

Use of the aqua complex $[fac-Mn(CO)_3(dppe)OH_2]BF_4$ for the preparation of a series of $fac-Mn(CO)_3(dppe)Z$ and $[fac-Mn(CO)_3(dppe)Z]BF_4$ complexes. X-ray crystal structures of three representative examples

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Abstract

The aqua ligand in the titled complex (prepared by a simple two-step, high-yield synthesis) is readily replaced by the desired anionic ligand Z^- , to give a six-coordinate neutral species $fac-Mn(CO)_3(dppe)Z$. Examples of such complexes where $Z=O-NO_2$, CN, OMe, OC(O)OMe, and OS(O)₂CF₃ (OTf) are reported herein. Neutral ligands also replace the aqua ligand to give ionic complexes $[fac-Mn(CO)_3(dppe)Z]BF_4$. Examples where $Z=2,6$ -dimethylphenyl (xylyl) isocyanide, acetonitrile, benzonitrile, and acrylonitrile are also reported herein. Crystal structures of $fac-Mn(CO)_3(dppe)NO_3$ (**2**), $[fac-Mn(CO)_3(dppe)(xylyl-NC)]BF_4$ (**7**), and $[fac-(CO)_3Mn(dppe)(PhCN)]BF_4$ (**9**), are reported. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The aqua complex $[fac-Mn(CO)_3(dppe)(OH_2)]BF_4$ (**1**), [1] provides a convenient starting compound en route to manganese complexes possessing a wide variety of functional groups directly σ -bonded to the metal. Treatment of the aqua complex **1**, with anionic species Z^- leads to neutral, six-coordinate complexes with Z σ -bonded to the metal. Products corresponding to simple anion exchange were not observed. Neutral ligands Z , also react with **1** producing complexes of the type, $[fac-Mn(CO)_3(dppe)Z]BF_4$.

2. Experimental

All reactions were carried out under an argon atmosphere using a Schlenk line. Solvents were used as received unless otherwise noted. Dppe was purchased

from Pressure Chemicals. $[Fac-Mn(CO)_3(dppe)-(OH_2)]BF_4$ (**1**), and $fac-Mn(CO)_3Mn(dppe)H$ were prepared by methods described in the literature [1,2]. Tri-fluoromethanesulfonic (triflic) acid was purchased from Aldrich. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR instrument employing 1.0 mm NaCl liquid cells unless noted otherwise. ¹H-NMR data were recorded using a Bruker AC-250 spectrometer with CDCl₃ chemical shifts recorded relative to Me₄Si. Melting points were obtained using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories and Chemisar Laboratories. Mass spectra were recorded on a Kratos MS-890 high-performance mass spectrometer. The purity of each of the new compounds was assured by careful examination of the spectroscopic data (particularly ¹H-NMR) and by thin-layer chromatography.

2.1. Preparation of $fac-(CO)_3Mn(dppe)O-NO_2$ (**2**)

The aqua complex **1** (86 mg, 0.13 mmol) was added to a round bottomed flask and dissolved in approxi-

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mately 15 ml of CHCl_3 . Excess KNO_3 (aq.) (1 ml of a saturated solution) was added and the mixture stirred for 4.5 h. All liquids were removed via rotary evaporation. The residue was stirred with CH_2Cl_2 and then filtered to remove excess KNO_3 and KBF_4 . The CH_2Cl_2 was removed by rotary evaporation. The addition of hexane, followed by rotary evaporation yielded the yellow solid **2** (72 mg, 90% yield). X-ray quality crystals were grown from CH_2Cl_2 –hexane.

Data 2: decomposition occurs at 168–170°C. IR (cm^{-1} , CHCl_3): $\nu(\text{C}=\text{O})$ 2034 s, 1968 s, 1925 s. $^1\text{H-NMR}$ (δ , CDCl_3): 7.6–7.3 (m, 20H, Ph), 3.0–2.7 (m, 4H, CH_2) MS (m/z): 515 ($[\text{Mn}(\text{dppe})\text{NO}_3]^+$), 453 ($[\text{Mn}(\text{dppe})]^+$). Anal. Calc. for $\text{C}_{29}\text{H}_{24}\text{MnNO}_6\text{P}_2 \cdot 1/4\text{H}_2\text{O}$: C, 57.7; H, 4.09; N, 2.32. Found: C, 57.2; H, 4.05; N, 2.28% (see Fig. 1 for crystal structure).

2.2. Preparation of *fac*-(CO)₃Mn(dppe)CN (**3**)

The aqua complex **1** (101 mg, 0.157 mmol) was dissolved in about 15 ml of CHCl_3 . A total of 20 drops of a saturated KCN (aq.) solution were added and the mixture stirred for 1 h 35 min. The solvents were removed by rotary evaporation and the residue vacuum dried to ensure water removal. The solid material was dissolved in CH_2Cl_2 and filtered to remove KBF_4 and excess KCN. Removal of CH_2Cl_2 yielded the yellow solid **3** (51 mg, 58% yield).

Data 3: decomposition occurs at 174–177°C. IR (cm^{-1} , CHCl_3): $\nu(\text{C}=\text{N})$ 2242m, $\nu(\text{C}=\text{O})$ 2030 s, 1960 s,

1920 s. $^1\text{H-NMR}$ (δ , CDCl_3): 7.67–7.35 (m, 20H, Ph), 3.96–3.62 (m, 4H, CH_2) MS (m/z): 537 ($[\text{Mn}(\text{CO})_3(\text{dppe})]^+$), 453 ($[\text{Mn}(\text{dppe})]^+$). Anal. Calc. for $\text{C}_{30}\text{H}_{24}\text{MnNO}_3\text{P}_2$: H, 4.3; N, 2.5. Found: H, 4.4; N, 2.5%. Carbon analysis was unsatisfactory.

2.3. Preparation of *fac*-(CO)₃Mn(dppe)OMe (**4**) and *fac*-(CO)₃Mn(dppe)OC(O)OMe (**5**)

The aqua complex **1** (114 mg, 0.178 mmol) was placed in a round-bottomed flask and 7.78 ml of freshly prepared 0.228 M NaOMe (prepared from 0.52g of Na dissolved in 99 ml of methanol) was added. Additional methanol was added to bring the total amount of solution to approximately 15 ml and the solution was stirred for 3 h 15 min and then rotovaped to yield **4** plus a small amount of **5** as indicated by IR spectroscopy [3,4]. The mixture **4** was converted completely to **5** by exposure to CO_2 (86 mg, 79% yield). The spectroscopic data agreed with that reported previously for **5** [4].

2.4. Preparation of *fac*-Mn(CO)₃(dppe)OTf (**6**)

The aqua complex **1** (83 mg, 0.13 mmol) was dissolved in about 15 ml of CHCl_3 . Excess triflic acid (0.050 ml, 0.57 mmol) was added via syringe and the mixture was stirred for 3 h. The solution was extracted with water to remove any excess acid and the CHCl_3 was removed via rotary evaporation. The residue was

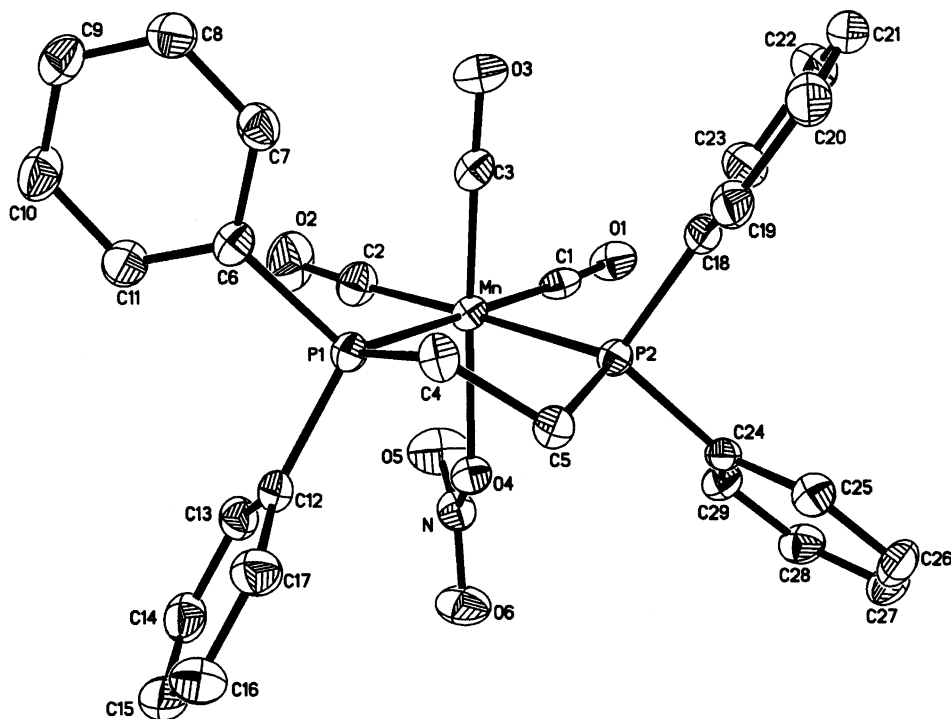


Fig. 1. ORTEP diagram of *fac*-Mn(CO)₃(dppe)NO₃ (**2**), indicating labeling scheme and 50% thermal ellipsoids.

dissolved in CH_2Cl_2 –hexane and the solvent removed via rotary evaporation, giving **6** as a yellow solid (89 mg, 100% yield).

Data 6: decomposition occurs at 169–171°C. IR (cm^{-1} , CHCl_3): $\nu(\text{C}=\text{O})$ 2040 s, 1974 s, 1928 s. $^1\text{H-NMR}$ (δ , CDCl_3): 7.65–7.30 (m, 20H, Ph), 3.00–2.79 (m, 4H, CH_2) MS (m/z): 537 ($[\text{Mn}(\text{CO})_3(\text{dppe})]^+$), 453 ($[\text{Mn}(\text{dppe})]^+$). Anal. Calc. for $\text{C}_{30}\text{H}_{24}\text{F}_3\text{MnO}_6\text{P}_2\text{S}$: C, 52.5; H, 3.52; S, 4.67. Found: C, 52.8; H, 3.78; S, 4.81%.

2.5. Alternative preparation of *fac*- $\text{Mn}(\text{CO})_3(\text{dppe})\text{OTf}$ (**6**) from *fac*- $\text{Mn}(\text{CO})_3(\text{dppe})\text{H}$

The hydride, *fac*- $\text{Mn}(\text{CO})_3(\text{dppe})\text{H}$ (220 mg, 0.409 mmol), was dissolved in about 15 ml of CHCl_3 . A slight excess of triflic acid (0.050 ml, 0.57 mmol) was added via syringe. Evolution of H_2 occurred immediately and the reaction was stirred for 2 h. The workup of the reaction mixture was conducted in a manner identical to the isolation of **6** described above; (272 mg, 97% yield).

2.6. Preparation of *[fac-(CO)₃Mn(dppe)(xylyl-N≡C)]BF₄* (**7**)

The aqua complex **1** (220 mg, 0.343 mmol) was dissolved in approximately 15 ml of CHCl_3 . Excess xylyl isocyanide (76 mg, 0.58 mmol) was added and the mixture was stirred for 25 min. The solvent was removed via rotary evaporation. Hexane was added, the mixture stirred and the hexane solution was decanted (4×3 ml), thereby removing excess isocyanide. Hexane was added again and removed via rotary evaporation yielding the white solid **7** (230 mg, 89% yield). X-ray quality crystals were obtained from CH_2Cl_2 –hexane.

Data 7: m.p. 240–243°C. IR (cm^{-1} , CHCl_3): $\nu(\text{C}\equiv\text{N})$ 2151 m, $\nu(\text{C}=\text{O})$ 2035 s, 1982 s, 1973 s. $^1\text{H-NMR}$ (δ , CDCl_3): 7.8–6.8 (m, 23H, Ph), 3.6–3.1 (m, 4H, CH_2), 1.62 (s, 6H, CH_3). MS (m/z): 668 ($[\text{Mn}(\text{CO})_3(\text{dppe})(\text{xylyl-NC})]^+$), 584 ($[\text{Mn}(\text{dppe})(\text{xylyl-NC})]^+$), 453 ($[\text{Mn}(\text{dppe})]^+$). Anal. Calc. for $\text{C}_{38}\text{H}_{33}\text{BF}_4\text{MnNO}_3\text{P}_2$: C, 60.4; H, 4.40. Found: C, 60.0; H 4.39%.

2.7. Preparation of *[fac-(CO)₃Mn(dppe)(CH₃CN)]BF₄* (**8**)

The aqua complex **1** (148 mg, 0.230 mmol) was dissolved in approximately 15 ml of CHCl_3 . Acetonitrile (0.060 ml, 1.1 mmol) was added via syringe and the mixture was stirred for 2 h during which time the color of the yellow solution faded significantly. The mixture was rotovaped yielding an oil, which was then stirred with hexane. Rotary evaporation of the hexane yielded the pale yellow solid **8** (133 mg, 87% yield).

Data 8: decomposition occurs at 110–114°C. IR (cm^{-1} , CHCl_3): $\nu(\text{C}\equiv\text{N})$ 2286 vw, $\nu(\text{C}=\text{O})$ 2039 s, 1970 s, 1952 s. $^1\text{H-NMR}$ (δ , acetone- d_6): 8.04–7.7 (m, 20H, Ph), 3.6–3.2 (m, 4H, CH_2), 1.72 (s, 3H, CH_3) MS (m/z): 578 ($[\text{Mn}(\text{CO})_3(\text{dppe})(\text{CH}_3\text{CN})]^+$), 537 ($[\text{Mn}(\text{CO})_3(\text{dppe})]^+$), 453 ($[\text{Mn}(\text{dppe})]^+$). Anal. Calc. for $\text{C}_{31}\text{H}_{27}\text{BF}_4\text{MnNO}_3\text{P}_2$: C, 56.0; H, 4.09; N, 1.8. Found: C, 55.4; H, 4.05; N, 1.8%.

2.8. Preparation of *[fac-(CO)₃Mn(dppe)(PhCN)]BF₄* (**9**)

The aqua complex **1** (103 mg, 0.161 mmol) was dissolved in approximately 15 ml of CHCl_3 . Benzonitrile (0.050 ml, 0.49 mmol) was added via syringe and the mixture was stirred for 20 min during which time the color of the yellow solution faded significantly. The chloroform was removed by rotary evaporation. The residue was stirred with hexane (8×2 ml) to dissolve excess benzonitrile. The remaining hexane was removed via rotary evaporator giving the pale yellow solid **9** (102 mg, 87% yield). X-ray quality crystals were obtained from CH_2Cl_2 –hexane.

Data 9: m.p. 172–173°C. IR (cm^{-1} , CHCl_3): $\nu(\text{C}\equiv\text{N})$ 2254 vw, $\nu(\text{C}=\text{O})$ 2038 s, 1969 s, 1957 s. $^1\text{H-NMR}$ (δ , CDCl_3): 7.8–6.55 (m, 25H, Ph), 3.7–3.0 (m, 4H, CH_2). MS (m/z): 640 ($[\text{Mn}(\text{CO})_3(\text{dppe})(\text{PhCN})]^+$), 537 ($[\text{Mn}(\text{CO})_3(\text{dppe})]^+$), 453 ($[\text{Mn}(\text{dppe})]^+$). Anal. Calc. for $\text{C}_{36}\text{H}_{29}\text{BF}_4\text{MnNO}_3\text{P}_2 \cdot 1/2\text{H}_2\text{O}$: C, 58.7; H, 4.11. Found: C, 58.8; H 4.20%.

2.9. Preparation of *[fac-(CO)₃Mn(dppe)(CH₂=CHCN)]BF₄* (**10**)

The aqua complex **1** (1.461 g, 2.278 mmol) was dissolved in approximately 50 ml of CHCl_3 . Acrylonitrile (3.0 ml, 45 mmol) was added via syringe and the mixture was stirred for 2 h during which time the color of the yellow solution faded significantly. The mixture was rotovaped to remove chloroform and excess acrylonitrile. A mixture of CH_2Cl_2 –hexane was added and then removed via rotary evaporator yielding the pale yellow solid **10** (1.436 g, 93% yield).

Data 10: m.p. (dec.) occurs at 82–86°C. IR (cm^{-1} , CHCl_3): $\nu(\text{C}\equiv\text{N})$ 2257 vw, $\nu(\text{C}=\text{O})$ 2038 s, 1971 s, 1957 s. $^1\text{H-NMR}$ (δ , CDCl_3): 7.8–7.2 (m, 20H, Ph), 5.87 [d, 1H, H_{cis} , $J(\text{H}_{\text{cis}}-\text{H}_{\text{gem}}) = 12$ Hz], 5.45 [d, 1H, H_{trans} , $J(\text{H}_{\text{trans}}-\text{H}_{\text{gem}}) = 18$ Hz], 5.03 (dd, 1H, H_{gem}), 3.65–2.85 (m, 4H, CH_2). MS (m/z): 590 ($[\text{Mn}(\text{CO})_3(\text{dppe})(\text{CH}_2=\text{CHCN})]^+$), 537 ($[\text{Mn}(\text{CO})_3(\text{dppe})]^+$), 453 ($[\text{Mn}(\text{dppe})]^+$). Anal. Calc. for $\text{C}_{32}\text{H}_{27}\text{BF}_4\text{MnNO}_3\text{P}_2$: C, 56.7; H, 4.0. Found: C, 56.3; H 4.4%.

2.10. X-ray diffraction studies of **2**, **7**, and **9**

Crystals of **2**, **7**, and **9** used for the X-ray diffraction experiments were grown from CH_2Cl_2 –hexane. When

attempts were made to cut crystals of **7**, they shattered and hence a larger than desirable crystal was used for the experiment. The crystals of **2** and **9** were of a more desirable size, namely less than 0.5 mm on an edge. All crystals were mounted on the tip of a glass fiber with epoxy resin.

Intensity data for **7** were collected at 21°C on a Siemens P3 diffractometer [5] with graphite-monochromated Mo K α radiation. Intensity data were collected using variable $\theta - 2\theta$ scans in ω out to a maximum θ value of 27.56°. The data were processed using the program XDISK. The data were corrected for decay, Lorentz and polarization effects as well as absorption (based on measured ψ scans). A hemisphere of intensity data for **2** were collected at 150 K on a Siemens SMART 2K CCD diffractometer [6] using graphite-monochromated Ag K α radiation, a detector distance of 3.905 cm from the crystal, 25-s frames at 0.3° intervals of ω , and a maximum θ value of 22.09°. A hemisphere of intensity data for **9** were collected at 175 K on a Siemens SMART 1K CCD diffractometer using graphite-monochromated Mo K α radiation, a detector distance of 5.010 cm and 30-s frames at 0.3° intervals of ω and a maximum θ value of 28.26°. The CCD data frames were processed using the program SAINT. All data were corrected for decay, Lorentz and polarization effects as well as absorption (based on the multi-scan technique using SADABS [7]).

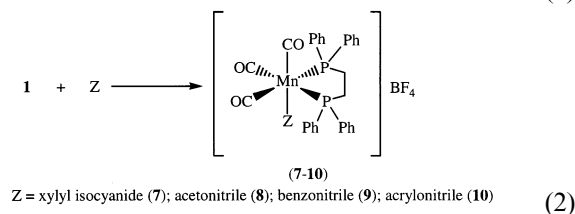
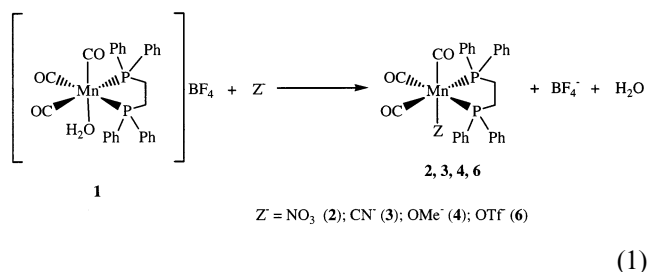
All structures were solved by a combination of direct methods using SHELXTL version 5.03 [8] and the difference Fourier technique and refined by full-matrix least-squares on F^2 [9]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Weights were assigned as $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = 0.33333F_o^2 + 0.66667F_c^2$ and $a = 0.0560$, $b = 0.00$ for **2**, $a = 0.0786$, $b = 1.4909$ for **7**, and $a = 0.0281$, $b = 33.6397$ for **9**. Positions of the hydrogen atoms for **7** were either calculated (based on geometric criteria) or located directly from the difference map. A riding model was imposed on the H-atom positions in subsequent refinements. For **2**, all H-atom positions on the chelated phosphine were calculated and treated with a riding model in the refinements. H1W was located directly from the difference map while H2W was calculated, based on hydrogen bonding distances from the water to the manganese complex. The H-atom positions on the water were held fixed. All aromatic and methylene H-atom positions in **9** were calculated and treated with a riding model in the refinements. H1W and H2W were located directly from the difference map and held fixed in subsequent refinements. In all cases, hydrogen atom isotropic temperature factors were defined as a^*U_{eq} of the adjacent atom where $a = 1.5$ for CH₃ and OH and 1.2 for all others.

In **2** the occupancy of the water molecule refined to nearly 0.25 and was fixed at this value in the final

refinement. A water molecule (0.5 total occupancy) is found in the crystalline lattice for **7**. The water oxygen in **7** appears disordered over two positions with the H-atoms shared between them. The anisotropic displacement parameter for O1WB was constrained to be equal to that of O1WA, otherwise OW1B had a tendency to be non-positive definite. The BF₄ anion in **7** is disordered with two major conformers located (occupancy set at 0.5 for F2–F4 and 1.0 for F1). The refinement of BF₄ did not proceed without difficulty; several restraints on bond distances and magnitude of displacement parameters were necessary. The BF₄ anion in **9** also shows disorder in two of the fluorines (occupancy set at 0.5 for F3 and F4). The refinements for all structures converged with crystallographic agreement factors summarized in Table 1.

3. Results and discussion

The one-pot synthesis of *fac*-Mn(CO)₃(dppe)H from Mn₂(CO)₁₀ and dppe in refluxing 1-pentanol [2], followed by its subsequent reaction with HBF₄, provides an easy two step route to the aqua complex **1** [1]. The general reactions in chloroform at room temperature (r.t.) to produce neutral complexes of the type; *fac*-Mn(CO)₃(dppe)Z and ionic complexes of the type; [*fac*-Mn(CO)₃(dppe)Z]BF₄ are depicted in Eq. (1) Eq. (2), respectively.



The triflate complex, **6**, was also prepared from the reaction of the hydride, *fac*-Mn(CO)₃(dppe)H, with an excess of triflic acid. Immediate hydrogen gas evolution was observed and **6** was separated from excess acid and isolated in quantitative yield.

The progress of these reactions was followed by IR spectroscopy. The IR spectra of complexes **2**–**10** exhibit three strong carbonyl bands consistent with a facial carbonyl arrangement. Complexes **3** and **7** have a medium intensity C $\equiv$ N band at 2242 and 2151 cm^{−1},

Table 1
Crystal data and structure refinement for **2**, **7** and **9**

	2	7	9
Empirical formula	C ₂₉ H ₂₄ NO ₆ P ₂ Mn·0.25(H ₂ O)	[C ₃₈ H ₃₃ MnNO ₃ P ₂]BF ₄	[C ₃₆ H ₂₉ NO ₃ P ₂ Mn]BF ₄ ·0.5(H ₂ O)
Formula weight	603.88	755.34	736.30
Temperature (K)	150(2)	294(2)	175(2)
Wavelength (Å)	0.56086	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
Unit cell			
<i>a</i> (Å)	12.9745(14)	10.987(2)	24.440(3)
<i>b</i> (Å)	14.3516(14)	12.906(3)	12.819(1)
<i>c</i> (Å)	15.327(2)	14.188(3)	21.836(2)
α (°)		78.99(3)	
β (°)	105.945(5)	67.83(3)	100.504(2)
γ (°)		86.89(3)	
<i>V</i> (Å ³)	2744.1(5)	1828.5(6)	6726.4
<i>Z</i>	4	2	8
ρ_{calc} (Mg m ^{−3})	1.462	1.372	1.454
μ (mm ^{−1})	0.338	0.506	0.549
<i>T</i> _{min} / <i>T</i> _{max}	0.8495/0.8769	0.7576/0.9194	0.8102/0.8749
<i>F</i> (000)	1242	776	3016
θ_{max} (°)	22.09	27.56	28.26
Independent reflections	6888	8450	8172
<i>R</i> _{int}	0.0989	0.0159	0.1215
Data/parameters	6887/361	8391/466	6819/463
<i>S</i>	0.979	1.023	1.101
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0459, <i>wR</i> ₂ = 0.1007	<i>R</i> ₁ = 0.0532, <i>wR</i> ₂ = 0.1437	<i>R</i> ₁ = 0.0685, <i>wR</i> ₂ = 0.1197
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0889, <i>wR</i> ₂ = 0.1199	<i>R</i> ₁ = 0.0947, <i>wR</i> ₂ = 0.2154	<i>R</i> ₁ = 0.1566, <i>wR</i> ₂ = 0.1623
Residual peak (e Å ^{−3})	0.687	0.952	0.394

respectively. The IR spectra of the nitriles **8**–**10** display very weak C≡N stretches between 2286 and 2254 cm^{−1}.

The ¹H-NMR spectra of all the complexes are relatively straightforward, displaying multiplets in the phenyl region as well as multiplets in the methylene region associated with the chelating dppe ligand. The ¹H-NMR spectra of complexes **7** and **8** show methyl signals at 1.62 and 1.72 ppm, respectively. The *H*_{trans}, *H*_{cis}, and *H*_{gem} protons of the acrylonitrile ligand appear as a doublet, a doublet and a doublet of doublets, respectively, in the 250 MHz ¹H-NMR spectrum. Apparently, *J*(*H*_{cis}–*H*_{trans}) is very small and accordingly, only doublets are observed for *H*_{cis} and *H*_{trans} in **10**.

The mass spectra of complexes **7**–**10** exhibit molecular ion peaks as well as the expected fragmentation peaks. The molecular ion peaks in the mass spectra of complexes **2**, **3**, and **6** are not observed; however, appropriate fragmentation peaks are found.

The methoxide complex **4** has been prepared previously and has been shown to insert CO₂ readily upon exposure to air [3]. The formation of the methoxide complex **4** was verified (without isolation) by IR spectroscopy and it was then converted in situ to the stable carbonato complex **5**.

The versatility of the readily available aqua complex **1** has been demonstrated by the ease of creating both

neutral and cationic manganese complexes from it, thus allowing access to complexes having a variety of functional groups σ-bonded to the manganese atom.

3.1. Molecular structures of **2**, **7**, and **9**

Crystallographic data for complexes **2**, **7**, and **9** are summarized in Table 1. The molecular structures of **2**, **7**, and **9** are shown in Figs. 1–3, respectively.

Selected bond distances and angles for the nitrate complex **2** are found in Table 2. To our knowledge, this is the first crystal structure of a manganese carbonyl complex containing a nitrate ligand. The complex crystallizes with 1/4H₂O in the lattice and exhibits O–H···O hydrogen bonding. The NO₃ ligand is bound terminally to Mn through O(4) at a distance of 2.050(2) Å. The complex has a O(4)–N distance of 1.300(3) Å and a Mn–O(4)–N bond angle of 123.8(2)°. These distances and angles are consistent with those of other non-carbonyl manganese complexes containing a terminal nitrate group [10–12].

Selected bond distances and angles for the isocyanide complex **7** are found in Table 3. A distance of 1.916(3) Å is found for the manganese–xylyl isocyanide carbon bond. The C≡N bond length is 1.154(3) Å and the bond

angle for Mn(1)–C(4)–N(1) is $177.4(2)^\circ$, demonstrating a linear linkage as expected. These distances and angles are consistent with those of other manganese isocyanide complexes [13–17].

Selected bond distances and angles for the benzonitrile complex **9** are given in Table 4. The complex crystallizes with $1/2\text{H}_2\text{O}$ in the lattice and exhibits O–H $\cdots$ F and C–H $\cdots$ O hydrogen bonds. This latter type

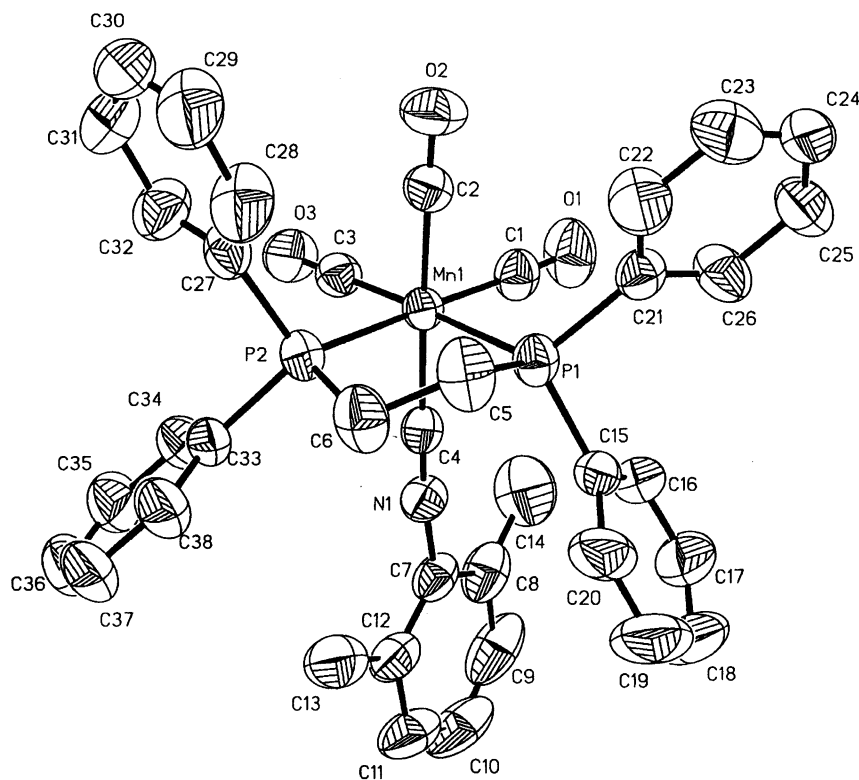


Fig. 2. ORTEP diagram of $[\text{fac-Mn}(\text{CO})_3(\text{dppe})(\text{xylyl-NC})]\text{BF}_4$ (**7**), indicating labeling scheme and 50% thermal ellipsoids.

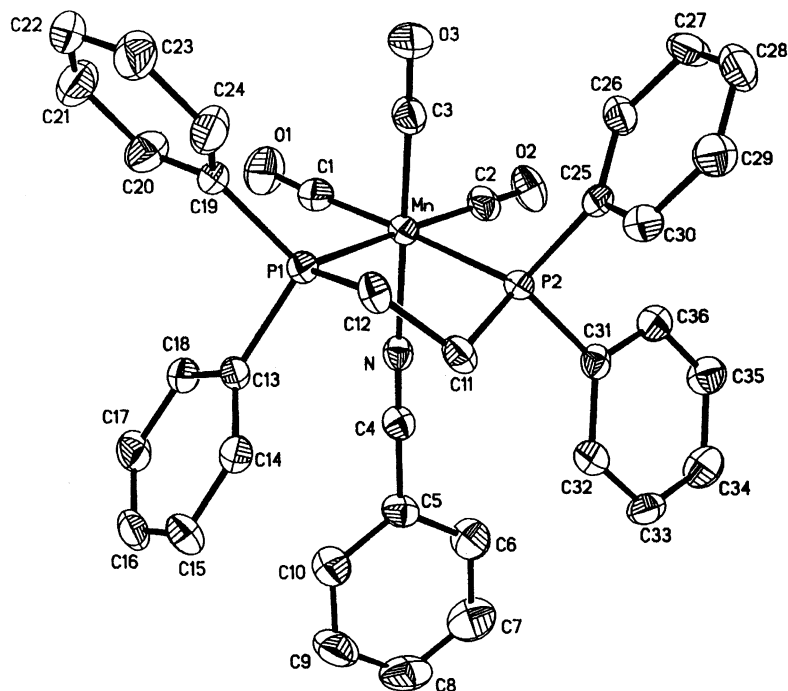


Fig. 3. ORTEP diagram of $[\text{fac}-(\text{CO})_3\text{Mn}(\text{dppe})(\text{PhCN})]\text{BF}_4$ (**9**), indicating labeling scheme and 50% thermal ellipsoids.

Table 2
Bond lengths (Å) and angles (°) for **2**

<i>Bond lengths</i>			
Mn–C(3)	1.789(3)	Mn–C(1)	1.820(3)
Mn–C(2)	1.834(3)	Mn–O(4)	2.050(2)
Mn–P(1)	2.322(1)	Mn–P(2)	2.324(1)
P(1)–C(4)	1.837(3)	P(2)–C(5)	1.829(3)
O(1)–C(1)	1.136(3)	O(2)–C(2)	1.147(3)
O(3)–C(3)	1.153(3)	O(4)–N	1.300(3)
O(5)–N	1.231(3)	O(6)–N	1.241(3)
C(4)–C(5)	1.533(4)		
<i>Bond angles</i>			
C(3)–Mn–C(1)	88.81(12)	C(3)–Mn–C(2)	89.65(12)
C(1)–Mn–C(2)	92.25(13)	C(3)–Mn–O(4)	172.89(10)
C(1)–Mn–O(4)	94.52(10)	C(2)–Mn–O(4)	96.49(10)
C(3)–Mn–P(1)	89.51(9)	C(1)–Mn–P(1)	176.20(8)
C(2)–Mn–P(1)	91.15(11)	O(4)–Mn–P(1)	86.78(6)
C(3)–Mn–P(2)	90.68(9)	C(1)–Mn–P(2)	92.09(8)
C(2)–Mn–P(2)	175.65(11)	O(4)–Mn–P(2)	82.94(5)
P(1)–Mn–P(2)	84.52(3)	O(5)–N–O(6)	123.3(2)
O(5)–N–O(4)	119.8(2)	O(6)–N–O(4)	116.9(2)
O(1)–C(1)–Mn	176.2(2)	O(2)–C(2)–Mn	176.7(3)
O(3)–C(3)–Mn	177.3(3)		
<i>Hydrogen bonding interactions for 2</i>			
	D⋯A	D–H	H⋯A Angle
O1W–H1W⋯O6 ^a	2.769(10)	0.91	1.98 144.0(7)
O1W–H2W⋯O5 ^b	3.126(10)	1.11	2.29 130.5(5)
O1W–H2W⋯O2 ^b	2.684(9)	1.11	1.87 126.6(5)
C4–H4B⋯O1W ^c	3.355(11)	0.99	2.51 142.9(3)

^a Symmetry operators: $x+1/2$, $-y+3/2$, $z+1/2$.

^b $-x+3/2$, $y-1/2$, $-z+1/2$.

^c x , y , z .

Table 3
Bond lengths (Å) and angles (°) for **7**

<i>Bond lengths</i>			
Mn(1)–C(3)	1.822(3)	Mn(1)–C(1)	1.827(3)
Mn(1)–C(2)	1.849(3)	Mn(1)–C(4)	1.916(3)
Mn(1)–P(2)	2.325(1)	Mn(1)–P(1)	2.337(1)
P(1)–C(5)	1.824(3)	P(1)–C(15)	1.826(3)
P(1)–C(21)	1.831(3)	P(2)–C(27)	1.817(3)
P(2)–C(33)	1.831(3)	P(2)–C(6)	1.833(3)
O(1)–C(1)	1.130(4)	O(2)–C(2)	1.129(3)
O(3)–C(3)	1.132(3)	N(1)–C(4)	1.154(3)
N(1)–C(7)	1.402(4)	C(5)–C(6)	1.490(5)
<i>Bond angles</i>			
C(3)–Mn(1)–C(1)	90.90(13)	C(3)–Mn(1)–C(2)	93.64(12)
C(1)–Mn(1)–C(2)	89.58(13)	C(3)–Mn(1)–C(4)	89.85(12)
C(1)–Mn(1)–C(4)	91.12(13)	C(2)–Mn(1)–C(4)	176.42(11)
C(3)–Mn(1)–P(2)	92.26(9)	C(1)–Mn(1)–P(2)	176.76(9)
C(2)–Mn(1)–P(2)	89.51(9)	C(4)–Mn(1)–P(2)	89.60(8)
C(3)–Mn(1)–P(1)	176.99(9)	C(1)–Mn(1)–P(1)	92.05(9)
C(2)–Mn(1)–P(1)	87.01(9)	C(4)–Mn(1)–P(1)	89.46(8)
P(2)–Mn(1)–P(1)	84.80(4)	C(4)–N(1)–C(7)	174.0(3)
O(1)–C(1)–Mn(1)	177.0(3)	O(2)–C(2)–Mn(1)	178.8(3)
O(3)–C(3)–Mn(1)	177.3(3)	N(1)–C(4)–Mn(1)	177.4(2)

Table 4
Bond lengths (Å) and angles (°) for **9**

<i>Bond lengths</i>			
Mn–C(3)	1.808(5)	Mn–C(1)	1.836(5)
Mn–C(2)	1.845(5)	Mn–N	1.996(4)
Mn–P(1)	2.332(1)	Mn–P(2)	2.348(1)
P(1)–C(19)	1.824(5)	P(1)–C(13)	1.832(5)
P(1)–C(12)	1.832(5)	P(2)–C(31)	1.830(5)
P(2)–C(25)	1.834(5)	P(2)–C(11)	1.836(5)
O(1)–C(1)	1.138(6)	O(2)–C(2)	1.138(6)
O(3)–C(3)	1.134(6)	N–C(4)	1.139(6)
C(4)–C(5)	1.449(7)		
<i>Bond angles</i>			
C(3)–Mn–C(1)	89.6(2)	C(3)–Mn–C(2)	92.7(2)
C(1)–Mn–C(2)	91.7(2)	C(3)–Mn–N	175.7(2)
C(1)–Mn–N	93.2(2)	C(2)–Mn–N	90.5(2)
C(3)–Mn–P(1)	86.4(2)	C(1)–Mn–P(1)	92.6(2)
C(2)–Mn–P(1)	175.7(2)	N–Mn–P(1)	90.22(12)
C(3)–Mn–P(2)	92.1(2)	C(1)–Mn–P(2)	176.6(2)
C(2)–Mn–P(2)	91.2(2)	N–Mn–P(2)	84.89(12)
P(1)–Mn–P(2)	84.60(5)	C(4)–N–Mn	176.5(4)
O(1)–C(1)–Mn	177.4(5)	O(2)–C(2)–Mn	178.4(4)
O(3)–C(3)–Mn	178.1(5)	N–C(4)–C(5)	178.8(5)
<i>Hydrogen bonding interactions for 9</i>			
	D⋯A	D–H	H⋯A Angle
O1WB–H1W⋯F2 ^a	3.23(4)	1.00	2.29 156(2)
C7–H7⋯O1WA ^b	3.21(3)	0.95	2.50 132(1)
C7–H7⋯O1WB ^b	3.39(4)	0.95	2.51 155(1)

^a Symmetry operators: $-x+2$, y , $-z+3/2$.

^b x , y , z .

of bonding is not uncommon and has been discussed elsewhere [18]. The benzonitrile group has a Mn–N distance of 1.996(4) Å. The bond angle for C(4)–N–Mn is 176.5(4)°, demonstrating a linear linkage as expected. The distances and angles with regard to the benzonitrile ligand are similar to those reported previously in the structure of [Mn(CO)(PhCN)(dmpe)₂]BPh₄ [19].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 136155–CCDC 136157. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Structure factors are available upon request from the authors.

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