chemical shifts of the methylene protons provide valuable evidence for the preferred site of mono-coordinated ambident ligands. One of the most instructive ^{1}H NMR studies [8] of this system involved the dppe complex, 6-exophenylcyclohexadienylmanganese(I), $[PhC_6H_6(dppe)Mn(NO)]PF_6$. At 25 °C, this complex showed the CH_2 protons of the dppe as two signals (δ 3.53 and 3.02) as expected. However at −75 °C four different signals were observed, which the authors ascribe to two non-equivalent axial and two non-equivalent equatorial protons, in accordance with a stable puckered C_1 structure. We examined the ^{1}H NMR of our pyridine complex, **11**, at −50 °C, but the two signals observed at room temperature remained essentially unchanged at the lower temperature.

The chemical shift data (Table 2) of the methylene protons on the dppe ligand, provide valuable diagnostic information as to the site (Table 1) of mono-coordination of ambident ligands. These data show a consistent pattern, particularly, with respect to the difference between the chemical shifts of the two sets of protons. For the 21 related complexes in which the Mn is coordinated to an oxygen atom, this difference ranges from 0.09 to 0.19 ppm or an average of 0.14 ppm. For the 10 complexes in which the Mn is attached to a nitrogen atom, either that of a pyridine or a nitrile nitrogen, this difference ranges from 0.32 to 0.43 ppm or an average of 0.39 ppm.

3.2. Infrared studies

In a previous paper [9], we analyzed the carbonyl stretching frequencies of 38 $[(CO)_3(dppe)MnZ]$ complexes. We were able to assign symmetry species A′, A″, and A′ in decreasing order of frequency, to the three carbonyl stretches in each of these related C_s complexes. The partial positive charge on the carbon atom of coordinated CO is the most important factor affecting the frequency; the more positive this charge, the larger the force constant and the higher the frequency. Data for the new complexes are shown in Table 2. These 29 complexes may be grouped into four categories (Table 3) depending on the nature of the ligand atom that is bonded to the Mn, namely cyano-nitrogen, pyridine-nitrogen, carboxyl-oxygen and phenolic-oxygen. This order is the descending order of frequencies (with one minor exception) for all three A′, A″, and A′ bonding modes. The largest difference in frequencies between the four categories of bonding types occurs with the lower A′ mode, which involves the equatorial COs moving in phase with respect to each other and out of phase with respect to the axial CO. The group of complexes with the highest frequencies of the four groups is the category in which a nitrile nitrogen atom is bonded to the Mn. The six complexes having such coordination have the relevant A′ stretching frequencies in the narrow range 1957–1961 cm^{-1} (noticeably shifted, as expected, from the values observed with ligands having free nitrile groups). The nitrile group's π* orbitals probably compete with the carbonyl π* orbitals in accepting back-donation from the Mn d-electrons, thus increasing the partial positive charge on the carbonyl carbon atoms with the net effect of increasing the carbonyl frequencies as compared to those with pyridine or oxygen-bonded ligands.

3.3. Competition for coordination sites on ambident ligands

Previous evaluations of the relative coordinating ability of some monodentate ligands have relied on the determination of equilibrium studies of substitution reactions, e.g., $(amine)W(CO)_5 + L \rightleftarrows LW(CO)_5 + amine$ [10]. The determination of the equilibrium constants by such studies is, however, rather limited and have to be carefully chosen because of analytical difficulties. The interest in unsymmetrical chelation in ambident ligands stems from their potential use in transition metal-catalyzed homogeneous reactions. The K^2 chelation of such ligands affords stability, but if one of the donor atoms is more easily dissociated than the other, the resulting vacated site on the K^1 complex may then be occupied by a substrate molecule, followed by a desired insertion reaction and a subsequent reconstitution of the original K^2 complex. One of the most frequently used ligand for such reactions is the bidentate P,N ligand,

Table 3
CO stretching frequencies from Table 2 of (various) $[(CO)_3(dppe)MnZ]$ complexes arranged according to Mn–Z bond

	Cyano "N" (**6**)		Pyridine "N" (**4**)		Carboxyl "O" (**15**)		Phenolic "O" (**3**)	
	Range	Median	Range	Median	Range	Median	Range	Median
A′	2038–2039	2038	2027–2030	2026	2025–2029	2027	2017–2021	2019
A″	1969–1971	1970	1955–1961	1959	1953–1962	1959	1942–1947	1945
A′	1958–1961	1960	1939–1944	1940	1907–1916	1913	1906–1912	1911

$(CH_3)_2NCH_2CH_2PPh_2$, (pn). It has been found, for example [11] that the rhodium-catalyzed hydroformylation of styrene gives a substantially better yield of aldehydes when pn rather than dppe is used as a chelating ligand and a similar result was found [12,13] in the case of the carbonylation of a Pt-K^2(N,P) pn complex. Studies of Ni [14], Ru [15], and heteronuclear Pt complexes [16] containing the pn ligand in its K^2(N,P) form have shown that the nitrogen site is more easily dissociated from the metal than the phosphorous atom.

Most studies involving mixed bidentate ligands, such as the ones cited above, have been devoted to investigating selective dissociation of the chelated K^2-complex to a corresponding K^1-complex. The results of such studies are generally consistent with hard-acid, soft-base (HASB) theory, with the central cationic metal acting as the hard acid, and the ligand, with two competing heteroatoms of differing hardness/softness, as the base [17]. In the case of a the K^2(N,P) pn complexes, the metal–N bond, as expected, and as the cited references show, dissociates preferentially. Although it may be reasonable to assume that preferred coordination is the reverse of preferred dissociation, it was nevertheless thought to be instructive to ascertain the preferred coordination site in the case of pn by reacting it with one mole of **1**.

Our studies show that when a solution of **1** is added dropwise to an equimolar solution of pn, the K^1(P) complex, **30**, is formed, essentially in quantitative yield. For purposes of comparing their ^{1}H NMR spectra, complexes **32** and **33** were also prepared. The difference in δ of the methyl protons attached to the trivalent and tetravalent N atoms in the complexes allows one to ascertain when and if the N is involved in the coordination of pn to the Mn. The fact that P of pn is preferred on coordination is consistent with the dissociation studies, which found that N dissociates before P in pn K^2 (P,N) complexes.

Our studies compare relative ligating ability of ambident ligands possessing combinations of carboxylate, phenolic, pyridine and nitrile groups competing for a single coordination site. When present as anions, usually in a two-phase system, the carboxylate (including the zwitter ions of amino acids) and phenolic ligands are preferred over the other type ligands. By using $NaHCO_3$ it is possible to coordinate 3-hydroxybenzoic acid exclusively at the carboxyl group, **23**, while with NaOH both functional groups are coordinated, **24**. The synthesis of **16** from 4-cyanopyridine indicates coordination at nitrile nitrogen in preference to pyridine nitrogen. In the absence of alkali or water, the nitrile group coordinates more rapidly than carboxyl of 3-hydroxybenzoic acid (**25**) or the hydroxyl of 3-cyanophenol (**20**). It would appear that a useful ambident chelating ligand for certain catalytic reactions might consist of a pyridine derivative having a suitably situated nitrile group, or one containing CN and $N(CH_3)_2$ groups. We have no plans to pursue this area of research.

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