Supplementary Information (ESI) for Chemical Communications

Reactivity of Electrophilic μ_2-Phosphinidene Complexes with Heterocumulenes: Formation of the First σ-π-Aminophosphaimine Complexes $[Mn_2(CO)_8\{\mu\text{-}\eta^1,\eta^2\text{-}P(N^iPr_2)=NR\}]$ and Diazoalkane Insertions into Metal-Phosphorus Bonds.

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Supplementary Material (ESI) for Chemical Communications

Experimental

General comments: All procedures were carried out using standard Schlenk techniques or in a glovebox under a nitrogen atmosphere. THF was distilled from Na/benzophenone. Dichloromethane and hexane were purified using solvent purification columns containing alumina (dichloromethane) or alumina and copper catalyst (hexane). Deuterated chloroform was vacuum distilled from $AlCl_3$ and then CaH_2. C_6D_6 was vacuum distilled from Na/benzophenone. NMR spectra were recorded at 400 MHz (^1H) or 161.975 ($^{31}P\{^1H\}$). $Cl_2PN^iPr_2$ was prepared according to the literature procedure.[1] $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were obtained from Strem Chemicals. All other reagents were obtained from Aldrich and were used as received.

a) **$[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$** (**1**): 2.067 g (5.300 mmol) of $Mn_2(CO)_{10}$ was added slowly to 1.900 g (14.054 mmol) of KC_8 in 20 mL of THF. The mixture was stirred for two hours and then was filtered through Celite. The solution was added dropwise via cannula to 1.070 g (5.300 mmol) of $Cl_2PN^iPr_2$ in 20 mL of THF at –80 ºC. After warming to room temperature the solution was stirred for 2 h and the solvent was then removed in vacuo. The residue was extracted repeatedly with ether (ca. 200 mL); the extracts were filtered through Celite and the solution was concentrated to ca. 40 mL and cooled to –45 ºC overnight. The solvent was then decanted and the red crystalline solid was dried in vacuo. Yield: 47 %. ^1H NMR (δ, C_6D_6, 25 ºC): 4.09 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, $CH(CH_3)_2$); 0.92 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, $CH(CH_3)_2$). ^{31}P NMR (δ, C_6D_6, 25 ºC): 731. IR (ν_{CO}, cm^{-1}, ether): 2073 (m); 2016(s); 1989 (s); 1959 (m); 1942 (s). Anal. Calcd. for $C_{14}H_{14}NO_8PMn_2$: C, 36.2; H, 3.0; N, 3.0. Found: C, 35.9; H, 3.0; N, 3.0.

b) **$[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}PN^iPr_2)]$** (**2a**): Solid $Co_2(CO)_8$ (3.044 g, 8.902 mmol) was added slowly to a suspension of 3.500 g (25.906 mmol) of KC_8 in 50 mL of THF. The mixture was stirred for 2 h and was then filtered through Celite. The solution was added dropwise at –15 to –10 °C to a THF solution of 1.798 g (8.898 mmol) $Cl_2PN^iPr_2$ and 3.422 g (8.902 mmol) of dppm. The mixture was warmed to room temperature, stirred for 1 h and then the solvent was removed in vacuo. The solid was extracted into 40 mL of a 1:1 mixture of ether and hexane; the extracts were filtered through Celite and then the solvent volume was decreased to approximately 20 mL. After cooling to –45 ºC overnight large brown crystals of **2a** had formed which were isolated by decanting the

solvent. Yield: 50 %. ^{1}H NMR (δ, C_6D_6, 25 ºC): 7.52-6.93 (br, m, 20H, $Ph_2PCH_2PPh_2$); 4.18 (br, s, 2H, $Ph_2PCH_2PPh_2$ or $CH(CH_3)_2$), 4.01 (br, s, 2H, $Ph_2PCH_2PPh_2$ or $CH(CH_3)_2$); 1.19 (br, s, 12H, $CH(CH_3)_2$). ^{31}P NMR (δ, C_6D_6, 25 ºC): 578 (br, s); 42 (d, $^{2}J_{PP}$ = 55.9 Hz). IR (ν_{CO}, cm^{-1}, ether): Anal. Calcd. For $C_{35}H_{30}NO_4P_3Co_2$: C, 56.9; H, 4.1; N 1.9. Found: C, 56.6; H, 3.8; N, 1.8.

c) **[$Mn_2(CO)_8(\mu,\eta^1,\eta^2$-P($N^iPr_2$)=N-R)]** (R = $SiMe_3$ (**3a**); $SnMe_3$ (**3b**); Ph (**3c**); adamantyl (**3d**): These compounds were prepared in a similar manner and only the synthesis of **3a** is described. 100 μL (0.754 mmol) of azidotrimethylsilane was added to a suspension of 351 mg (0.755 mmol) of [$Mn_2(CO)_8(\mu$-PN^iPr_2)] in 5 mL of ether. The mixture was stirred overnight and then the solvent was removed in vacuo. The residue was extracted into a minimum volume of ether, filtered and then cooled to –45 ºC overnight resulting in the formation of a red crystalline solid. **3a** (R = $SiMe_3$): Yield 69 %. ^{1}H NMR (δ, $CDCl_3$, 25 ºC): 4.33 (s, br, 2H, $CH(CH_3)_2$); 1.48 (s, br, 12H, $CH(CH_3)_2$); 0.18 (s, br, 9H, $Si(CH_3)_3$). ^{31}P NMR (δ, $CDCl_3$, 25 ºC): 216. IR (ν_{CO}, cm^{-1}, ether): 2075 (m); 2024 (s); 2018 (s), 1989 (s); 1974 (s), 1962 (s), 1943 (m). Anal. Calcd. for $C_{17}H_{25}N_2O_8PSiMn_2$: C, 36.8; H, 4.5; N, 5.1. Found: C, 36.6; H, 4.0; N, 4.7. Mass spectrum: Calcd. M^+ m/z = 554.3; found m/z = 554.4. **3b** (R = $SnMe_3$): Yield 75 %. ^{1}H NMR (δ, C_6D_6, 25 ºC): 3.93 (sept., $^{3}J_{HH}$ = 6.7 Hz, 2H, $CH(CH_3)_2$); 1.02 (d, $^{3}J_{HH}$ = 6.7 Hz, 12H, $CH(CH_3)_2$); 0.18 (pseudotriplet, $^{2}J_{SnH}$ = 55.2 Hz, 9H, $Sn(CH_3)_3$). ^{31}P NMR (δ, C_6D_6, 25 ºC): 220. IR (ν_{CO}, cm^{-1}, ether): 2070 (m); 2017 (s); 1982 (s); 1966 (s); 1955 (m); 1935 (m). Anal. Calcd. for $C_{17}H_{23}N_2O_8SnMn_2$: C, 31.8; H, 3.6; N, 4.4. Found: 31.9; H, 3.6; N, 4.4. **3c** (R = Ph): Yield: 70 %. ^{1}H NMR (δ, C_6D_6, 25 ºC): 6.93 (m, 2H, C_6H_5); 6.73 (m, 3H, C_6H_5); 3.41 (sept., $^{3}J_{HH}$ = 6.9 Hz, 2H, $CH(CH_3)_2$); 0.82 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$). ^{31}P NMR (δ, C_6D_6, 25 ºC): 197. IR (ν_{CO}, cm^{-1}, ether): 2078 (m); 2029 (s); 1992 (s); 1977 (s); 1963 (s); 1942 (m). Anal. Calcd. for $C_{20}H_{19}N_2O_8PMn_2$: C, 43.2; H, 3.4; N, 5.0. Found: C, 43.0; H, 3.6; N, 4.6. **3d** (R = adamantyl): Note – reaction mixture stirred in THF for four days. Yield 75 %. ^{1}H NMR (δ, C_6D_6, 25 ºC). 3.31 (sept., $^{3}J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$); 1.94-1.91 (m, 6H, CH_2); 1.45 (s, 6H, CH_2); 0.99 (br s, 12H, $CH(CH_3)_2$). ^{31}P NMR (δ, C_6D_6, 25 ºC): 155. Anal. Calcd. for $C_{24}H_{27}N_2O_8PMn_2$:

C, 47.1; H, 4.4; N, 4.6. Found: C, 47.2; H, 4.9; N, 4.8. Mass spectrum: Calcd. M^+ m/z = 612.3; found m/z = 612.0.

d) **$[Co_2(CO)_4(\mu,\eta^1\text{-}\eta^2\text{-}P(NR_2)=CH_2)(\mu\text{-dppm})]$ (NR_2 = N^iPr_2 (4a), TMP (4b))**: These complexes were prepared in a similar manner and only the synthesis of **4a** is described. Diazomethane was generated by adding three drops of 6.0 M aqueous KOH to a methanol suspension of 300 mg (1.400 mmol) of Diazald. The diazomethane vapor was passed through a solution of 300 mg (0.402 mmol) $[Co_2(CO)_2(\mu\text{-dppm})(\mu\text{-}PN^iPr_2)]$ in 10 ml of THF at –80 ºC and the mixture was then stirred at room temperature for 20 minutes. The solvent was removed in vacuo and the residue was then extracted with hexane (ca. 5×5 ml). The hexane extracts were filtered through Celite and concentrated in vacuo to ca. 2 ml and then cooled to –45 ºC overnight, resulting in the formation of a brown crystalline powder. Analytically pure material was obtained by recrystallization from ether at –45 °C. **4a**: Yield: 45 %. ^{1}H NMR (δ, $CDCl_3$, 25 ºC): 7.70-7.12 (m, 20 H, C_6H_5); 4.20 (dt, $^2J_{HH}$ = 14.0 Hz, $^2J_{PH}$ = 9.8 Hz, 1H, $Ph_2PCH_2PPh_2$); 3.89 (sept., $^3J_{HH}$ = 6.7 Hz, 2H, $CH(CH_3)_2$); 3.73 (dt, $^2J_{HH}$ = 14.1 Hz, $^2J_{PH}$ = 9.4 Hz, 1H, $Ph_2PCH_2PPh_2$); 2.01 (dd, $^2J_{HH}$ = 5.9 Hz, J_{HP} = 10.8 Hz, 1H, =C*H*H); 1.41 (d, $^3J_{HH}$ = 6.7 Hz, 6H, $CH(CH_3)_2$); 1.27 (d, $^3J_{HH}$ = 6.7 Hz, 6H, $CH(CH_3)_2$), 0.71 (ddd, $^2J_{HH}$ = 5.9 Hz, $^2J_{PH}$ = 15.4 Hz, $^3J_{PH}$ = 20.2 Hz, 1H, =C*H*H). ^{31}P NMR (δ, $CDCl_3$, 25 ºC): 247 (m); 46 (m), 38 (m). ^{13}C NMR (δ, $CDCl_3$, 25 ºC): 133.6 (d, J_{PC}= 13.7 Hz, C_6H_5); 132.3 (d, J_{PC}= 12.2 Hz, C_6H_5); 132.1 (d, J_{PC}= 12.1 Hz, C_6H_5); 131.5 (d, J_{PC}= 11.4 Hz, C_6H_5); 130.0 (d, J_{PC}= 39.4 Hz, C_6H_5); 129.5 (d, J_{PC}= 25.6 Hz, C_6H_5); 128.6 (s, C_6H_5); 128.5 (s, C_6H_5); 128.4 (s, C_6H_5); 128.3 (s, C_6H_5); 50.3 (s, $CH(CH_3)_2$); 24.0 (br, P=CH_2); 22.3 (s, $CH(CH_3)_2$). IR (ν_{CO}, cm^{-1}, ether): 1995 (s); 1958 (s); 1945 (s); 1906 (s). Anal. Calcd. for $C_{36}H_{41}NO_4P_3Co_2$: C, 56.7; H, 5.4; N, 1.3. Found: C, 56.9; H, 5.1; N, 1.6. Yield: **4b**: Yield: 52 %. ^{1}H NMR (δ, $CDCl_3$, 25 ºC): 7.76-7.09 (m, 20H, C_6H_5); 4.02 (dt, $^2J_{HH}$ = 14.2 Hz, $^2J_{PH}$ = 9.9 Hz, 1H, $Ph_2CH_2Ph_2$); 3.62 (dt, $^2J_{HH}$ = 14.4 Hz, $^2J_{PH}$ = 9.5 Hz, 1H, $Ph_2CH_2Ph_2$); 1.80-1.66 (m, 13H, CH_3/CH_2 of TMP and =C*H*H); 0.52 (ddd, $^2J_{HH}$ = 5.3 Hz, $^2J_{PH}$ = 14.3 Hz, $^3J_{PH}$ = 25.6 Hz, 1H, $Ph_2CH_2Ph_2$). ^{31}P NMR (δ, $CDCl_3$, 25 ºC): 228 (m), 51 (m), 42 (m). ^{13}C NMR (δ, $CDCl_3$, 25 ºC): 133.8 (d, J_{PC}=13.4 Hz, C_6H_5); 132.0 (d, J_{PC}= 12.3 Hz, C_6H_5); 131.5 (d, J_{PC}=11.3 Hz, C_6H_5); 130.0 (d, J_{PC}=34.1 Hz, C_6H_5); 129.5 (d, 129.5, J_{PC}=32.5 Hz, C_6H_5);

128.8 (s, C_6H_5); 128.7 (s, C_6H_5); 128.6 (s, C_6H_5); 128.4 (s, C_6H_5); 59.0 (s, CH_2); 41.6 (s, CH_2); 31.7 (s, $=CH_2$); 17.5 (s, CH_3). IR (ν_{CO}, cm^{-1}, ether): 1985 (s); 1968 (s); 1955 (sh), 1900 (s). Anal. Calcd. for $C_{40}H_{45}NO_4P_3Co_2$: C, 59.0; H, 5.6; N, 1.7. Found: C, 58.8; H, 5.3; N, 1.6.

e) **$[Mn_2(CO)_8(\mu,\eta^2\text{-}P(N^iPr_2)=N\text{-}N=CPh_2)]$** (**5**): 125 mg (0.645 mmol) of diphenyldiazomethane in 2 mL of THF was added at –45 ºC to 300 mg (0.645 mmol) $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ in 2 mL of THF. The mixture was kept at –45 ºC for one hour and then was stirred at room temperature for one hour. The solvent was removed in vacuo and the solid was crystallized from a minimum volume of ether at –45 ºC. Yield: 60 %. ^1H NMR (δ, C_6D_6, 25 ºC): 7.85 (m, 2H, C_6H_5); 7.10-6.93 (m, 8H, C_6H_5); 3.73 (sept., $^3J_{HH}$ = 6.9 Hz, 2H, $CH(CH_3)_2$); 3.25 (q, $^3J_{HH}$ = 7.0 Hz, $O(CH_2CH_3)_2$); 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$); 1.15 (t, $^3J_{HH}$ = 7.0 Hz, $O(CH_2CH_3)_2$); 1.00 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$). ^{31}P NMR (δ, C_6D_6, 25 °C): 285. IR (ν_{CO}, cm^{-1}, ether): 2084 (w); 2009 (s); 1965 (m); 1921 (m); 1906 (m). Note: this complex has a variable amount of co-crystallised ether and a proper elemental analysis could not be obtained. Mass spectrum: Calcd. M^+ m/z = 659.4; found m/z = 660.1.

References

1. R. B. King, N. D. Sadanani *Synth. React. Inorg. Met.-Org. Chem*. **1985**, *15(2)*, 149.

Supplementary Material (ESI) for Chemical Communications

Crystallographic Data for Compounds **1**, **3a**, **3c**, **4b**, **5.**

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ (**1**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn(1)	2987(1)	7284(1)	1548(1)	20(1)
Mn(2)	2536(1)	8421(1)	3442(1)	21(1)
P(1)	1682(1)	6293(1)	2505(1)	19(1)
N(1)	1210(2)	4568(1)	2495(1)	23(1)
O(1)	6782(2)	6193(1)	2115(1)	31(1)
O(2)	5413(2)	9970(1)	1303(1)	52(1)
O(3)	-843(2)	8271(1)	884(1)	37(1)
O(4)	2589(2)	5156(1)	-237(1)	40(1)
O(5)	6440(2)	7637(1)	4187(1)	36(1)
O(6)	1084(2)	8553(1)	5197(1)	39(1)
O(7)	4849(2)	11363(1)	3534(1)	49(1)
O(8)	-1255(2)	9541(1)	2876(1)	34(1)
C(1)	5344(2)	6630(1)	1902(1)	24(1)
C(2)	4499(2)	8955(2)	1411(1)	32(1)
C(3)	595(2)	7907(1)	1164(1)	26(1)
C(4)	2753(2)	5996(2)	454(1)	27(1)
C(5)	4948(2)	7914(1)	3887(1)	26(1)
C(6)	1661(2)	8519(1)	4523(1)	28(1)
C(7)	3969(2)	10236(2)	3501(1)	32(1)
C(8)	170(2)	9079(1)	3068(1)	26(1)
C(9)	874(2)	4016(2)	3297(1)	30(1)
C(10)	2726(2)	4509(2)	4038(1)	35(1)
C(11)	-1089(2)	4403(2)	3634(1)	38(1)
C(12)	1033(2)	3421(1)	1606(1)	27(1)
C(13)	-1013(2)	2407(2)	1385(1)	38(1)
C(14)	2831(2)	2603(2)	1603(1)	41(1)

Table 2. Bond lengths [Å] and angles [°] for $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ (**1**).

Mn(1)-C(4)	1.7990(13)
Mn(1)-C(1)	1.8391(12)
Mn(1)-C(2)	1.8405(14)
Mn(1)-C(3)	1.8570(13)
Mn(1)-P(1)	2.1439(4)
Mn(1)-Mn(2)	2.9193(4)
Mn(2)-C(6)	1.8139(14)
Mn(2)-C(7)	1.8369(14)
Mn(2)-C(5)	1.8443(13)
Mn(2)-C(8)	1.8547(13)
Mn(2)-P(1)	2.1376(4)
P(1)-N(1)	1.6242(10)
N(1)-C(9)	1.4886(15)
N(1)-C(12)	1.5069(16)
O(1)-C(1)	1.1394(15)
O(2)-C(2)	1.1318(17)
O(3)-C(3)	1.1364(16)
O(4)-C(4)	1.1470(17)
O(5)-C(5)	1.1384(16)
O(6)-C(6)	1.1445(17)
O(7)-C(7)	1.1395(18)
O(8)-C(8)	1.1371(16)
C(9)-C(10)	1.5195(19)
C(9)-C(11)	1.5195(19)
C(12)-C(14)	1.5116(18)
C(12)-C(13)	1.5157(19)
C(4)-Mn(1)-C(1)	89.07(6)
C(4)-Mn(1)-C(2)	103.24(6)
C(1)-Mn(1)-C(2)	90.51(6)
C(4)-Mn(1)-C(3)	89.50(6)
C(1)-Mn(1)-C(3)	178.57(5)
C(2)-Mn(1)-C(3)	89.98(6)

C(4)-Mn(1)-P(1)	112.07(4)
C(1)-Mn(1)-P(1)	85.86(4)
C(2)-Mn(1)-P(1)	144.41(5)
C(3)-Mn(1)-P(1)	94.53(4)
C(4)-Mn(1)-Mn(2)	158.96(4)
C(1)-Mn(1)-Mn(2)	90.04(4)
C(2)-Mn(1)-Mn(2)	97.78(5)
C(3)-Mn(1)-Mn(2)	91.23(4)
P(1)-Mn(1)-Mn(2)	46.922(10)
C(6)-Mn(2)-C(7)	107.85(6)
C(6)-Mn(2)-C(5)	89.64(6)
C(7)-Mn(2)-C(5)	88.37(6)
C(6)-Mn(2)-C(8)	88.24(6)
C(7)-Mn(2)-C(8)	88.23(6)
C(5)-Mn(2)-C(8)	175.25(5)
C(6)-Mn(2)-P(1)	113.29(4)
C(7)-Mn(2)-P(1)	138.84(5)
C(5)-Mn(2)-P(1)	90.91(4)
C(8)-Mn(2)-P(1)	93.84(4)
C(6)-Mn(2)-Mn(1)	159.97(4)
C(7)-Mn(2)-Mn(1)	91.91(5)
C(5)-Mn(2)-Mn(1)	94.25(4)
C(8)-Mn(2)-Mn(1)	89.18(4)
P(1)-Mn(2)-Mn(1)	47.104(9)
N(1)-P(1)-Mn(2)	140.12(4)
N(1)-P(1)-Mn(1)	129.61(4)
Mn(2)-P(1)-Mn(1)	85.974(14)
C(9)-N(1)-C(12)	116.53(10)
C(9)-N(1)-P(1)	125.04(9)
C(12)-N(1)-P(1)	118.41(8)
O(1)-C(1)-Mn(1)	178.46(11)
O(2)-C(2)-Mn(1)	178.20(16)
O(3)-C(3)-Mn(1)	176.39(11)
O(4)-C(4)-Mn(1)	178.81(13)
O(5)-C(5)-Mn(2)	177.77(12)

O(6)-C(6)-Mn(2)	178.59(13)
O(7)-C(7)-Mn(2)	179.58(14)
O(8)-C(8)-Mn(2)	176.51(11)
N(1)-C(9)-C(10)	111.96(11)
N(1)-C(9)-C(11)	111.28(10)
C(10)-C(9)-C(11)	112.93(12)
N(1)-C(12)-C(14)	110.38(11)
N(1)-C(12)-C(13)	111.34(11)
C(14)-C(12)-C(13)	112.98(12)

Symmetry transformations used to generate equivalent atoms:

Table 3. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ (**1**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	19(1)	19(1)	22(1)	5(1)	4(1)	3(1)
Mn(2)	22(1)	19(1)	21(1)	2(1)	1(1)	4(1)
P(1)	20(1)	18(1)	20(1)	4(1)	3(1)	3(1)
N(1)	23(1)	20(1)	27(1)	7(1)	4(1)	5(1)
O(1)	26(1)	36(1)	32(1)	8(1)	4(1)	11(1)
O(2)	34(1)	35(1)	100(1)	34(1)	21(1)	6(1)
O(3)	34(1)	47(1)	33(1)	12(1)	4(1)	18(1)
O(4)	44(1)	44(1)	28(1)	-1(1)	7(1)	9(1)
O(5)	30(1)	40(1)	37(1)	10(1)	-1(1)	11(1)
O(6)	44(1)	50(1)	25(1)	6(1)	7(1)	16(1)
O(7)	46(1)	27(1)	66(1)	14(1)	-11(1)	-4(1)
O(8)	33(1)	37(1)	32(1)	3(1)	0(1)	15(1)
C(1)	25(1)	23(1)	23(1)	4(1)	5(1)	3(1)
C(2)	24(1)	28(1)	49(1)	14(1)	10(1)	8(1)
C(3)	28(1)	28(1)	23(1)	7(1)	6(1)	6(1)
C(4)	26(1)	30(1)	27(1)	8(1)	6(1)	6(1)
C(5)	27(1)	25(1)	24(1)	3(1)	3(1)	4(1)
C(6)	28(1)	28(1)	24(1)	1(1)	0(1)	8(1)
C(7)	30(1)	26(1)	37(1)	6(1)	-5(1)	5(1)
C(8)	29(1)	23(1)	22(1)	1(1)	3(1)	5(1)
C(9)	33(1)	29(1)	31(1)	14(1)	8(1)	6(1)
C(10)	42(1)	39(1)	28(1)	12(1)	5(1)	12(1)
C(11)	37(1)	47(1)	37(1)	19(1)	15(1)	10(1)
C(12)	31(1)	22(1)	27(1)	3(1)	3(1)	3(1)
C(13)	40(1)	34(1)	34(1)	5(1)	0(1)	-5(1)
C(14)	45(1)	41(1)	38(1)	3(1)	7(1)	21(1)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Mn_2(CO)_8(\mu\text{-}PN^iPr_2)]$ (**1**).

	x	y	z	U(eq)
H(9)	689	2917	3090	35
H(10A)	3966	4339	3771	42
H(10B)	2581	3945	4486	42
H(10C)	2825	5560	4333	42
H(11A)	-964	5475	3856	45
H(11B)	-1334	3952	4126	45
H(11C)	-2237	4032	3135	45
H(12)	1099	3952	1123	33
H(13A)	-1094	1820	1825	46
H(13B)	-1149	1749	775	46
H(13C)	-2118	2994	1414	46
H(14A)	4108	3311	1760	49
H(14B)	2778	1942	1000	49
H(14C)	2773	2027	2048	49

Table 5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for [$Mn_2(CO)_8(\mu$–η^1,η^2-P(N^iPr_2)=NTMS)] (**3a**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn(1)	1809(1)	4566(1)	1868(1)	16(1)
Mn(2)	3769(1)	4297(1)	2932(1)	17(1)
P(1)	2855(1)	5600(1)	3259(1)	15(1)
Si(1)	1273(1)	4593(1)	3884(1)	19(1)
N(1)	2966(1)	7150(1)	3446(1)	17(1)
N(2)	1924(1)	5053(1)	3263(1)	18(1)
O(1)	-213(1)	4278(1)	887(1)	38(1)
O(2)	1966(1)	1749(1)	2204(1)	30(1)
O(3)	2230(1)	3996(1)	221(1)	31(1)
O(4)	1440(1)	7255(1)	1199(1)	28(1)
O(5)	3453(1)	2432(1)	4227(1)	36(1)
O(6)	4039(1)	2142(1)	1825(1)	38(1)
O(7)	5656(1)	4655(1)	4356(1)	33(1)
O(8)	4184(1)	6038(1)	1633(1)	33(1)
C(1)	567(1)	4376(1)	1289(1)	25(1)
C(2)	1943(1)	2826(1)	2132(1)	22(1)
C(3)	2070(1)	4223(1)	859(1)	22(1)
C(4)	1618(1)	6254(1)	1491(1)	20(1)
C(5)	3551(1)	3143(1)	3724(1)	24(1)
C(6)	3939(1)	2970(1)	2249(1)	25(1)
C(7)	4930(1)	4514(1)	3799(1)	23(1)
C(8)	4006(1)	5405(1)	2133(1)	22(1)
C(9)	2221(1)	7850(1)	3620(1)	21(1)
C(10)	2431(1)	7939(1)	4659(1)	28(1)
C(11)	1987(1)	9149(1)	3155(1)	26(1)
C(12)	3826(1)	7773(1)	3476(1)	22(1)
C(13)	3678(1)	8578(1)	2609(1)	30(1)
C(14)	4332(1)	8524(1)	4369(1)	31(1)
C(15)	729(1)	3015(1)	3462(1)	29(1)

C(16)	324(1)	5750(1)	3726(1)	32(1)
C(17)	2026(1)	4446(1)	5144(1)	31(1)

Table 6. Bond lengths [Å] and angles [°] for $[Mn_2(CO)_8(\mu-\eta^1,\eta^2\text{-}P(N^iPr_2)=NTMS)]$ (**3a**) .

Mn(1)-C(3)	1.8113(12)
Mn(1)-C(1)	1.8143(12)
Mn(1)-C(4)	1.8551(12)
Mn(1)-C(2)	1.8674(12)
Mn(1)-N(2)	2.1717(9)
Mn(1)-P(1)	2.4084(3)
Mn(1)-Mn(2)	2.8888(3)
Mn(2)-C(7)	1.8120(12)
Mn(2)-C(6)	1.8358(12)
Mn(2)-C(8)	1.8466(12)
Mn(2)-C(5)	1.8560(12)
Mn(2)-P(1)	2.1857(3)
P(1)-N(2)	1.5756(9)
P(1)-N(1)	1.6512(9)
Si(1)-N(2)	1.7297(9)
Si(1)-C(17)	1.8617(13)
Si(1)-C(15)	1.8633(13)
Si(1)-C(16)	1.8656(13)
N(1)-C(12)	1.4873(13)
N(1)-C(9)	1.4935(13)
O(1)-C(1)	1.1431(15)
O(2)-C(2)	1.1364(15)
O(3)-C(3)	1.1435(15)
O(4)-C(4)	1.1357(15)
O(5)-C(5)	1.1356(15)
O(6)-C(6)	1.1397(15)
O(7)-C(7)	1.1416(15)
O(8)-C(8)	1.1394(15)
C(9)-C(11)	1.5213(16)
C(9)-C(10)	1.5247(16)
C(12)-C(14)	1.5265(17)
C(12)-C(13)	1.5333(17)

C(3)-Mn(1)-C(1)	96.36(5)
C(3)-Mn(1)-C(4)	88.77(5)
C(1)-Mn(1)-C(4)	86.46(5)
C(3)-Mn(1)-C(2)	87.22(5)
C(1)-Mn(1)-C(2)	90.50(5)
C(4)-Mn(1)-C(2)	174.67(5)
C(3)-Mn(1)-N(2)	163.45(4)
C(1)-Mn(1)-N(2)	100.18(5)
C(4)-Mn(1)-N(2)	91.88(4)
C(2)-Mn(1)-N(2)	92.96(4)
C(3)-Mn(1)-P(1)	124.41(4)
C(1)-Mn(1)-P(1)	136.21(4)
C(4)-Mn(1)-P(1)	79.86(3)
C(2)-Mn(1)-P(1)	105.31(4)
N(2)-Mn(1)-P(1)	39.82(2)
C(3)-Mn(1)-Mn(2)	85.74(4)
C(1)-Mn(1)-Mn(2)	167.17(4)
C(4)-Mn(1)-Mn(2)	106.27(3)
C(2)-Mn(1)-Mn(2)	76.93(3)
N(2)-Mn(1)-Mn(2)	78.20(2)
P(1)-Mn(1)-Mn(2)	47.680(8)
C(7)-Mn(2)-C(6)	101.30(5)
C(7)-Mn(2)-C(8)	90.82(5)
C(6)-Mn(2)-C(8)	88.51(5)
C(7)-Mn(2)-C(5)	88.89(5)
C(6)-Mn(2)-C(5)	89.82(6)
C(8)-Mn(2)-C(5)	178.21(5)
C(7)-Mn(2)-P(1)	108.07(4)
C(6)-Mn(2)-P(1)	150.34(4)
C(8)-Mn(2)-P(1)	95.00(4)
C(5)-Mn(2)-P(1)	86.77(4)
C(7)-Mn(2)-Mn(1)	162.61(4)
C(6)-Mn(2)-Mn(1)	96.08(4)
C(8)-Mn(2)-Mn(1)	90.10(4)
C(5)-Mn(2)-Mn(1)	90.71(4)

P(1)-Mn(2)-Mn(1)	54.562(9)
N(2)-P(1)-N(1)	113.15(5)
N(2)-P(1)-Mn(2)	118.04(4)
N(1)-P(1)-Mn(2)	128.69(3)
N(2)-P(1)-Mn(1)	61.97(3)
N(1)-P(1)-Mn(1)	126.23(4)
Mn(2)-P(1)-Mn(1)	77.758(11)
N(2)-Si(1)-C(17)	110.00(5)
N(2)-Si(1)-C(15)	109.93(5)
C(17)-Si(1)-C(15)	108.28(6)
N(2)-Si(1)-C(16)	111.30(5)
C(17)-Si(1)-C(16)	109.84(7)
C(15)-Si(1)-C(16)	107.41(6)
C(12)-N(1)-C(9)	123.10(9)
C(12)-N(1)-P(1)	118.09(7)
C(9)-N(1)-P(1)	118.74(7)
P(1)-N(2)-Si(1)	149.12(6)
P(1)-N(2)-Mn(1)	78.21(4)
Si(1)-N(2)-Mn(1)	131.22(5)
O(1)-C(1)-Mn(1)	176.83(11)
O(2)-C(2)-Mn(1)	173.21(11)
O(3)-C(3)-Mn(1)	179.41(11)
O(4)-C(4)-Mn(1)	174.42(10)
O(5)-C(5)-Mn(2)	177.36(11)
O(6)-C(6)-Mn(2)	179.52(11)
O(7)-C(7)-Mn(2)	178.91(11)
O(8)-C(8)-Mn(2)	176.07(11)
N(1)-C(9)-C(11)	114.60(9)
N(1)-C(9)-C(10)	111.35(9)
C(11)-C(9)-C(10)	111.25(10)
N(1)-C(12)-C(14)	113.51(10)
N(1)-C(12)-C(13)	113.11(9)
C(14)-C(12)-C(13)	111.42(10)

Symmetry transformations used to generate equivalent atoms:

Supplementary Material (ESI) for Chemical Communications

Table 7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Mn_2(CO)_8(\mu–\eta^1,\eta^2\text{-}P(N^iPr_2)=NTMS)]$ (**3a**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	15(1)	17(1)	16(1)	0(1)	6(1)	-1(1)
Mn(2)	15(1)	18(1)	18(1)	0(1)	6(1)	1(1)
P(1)	14(1)	16(1)	16(1)	0(1)	6(1)	0(1)
Si(1)	17(1)	21(1)	20(1)	3(1)	9(1)	0(1)
N(1)	16(1)	16(1)	21(1)	-1(1)	8(1)	-1(1)
N(2)	17(1)	21(1)	18(1)	0(1)	8(1)	-2(1)
O(1)	20(1)	49(1)	38(1)	6(1)	4(1)	-7(1)
O(2)	34(1)	20(1)	34(1)	1(1)	12(1)	-3(1)
O(3)	43(1)	29(1)	26(1)	-3(1)	19(1)	0(1)
O(4)	35(1)	24(1)	25(1)	4(1)	11(1)	5(1)
O(5)	33(1)	34(1)	39(1)	14(1)	13(1)	1(1)
O(6)	31(1)	37(1)	45(1)	-17(1)	12(1)	3(1)
O(7)	21(1)	44(1)	29(1)	3(1)	3(1)	-3(1)
O(8)	33(1)	41(1)	27(1)	6(1)	13(1)	-5(1)
C(1)	23(1)	26(1)	24(1)	3(1)	8(1)	-2(1)
C(2)	21(1)	24(1)	20(1)	-2(1)	8(1)	-3(1)
C(3)	23(1)	18(1)	23(1)	0(1)	8(1)	-2(1)
C(4)	19(1)	24(1)	18(1)	-1(1)	8(1)	0(1)
C(5)	19(1)	23(1)	27(1)	2(1)	6(1)	3(1)
C(6)	18(1)	28(1)	29(1)	-3(1)	7(1)	1(1)
C(7)	22(1)	25(1)	23(1)	2(1)	10(1)	2(1)
C(8)	18(1)	27(1)	20(1)	-2(1)	6(1)	1(1)
C(9)	20(1)	20(1)	24(1)	0(1)	11(1)	3(1)
C(10)	35(1)	27(1)	26(1)	-2(1)	16(1)	5(1)
C(11)	26(1)	21(1)	31(1)	2(1)	11(1)	5(1)
C(12)	18(1)	20(1)	29(1)	-1(1)	10(1)	-3(1)
C(13)	28(1)	28(1)	39(1)	7(1)	19(1)	-2(1)
C(14)	24(1)	27(1)	38(1)	-8(1)	6(1)	-6(1)
C(15)	31(1)	27(1)	33(1)	1(1)	15(1)	-9(1)
C(16)	24(1)	34(1)	44(1)	5(1)	19(1)	5(1)

C(17)	33(1)	37(1)	22(1)	6(1)	10(1)	-3(1)

Table 8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Mn_2(CO)_8(\mu–\eta^1,\eta^2\text{-}P(N^iPr_2)=NTMS)]$ (**3a**).

	x	y	z	U(eq)
H(9)	1650	7320	3340	25
H(10A)	2639	7108	4951	33
H(10B)	1871	8193	4747	33
H(10C)	2916	8573	4946	33
H(11A)	2518	9718	3428	31
H(11B)	1455	9506	3252	31
H(11C)	1834	9058	2485	31
H(12)	4251	7067	3473	27
H(13A)	3275	8118	2051	36
H(13B)	4275	8741	2569	36
H(13C)	3389	9389	2652	36
H(14A)	3963	9268	4386	38
H(14B)	4932	8805	4386	38
H(14C)	4425	7980	4910	38
H(15A)	331	3073	2798	35
H(15B)	360	2763	3814	35
H(15C)	1212	2379	3551	35
H(16A)	588	6578	3982	38
H(16B)	-56	5438	4053	38
H(16C)	-61	5840	3061	38
H(17A)	2497	3794	5226	37
H(17B)	1650	4202	5492	37
H(17C)	2327	5264	5376	37

Table 9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[Mn_2(CO)_8(\mu\text{–}\eta^1,\eta^2\text{-P(N}^i\text{Pr}_2\text{)=NPh)}]$ (**3c**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn(1)	8906(1)	4219(1)	1197(1)	22(1)
Mn(2)	6604(1)	2549(1)	666(1)	22(1)
P(1)	8701(1)	2056(1)	1357(1)	18(1)
O(1)	6615(2)	4385(1)	-167(1)	58(1)
O(2)	4520(1)	4484(1)	1105(1)	33(1)
O(5)	11551(1)	5452(1)	1791(1)	44(1)
O(7)	8668(1)	768(1)	163(1)	44(1)
O(9)	3878(1)	1101(1)	204(1)	46(1)
O(14)	6963(1)	4696(1)	1976(1)	46(1)
O(15)	10807(1)	3604(1)	411(1)	50(1)
O(16)	7578(1)	6673(1)	674(1)	48(1)
N(1)	10007(1)	864(1)	1463(1)	21(1)
N(2)	7015(1)	1467(1)	1317(1)	21(1)
C(4)	5343(1)	3768(1)	951(1)	26(1)
C(6)	8107(2)	5729(1)	868(1)	33(1)
C(8)	7896(1)	1416(1)	367(1)	30(1)
C(10)	10519(1)	4982(1)	1560(1)	31(1)
C(11)	4935(1)	1637(1)	390(1)	31(1)
C(12)	10094(1)	3831(1)	712(1)	32(1)
C(13)	6344(1)	351(1)	1528(1)	23(1)
C(17)	6611(2)	3691(2)	161(1)	37(1)
C(18)	11532(1)	1139(1)	1744(1)	28(1)
C(19)	7677(1)	4522(1)	1670(1)	30(1)
C(20)	12613(1)	1914(1)	1460(1)	37(1)
C(21)	9687(1)	-595(1)	1332(1)	24(1)
C(22)	5678(1)	-723(1)	1252(1)	32(1)
C(23)	11359(2)	1810(1)	2224(1)	37(1)
C(24)	9623(2)	-1480(1)	1774(1)	32(1)
C(26)	10845(2)	-1133(1)	1016(1)	35(1)

C(27)	6314(1)	343(1)	2024(1)	33(1)
C(28)	5627(2)	-735(2)	2239(1)	49(1)
C(29)	5000(2)	-1799(1)	1475(1)	47(1)
C(30)	4971(2)	-1799(2)	1966(1)	55(1)

Table 10. Bond lengths [Å] and angles [°] for $[Mn_2(CO)_8(\mu\text{–}\eta^1,\eta^2\text{-}P(N^iPr_2)=NPh)]$ (**3c**).

Mn(1)-C(10)	1.8066(13)
Mn(1)-C(6)	1.8349(13)
Mn(1)-C(19)	1.8390(13)
Mn(1)-C(12)	1.8568(14)
Mn(1)-P(1)	2.1753(4) Å
Mn(1)-Mn(2)	2.8751(3)
Mn(2)-C(17)	1.8059(13)
Mn(2)-C(11)	1.8117(13)
Mn(2)-C(8)	1.8614(13)
Mn(2)-C(4)	1.8743(12)
Mn(2)-N(2)	2.1031(9)
Mn(2)-P(1)	2.5574(4)
P(1)-N(2)	1.5861(9)
P(1)-N(1)	1.6396(9)
O(1)-C(17)	1.1429(17)
O(2)-C(4)	1.1333(15)
O(5)-C(10)	1.1481(16)
O(7)-C(8)	1.1348(16)
O(9)-C(11)	1.1392(16)
O(14)-C(19)	1.1389(17)
O(15)-C(12)	1.1350(17)
O(16)-C(6)	1.1420(16)
N(1)-C(21)	1.4916(13)
N(1)-C(18)	1.4984(14)
N(2)-C(13)	1.4071(13)
C(13)-C(22)	1.3916(17)
C(13)-C(27)	1.3956(17)
C(18)-C(20)	1.5183(18)
C(18)-C(23)	1.5221(19)
C(21)-C(24)	1.5207(17)
C(21)-C(26)	1.5262(16)
C(22)-C(29)	1.3943(18)
C(27)-C(28)	1.3895(19)

C(28)-C(30)	1.376(3)
C(29)-C(30)	1.383(3)

C(10)-Mn(1)-C(6)	100.31(6)
C(10)-Mn(1)-C(19)	91.10(6)
C(6)-Mn(1)-C(19)	90.53(6)
C(10)-Mn(1)-C(12)	91.23(6)
C(6)-Mn(1)-C(12)	90.75(6)
C(19)-Mn(1)-C(12)	177.11(5)
C(10)-Mn(1)-P(1)	111.33(4)
C(6)-Mn(1)-P(1)	148.23(4)
C(19)-Mn(1)-P(1)	86.29(4)
C(12)-Mn(1)-P(1)	91.26(4)
C(10)-Mn(1)-Mn(2)	169.73(4)
C(6)-Mn(1)-Mn(2)	89.62(4)
C(19)-Mn(1)-Mn(2)	91.40(4)
C(12)-Mn(1)-Mn(2)	86.02(4)
P(1)-Mn(1)-Mn(2)	58.917(10)
C(17)-Mn(2)-C(11)	92.82(6)
C(17)-Mn(2)-C(8)	87.28(6)
C(11)-Mn(2)-C(8)	91.45(5)
C(17)-Mn(2)-C(4)	90.05(6)
C(11)-Mn(2)-C(4)	90.06(5)
C(8)-Mn(2)-C(4)	177.00(5)
C(17)-Mn(2)-N(2)	167.49(5)
C(11)-Mn(2)-N(2)	99.68(5)
C(8)-Mn(2)-N(2)	92.43(5)
C(4)-Mn(2)-N(2)	89.88(4)
C(17)-Mn(2)-P(1)	129.85(4)
C(11)-Mn(2)-P(1)	134.90(4)
C(8)-Mn(2)-P(1)	78.67(4)
C(4)-Mn(2)-P(1)	102.05(4)
N(2)-Mn(2)-P(1)	38.25(2)
C(17)-Mn(2)-Mn(1)	89.16(5)
C(11)-Mn(2)-Mn(1)	170.47(4)

C(8)-Mn(2)-Mn(1)	97.96(4)
C(4)-Mn(2)-Mn(1)	80.61(4)
N(2)-Mn(2)-Mn(1)	78.49(3)
P(1)-Mn(2)-Mn(1)	46.758(9)
N(2)-P(1)-N(1)	112.82(5)
N(2)-P(1)-Mn(1)	116.03(3)
N(1)-P(1)-Mn(1)	130.81(4)
N(2)-P(1)-Mn(2)	55.18(3)
N(1)-P(1)-Mn(2)	134.25(4)
Mn(1)-P(1)-Mn(2)	74.325(10)
C(21)-N(1)-C(18)	115.59(8)
C(21)-N(1)-P(1)	121.81(7)
C(18)-N(1)-P(1)	122.25(7)
C(13)-N(2)-P(1)	133.65(8)
C(13)-N(2)-Mn(2)	136.05(7)
P(1)-N(2)-Mn(2)	86.57(4)
O(2)-C(4)-Mn(2)	176.46(11)
O(16)-C(6)-Mn(1)	177.89(14)
O(7)-C(8)-Mn(2)	176.24(12)
O(5)-C(10)-Mn(1)	179.25(12)
O(9)-C(11)-Mn(2)	177.47(13)
O(15)-C(12)-Mn(1)	179.05(13)
C(22)-C(13)-C(27)	119.51(11)
C(22)-C(13)-N(2)	121.41(11)
C(27)-C(13)-N(2)	119.06(11)
O(1)-C(17)-Mn(2)	178.22(15)
N(1)-C(18)-C(20)	113.17(10)
N(1)-C(18)-C(23)	111.27(10)
C(20)-C(18)-C(23)	112.73(11)
O(14)-C(19)-Mn(1)	177.36(12)
N(1)-C(21)-C(24)	111.63(9)
N(1)-C(21)-C(26)	110.63(9)
C(24)-C(21)-C(26)	111.88(10)
C(13)-C(22)-C(29)	119.67(14)
C(28)-C(27)-C(13)	120.00(14)

C(30)-C(28)-C(27)	120.47(16)
C(30)-C(29)-C(22)	120.51(15)
C(28)-C(30)-C(29)	119.84(13)

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Mn_2(CO)_8(\mu\text{–}\eta^1,\eta^2\text{-}P(N^iPr_2)=NPh)]$ (**3c**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	22(1)	17(1)	27(1)	2(1)	1(1)	0(1)
Mn(2)	22(1)	25(1)	19(1)	2(1)	1(1)	-1(1)
P(1)	19(1)	17(1)	18(1)	0(1)	2(1)	1(1)
O(1)	60(1)	73(1)	39(1)	29(1)	0(1)	-6(1)
O(2)	31(1)	31(1)	39(1)	2(1)	4(1)	6(1)
O(5)	32(1)	30(1)	65(1)	-9(1)	-11(1)	-1(1)
O(7)	36(1)	66(1)	31(1)	-16(1)	9(1)	4(1)
O(9)	33(1)	49(1)	52(1)	-14(1)	-9(1)	-4(1)
O(14)	42(1)	54(1)	44(1)	-21(1)	13(1)	-4(1)
O(15)	47(1)	59(1)	48(1)	2(1)	24(1)	-8(1)
O(16)	51(1)	30(1)	62(1)	15(1)	-5(1)	4(1)
N(1)	20(1)	18(1)	25(1)	0(1)	1(1)	2(1)
N(2)	21(1)	20(1)	21(1)	2(1)	1(1)	0(1)
C(4)	25(1)	24(1)	27(1)	6(1)	-2(1)	-1(1)
C(6)	31(1)	25(1)	43(1)	5(1)	0(1)	-2(1)
C(8)	27(1)	41(1)	21(1)	-3(1)	1(1)	-3(1)
C(10)	29(1)	20(1)	44(1)	-1(1)	1(1)	2(1)
C(11)	29(1)	34(1)	28(1)	-3(1)	1(1)	2(1)
C(12)	31(1)	29(1)	38(1)	6(1)	6(1)	-5(1)
C(13)	18(1)	21(1)	32(1)	6(1)	6(1)	4(1)
C(17)	35(1)	45(1)	29(1)	9(1)	-1(1)	-2(1)
C(18)	21(1)	23(1)	37(1)	1(1)	-4(1)	3(1)
C(19)	28(1)	24(1)	36(1)	-6(1)	0(1)	-1(1)
C(20)	20(1)	31(1)	60(1)	2(1)	6(1)	1(1)
C(21)	24(1)	19(1)	30(1)	-4(1)	5(1)	2(1)
C(22)	23(1)	23(1)	49(1)	4(1)	2(1)	0(1)
C(23)	40(1)	33(1)	33(1)	0(1)	-12(1)	0(1)
C(24)	34(1)	21(1)	43(1)	6(1)	9(1)	5(1)
C(26)	32(1)	33(1)	40(1)	-10(1)	11(1)	6(1)
C(27)	30(1)	38(1)	34(1)	11(1)	12(1)	10(1)

C(28)	38(1)	59(1)	55(1)	33(1)	24(1)	16(1)
C(29)	25(1)	26(1)	87(1)	15(1)	3(1)	-3(1)
C(30)	30(1)	48(1)	91(1)	40(1)	19(1)	3(1)

Table 12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Mn_2(CO)_8(\mu–\eta^1,\eta^2\text{-}P(N^iPr_2)=NPh)]$ (**3c**).

	x	y	z	U(eq)
H(18)	12011	225	1820	33
H(20A)	12647	1465	1150	56
H(20B)	13638	1922	1640	56
H(20C)	12250	2856	1408	56
H(21)	8657	-632	1139	29
H(22)	5684	-724	914	38
H(23A)	10960	2740	2169	55
H(23B)	12356	1849	2420	55
H(23C)	10649	1274	2391	55
H(24A)	10647	-1553	1952	48
H(24B)	9251	-2395	1676	48
H(24C)	8929	-1064	1980	48
H(26A)	10866	-529	739	52
H(26B)	10553	-2057	905	52
H(26C)	11860	-1159	1202	52
H(27)	6763	1074	2215	40
H(28)	5611	-738	2577	59
H(29)	4555	-2538	1287	56
H(30)	4499	-2530	2115	66

Table 13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^1,\eta^2\text{- P(TMP)=CH}_2)]$ (**4b**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	1090(1)	2898(1)	2901(1)	19(1)
Co(2)	1521(1)	4300(1)	3818(1)	18(1)
P(1)	1248(1)	4404(1)	2327(1)	18(1)
P(2)	2023(1)	5107(1)	3372(1)	17(1)
P(3)	932(1)	3165(1)	3735(1)	20(1)
O(1)	1974(1)	1689(2)	3042(1)	36(1)
O(2)	498(1)	1035(2)	2220(1)	45(1)
O(3)	2049(1)	3486(2)	4940(1)	41(1)
O(4)	1031(1)	6589(2)	3937(1)	33(1)
N(1)	751(1)	2243(2)	4212(1)	27(1)
C(2A)	523(1)	3701(2)	3150(1)	23(1)
C(1)	1629(1)	2182(2)	3005(1)	26(1)
C(2)	736(1)	1755(2)	2481(1)	28(1)
C(3)	1852(1)	3743(2)	4480(1)	26(1)
C(4)	1220(1)	5693(2)	3858(1)	22(1)
C(5)	1831(1)	5023(2)	2569(1)	20(1)
C(6)	895(1)	5803(2)	2205(1)	20(1)
C(7)	477(1)	5748(2)	1813(1)	31(1)
C(8)	200(1)	6790(2)	1710(1)	36(1)
C(9)	330(1)	7899(2)	2007(1)	32(1)
C(10)	737(1)	7955(2)	2409(1)	28(1)
C(11)	1020(1)	6915(2)	2507(1)	23(1)
C(12)	1288(1)	3933(2)	1587(1)	22(1)
C(13)	1293(1)	4796(2)	1145(1)	31(1)
C(14)	1371(1)	4405(2)	611(1)	36(1)
C(15)	1440(1)	3160(2)	508(1)	36(1)
C(16)	1439(1)	2291(2)	941(1)	35(1)
C(17)	1362(1)	2676(2)	1478(1)	29(1)
C(18)	2595(1)	4427(2)	3459(1)	19(1)

C(19)	2900(1)	4919(2)	3151(1)	24(1)
C(20)	3322(1)	4371(2)	3186(1)	27(1)
C(21)	3445(1)	3337(2)	3539(1)	27(1)
C(22)	3148(1)	2856(2)	3854(1)	34(1)
C(23)	2722(1)	3396(2)	3814(1)	29(1)
C(24)	2160(1)	6752(2)	3552(1)	20(1)
C(25)	2251(1)	7660(2)	3166(1)	26(1)
C(26)	2357(1)	8881(2)	3356(1)	30(1)
C(27)	2378(1)	9216(2)	3928(1)	31(1)
C(28)	2289(1)	8326(2)	4317(1)	31(1)
C(29)	2180(1)	7109(2)	4130(1)	26(1)
C(30)	891(1)	889(2)	4300(1)	36(1)
C(31)	956(1)	538(3)	4945(1)	53(1)
C(32)	573(1)	937(3)	5223(1)	61(1)
C(33)	496(1)	2331(3)	5145(1)	53(1)
C(34)	390(1)	2759(3)	4506(1)	37(1)
C(35)	1346(1)	654(2)	4137(1)	49(1)
C(36)	538(1)	25(2)	3921(1)	45(1)
C(37)	-92(1)	2364(3)	4199(1)	46(1)
C(38)	404(1)	4194(3)	4515(1)	43(1)

Table 14. Bond lengths [Å] and angles [°] for $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^1,\eta^2\text{- P(TMP)=CH}_2)]$ (**4b**).

Co(1)-C(1)	1.766(2)
Co(1)-C(2)	1.775(2)
Co(1)-C(2A)	2.105(2)
Co(1)-P(3)	2.1321(6)
Co(1)-P(1)	2.2135(6)
Co(1)-Co(2)	2.7143(5)
Co(2)-C(4)	1.755(2)
Co(2)-C(3)	1.762(2)
Co(2)-P(3)	2.1232(6)
Co(2)-P(2)	2.1948(6)
P(1)-C(6)	1.8196(19)
P(1)-C(12)	1.8392(19)
P(1)-C(5)	1.8498(19)
P(2)-C(24)	1.831(2)
P(2)-C(18)	1.8400(19)
P(2)-C(5)	1.8525(18)
P(3)-N(1)	1.6691(17)
P(3)-C(2A)	1.737(2)
O(1)-C(1)	1.151(2)
O(2)-C(2)	1.138(3)
O(3)-C(3)	1.149(2)
O(4)-C(4)	1.148(2)
N(1)-C(30)	1.506(3)
N(1)-C(34)	1.512(3)
C(6)-C(11)	1.392(3)
C(6)-C(7)	1.396(3)
C(7)-C(8)	1.381(3)
C(8)-C(9)	1.387(3)
C(9)-C(10)	1.382(3)
C(10)-C(11)	1.389(3)
C(12)-C(13)	1.391(3)
C(12)-C(17)	1.391(3)
C(13)-C(14)	1.388(3)

C(14)-C(15)	1.373(4)
C(15)-C(16)	1.377(3)
C(16)-C(17)	1.391(3)
C(18)-C(23)	1.383(3)
C(18)-C(19)	1.392(3)
C(19)-C(20)	1.386(3)
C(20)-C(21)	1.382(3)
C(21)-C(22)	1.378(3)
C(22)-C(23)	1.392(3)
C(24)-C(25)	1.394(3)
C(24)-C(29)	1.398(3)
C(25)-C(26)	1.392(3)
C(26)-C(27)	1.378(3)
C(27)-C(28)	1.384(3)
C(28)-C(29)	1.387(3)
C(30)-C(35)	1.523(4)
C(30)-C(31)	1.532(3)
C(30)-C(36)	1.539(3)
C(31)-C(32)	1.507(5)
C(32)-C(33)	1.510(5)
C(33)-C(34)	1.535(3)
C(34)-C(38)	1.532(4)
C(34)-C(37)	1.536(3)

C(1)-Co(1)-C(2)	101.91(10)
C(1)-Co(1)-C(2A)	156.49(8)
C(2)-Co(1)-C(2A)	90.33(9)
C(1)-Co(1)-P(3)	108.10(7)
C(2)-Co(1)-P(3)	112.14(7)
C(2A)-Co(1)-P(3)	48.40(6)
C(1)-Co(1)-P(1)	94.94(7)
C(2)-Co(1)-P(1)	110.01(7)
C(2A)-Co(1)-P(1)	99.65(6)
P(3)-Co(1)-P(1)	125.62(2)
C(1)-Co(1)-Co(2)	81.83(7)

C(2)-Co(1)-Co(2)	161.57(7)
C(2A)-Co(1)-Co(2)	80.53(6)
P(3)-Co(1)-Co(2)	50.222(18)
P(1)-Co(1)-Co(2)	87.41(2)
C(4)-Co(2)-C(3)	116.14(9)
C(4)-Co(2)-P(3)	93.15(7)
C(3)-Co(2)-P(3)	101.16(7)
C(4)-Co(2)-P(2)	96.39(7)
C(3)-Co(2)-P(2)	103.63(7)
P(3)-Co(2)-P(2)	146.02(2)
C(4)-Co(2)-Co(1)	110.04(6)
C(3)-Co(2)-Co(1)	126.87(7)
P(3)-Co(2)-Co(1)	50.511(16)
P(2)-Co(2)-Co(1)	95.70(2)
C(6)-P(1)-C(12)	103.27(9)
C(6)-P(1)-C(5)	103.96(9)
C(12)-P(1)-C(5)	97.91(8)
C(6)-P(1)-Co(1)	119.73(6)
C(12)-P(1)-Co(1)	116.38(7)
C(5)-P(1)-Co(1)	112.72(6)
C(24)-P(2)-C(18)	101.09(8)
C(24)-P(2)-C(5)	106.73(9)
C(18)-P(2)-C(5)	100.20(8)
C(24)-P(2)-Co(2)	114.19(6)
C(18)-P(2)-Co(2)	121.19(6)
C(5)-P(2)-Co(2)	111.65(6)
N(1)-P(3)-C(2A)	116.44(10)
N(1)-P(3)-Co(2)	131.51(6)
C(2A)-P(3)-Co(2)	108.92(8)
N(1)-P(3)-Co(1)	135.05(7)
C(2A)-P(3)-Co(1)	64.98(7)
Co(2)-P(3)-Co(1)	79.27(2)
C(30)-N(1)-C(34)	119.60(18)
C(30)-N(1)-P(3)	122.34(15)
C(34)-N(1)-P(3)	117.63(15)

P(3)-C(2A)-Co(1)	66.62(7)
O(1)-C(1)-Co(1)	176.24(18)
O(2)-C(2)-Co(1)	177.8(2)
O(3)-C(3)-Co(2)	172.7(2)
O(4)-C(4)-Co(2)	173.84(17)
P(1)-C(5)-P(2)	113.61(10)
C(11)-C(6)-C(7)	118.67(18)
C(11)-C(6)-P(1)	122.22(15)
C(7)-C(6)-P(1)	119.06(15)
C(8)-C(7)-C(6)	120.7(2)
C(7)-C(8)-C(9)	120.1(2)
C(10)-C(9)-C(8)	119.7(2)
C(9)-C(10)-C(11)	120.2(2)
C(10)-C(11)-C(6)	120.46(19)
C(13)-C(12)-C(17)	118.18(19)
C(13)-C(12)-P(1)	122.62(16)
C(17)-C(12)-P(1)	118.89(15)
C(14)-C(13)-C(12)	120.4(2)
C(15)-C(14)-C(13)	120.7(2)
C(14)-C(15)-C(16)	119.8(2)
C(15)-C(16)-C(17)	119.8(2)
C(12)-C(17)-C(16)	121.1(2)
C(23)-C(18)-C(19)	118.83(18)
C(23)-C(18)-P(2)	120.96(15)
C(19)-C(18)-P(2)	120.17(14)
C(20)-C(19)-C(18)	120.84(18)
C(21)-C(20)-C(19)	119.83(19)
C(22)-C(21)-C(20)	119.81(19)
C(21)-C(22)-C(23)	120.4(2)
C(18)-C(23)-C(22)	120.30(19)
C(25)-C(24)-C(29)	117.96(18)
C(25)-C(24)-P(2)	125.54(15)
C(29)-C(24)-P(2)	116.49(15)
C(26)-C(25)-C(24)	120.31(19)
C(27)-C(26)-C(25)	121.0(2)

C(26)-C(27)-C(28)	119.4(2)
C(27)-C(28)-C(29)	119.9(2)
C(28)-C(29)-C(24)	121.38(19)
N(1)-C(30)-C(35)	111.34(18)
N(1)-C(30)-C(31)	110.1(2)
C(35)-C(30)-C(31)	106.0(2)
N(1)-C(30)-C(36)	110.86(18)
C(35)-C(30)-C(36)	107.7(2)
C(31)-C(30)-C(36)	110.76(19)
C(32)-C(31)-C(30)	114.2(2)
C(31)-C(32)-C(33)	109.7(2)
C(32)-C(33)-C(34)	114.0(2)
N(1)-C(34)-C(38)	110.42(18)
N(1)-C(34)-C(33)	108.6(2)
C(38)-C(34)-C(33)	106.5(2)
N(1)-C(34)-C(37)	112.7(2)
C(38)-C(34)-C(37)	107.5(2)
C(33)-C(34)-C(37)	110.9(2)

Symmetry transformations used to generate equivalent atoms:

Table 15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^1,\eta^2\text{-P P(TMP)=CH}_2)]$ (**4b**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	23(1)	17(1)	18(1)	1(1)	4(1)	1(1)
Co(2)	17(1)	19(1)	17(1)	2(1)	5(1)	0(1)
P(1)	19(1)	18(1)	17(1)	1(1)	4(1)	2(1)
P(2)	16(1)	18(1)	17(1)	3(1)	4(1)	1(1)
P(3)	20(1)	21(1)	20(1)	2(1)	5(1)	-1(1)
O(1)	35(1)	34(1)	38(1)	-3(1)	7(1)	14(1)
O(2)	54(1)	28(1)	47(1)	-7(1)	-5(1)	-8(1)
O(3)	37(1)	62(1)	22(1)	13(1)	5(1)	9(1)
O(4)	34(1)	28(1)	37(1)	-4(1)	10(1)	6(1)
N(1)	25(1)	33(1)	24(1)	5(1)	6(1)	-7(1)
C(2A)	20(1)	23(1)	26(1)	1(1)	3(1)	2(1)
C(1)	34(1)	22(1)	21(1)	1(1)	5(1)	3(1)
C(2)	36(1)	20(1)	27(1)	2(1)	4(1)	3(1)
C(3)	23(1)	32(1)	24(1)	4(1)	9(1)	1(1)
C(4)	22(1)	25(1)	20(1)	-1(1)	5(1)	-2(1)
C(5)	18(1)	25(1)	17(1)	3(1)	4(1)	0(1)
C(6)	20(1)	19(1)	22(1)	5(1)	6(1)	2(1)
C(7)	25(1)	26(1)	37(1)	1(1)	-1(1)	2(1)
C(8)	23(1)	38(1)	45(1)	6(1)	-1(1)	7(1)
C(9)	30(1)	27(1)	39(1)	9(1)	10(1)	11(1)
C(10)	32(1)	22(1)	32(1)	2(1)	11(1)	5(1)
C(11)	24(1)	23(1)	24(1)	2(1)	6(1)	3(1)
C(12)	21(1)	27(1)	16(1)	0(1)	1(1)	2(1)
C(13)	36(1)	30(1)	28(1)	3(1)	8(1)	-1(1)
C(14)	40(1)	47(2)	22(1)	7(1)	8(1)	-1(1)
C(15)	36(1)	54(2)	19(1)	-5(1)	7(1)	0(1)
C(16)	43(1)	38(1)	25(1)	-7(1)	7(1)	6(1)
C(17)	35(1)	31(1)	20(1)	0(1)	5(1)	7(1)
C(18)	17(1)	21(1)	18(1)	0(1)	3(1)	1(1)

C(19)	24(1)	19(1)	31(1)	4(1)	9(1)	1(1)
C(20)	23(1)	25(1)	36(1)	-1(1)	13(1)	-2(1)
C(21)	22(1)	34(1)	25(1)	-3(1)	4(1)	9(1)
C(22)	33(1)	41(1)	32(1)	15(1)	11(1)	17(1)
C(23)	28(1)	35(1)	27(1)	13(1)	12(1)	10(1)
C(24)	15(1)	19(1)	25(1)	2(1)	4(1)	2(1)
C(25)	29(1)	24(1)	28(1)	3(1)	14(1)	3(1)
C(26)	31(1)	19(1)	42(1)	6(1)	16(1)	4(1)
C(27)	28(1)	21(1)	41(1)	-1(1)	5(1)	-2(1)
C(28)	36(1)	27(1)	27(1)	-1(1)	-2(1)	-2(1)
C(29)	27(1)	26(1)	23(1)	4(1)	0(1)	-3(1)
C(30)	38(1)	31(1)	35(1)	12(1)	0(1)	-10(1)
C(31)	58(2)	52(2)	40(1)	24(1)	-8(1)	-24(1)
C(32)	61(2)	86(2)	33(1)	21(1)	2(1)	-37(2)
C(33)	44(2)	89(2)	28(1)	5(1)	13(1)	-21(2)
C(34)	27(1)	57(2)	28(1)	0(1)	11(1)	-11(1)
C(35)	48(2)	31(1)	70(2)	23(1)	13(1)	9(1)
C(36)	51(2)	35(1)	45(1)	6(1)	0(1)	-13(1)
C(37)	25(1)	71(2)	43(1)	3(1)	7(1)	-10(1)
C(38)	41(1)	56(2)	39(1)	-10(1)	22(1)	-2(1)

Table 16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Co_2(CO)_4(\mu\text{-dppm})(\mu\text{-}\eta^1,\eta^2\text{- P(TMP)=CH}_2)]$ (**4b**).

	x	y	z	U(eq)
H(2A)	502(7)	4530(20)	3064(9)	23(6)
H(2)	232(8)	3250(20)	3038(10)	28(6)
H(5B)	1844	5873	2405	24
H(5A)	2042	4481	2411	24
H(7)	382	4985	1615	37
H(8)	-81	6747	1435	44
H(9)	140	8618	1934	38
H(10)	824	8708	2619	33
H(11)	1301	6963	2781	28
H(13)	1243	5659	1208	37
H(14)	1377	5005	314	44
H(15)	1488	2900	140	43
H(16)	1490	1430	874	42
H(17)	1360	2072	1774	34
H(19)	2819	5638	2913	29
H(20)	3526	4706	2968	32
H(21)	3734	2959	3564	32
H(22)	3235	2153	4101	41
H(23)	2519	3055	4030	35
H(25)	2241	7444	2771	31
H(26)	2415	9493	3088	35
H(27)	2453	10051	4053	37
H(28)	2303	8547	4712	38
H(29)	2117	6506	4399	31
H(31B)	992	-383	4984	63
H(31A)	1241	927	5162	63
H(32B)	648	731	5644	73
H(32A)	293	481	5041	73
H(33B)	771	2777	5355	63

H(33A)	241	2577	5326	63
H(35C)	1562	1306	4310	59
H(35B)	1306	674	3712	59
H(35A)	1462	-169	4283	59
H(36C)	454	368	3525	54
H(36B)	268	-31	4088	54
H(36A)	669	-813	3906	54
H(37C)	-122	1452	4225	56
H(37B)	-147	2615	3788	56
H(37A)	-313	2773	4387	56
H(38C)	292	4515	4119	52
H(38B)	717	4476	4659	52
H(38A)	213	4510	4772	52

Table 17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $[Mn_2(CO)_8(\mu\text{-}\{P(N^iPr_2)=N\text{-}N(=CPh_2)\}]$ (**5**).U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mn(1)	4841(1)	3493(1)	3292(1)	18(1)
Mn(2)	2984(1)	3100(1)	1334(1)	17(1)
P(1)	4116(1)	4374(1)	2387(1)	16(1)
O(1)	6582(1)	3350(1)	2225(1)	44(1)
O(2)	5246(1)	2118(1)	4016(1)	39(1)
O(3)	6533(1)	4065(1)	5260(1)	37(1)
O(4)	2809(1)	3545(1)	4027(1)	28(1)
O(5)	2279(1)	2148(1)	2660(1)	35(1)
O(6)	4002(1)	3837(1)	-26(1)	30(1)
O(7)	1182(1)	2560(1)	-608(1)	37(1)
O(8)	4709(1)	2107(1)	1246(1)	34(1)
N(1)	4834(1)	5033(1)	2318(1)	19(1)
N(2)	2743(1)	4509(1)	1722(1)	18(1)
N(3)	2076(1)	3925(1)	1555(1)	17(1)
C(1)	5918(2)	3406(1)	2628(1)	27(1)
C(2)	5084(2)	2643(1)	3722(1)	26(1)
C(3)	5882(2)	3841(1)	4493(1)	25(1)
C(4)	3571(2)	3523(1)	3727(1)	21(1)
C(5)	2518(2)	2540(1)	2184(1)	24(1)
C(6)	3611(2)	3591(1)	518(1)	21(1)
C(7)	1847(2)	2781(1)	150(1)	24(1)
C(8)	4040(2)	2485(1)	1300(1)	24(1)
C(9)	995(1)	4009(1)	1515(1)	17(1)
C(10)	550(1)	4647(1)	1736(1)	19(1)
C(11)	1138(2)	4992(1)	2670(1)	26(1)
C(12)	698(2)	5584(1)	2843(2)	30(1)
C(13)	-324(2)	5846(1)	2095(2)	28(1)
C(14)	-916(2)	5504(1)	1176(1)	28(1)
C(15)	-496(2)	4905(1)	1000(1)	23(1)

C(16)	134(1)	3456(1)	1259(1)	20(1)
C(17)	-50(2)	3130(1)	2079(1)	28(1)
C(18)	-889(2)	2637(1)	1861(2)	35(1)
C(19)	-1564(2)	2474(1)	827(2)	36(1)
C(20)	-1400(2)	2802(1)	8(2)	33(1)
C(21)	-554(2)	3296(1)	217(1)	26(1)
C(22)	6139(1)	5066(1)	2968(1)	21(1)
C(23)	6863(2)	5202(1)	2292(2)	35(1)
C(24)	6389(2)	5545(1)	3871(2)	37(1)
C(25)	4288(2)	5638(1)	1713(1)	22(1)
C(26)	3403(2)	5958(1)	2116(1)	28(1)
C(27)	3766(2)	5515(1)	531(1)	26(1)
O(1A)	-474(2)	5022(2)	4693(2)	32(1)
C(1A)	367(6)	5475(4)	5332(6)	39(2)
C(2A)	-195(4)	6146(2)	5128(4)	45(1)
C(3A)	21(5)	4388(4)	4747(6)	33(2)
C(4A)	-944(4)	3926(2)	4105(4)	41(1)

Table 18. Bond lengths [Å] and angles [°] for $[Mn_2(CO)_8(\mu\text{-}\{P(N^iPr_2)=N\text{-}N(=CPh_2)\}]$ (**5**).

Mn(1)-C(3)	1.8037(18)
Mn(1)-C(2)	1.8320(18)
Mn(1)-C(4)	1.8449(18)
Mn(1)-C(1)	1.8525(19)
Mn(1)-P(1)	2.1845(5)
Mn(1)-Mn(2)	2.8945(4)
Mn(2)-C(8)	1.8103(18)
Mn(2)-C(7)	1.8116(17)
Mn(2)-C(6)	1.8631(17)
Mn(2)-C(5)	1.8646(18)
Mn(2)-N(3)	2.1034(13)
P(1)-N(2)	1.5931(14)
P(1)-N(1)	1.6309(14)
O(1)-C(1)	1.138(2)
O(2)-C(2)	1.144(2)
O(3)-C(3)	1.147(2)
O(4)-C(4)	1.141(2)
O(5)-C(5)	1.140(2)
O(6)-C(6)	1.139(2)
O(7)-C(7)	1.142(2)
O(8)-C(8)	1.144(2)
N(1)-C(22)	1.497(2)
N(1)-C(25)	1.504(2)
N(2)-N(3)	1.4176(18)
N(3)-C(9)	1.301(2)
C(9)-C(10)	1.492(2)
C(9)-C(16)	1.492(2)
C(10)-C(15)	1.395(2)
C(10)-C(11)	1.401(2)
C(11)-C(12)	1.383(3)
C(12)-C(13)	1.386(3)
C(13)-C(14)	1.382(3)
C(14)-C(15)	1.388(2)

C(16)-C(17)	1.393(2)
C(16)-C(21)	1.395(2)
C(17)-C(18)	1.387(3)
C(18)-C(19)	1.384(3)
C(19)-C(20)	1.382(3)
C(20)-C(21)	1.394(3)
C(22)-C(23)	1.517(2)
C(22)-C(24)	1.519(2)
C(25)-C(27)	1.521(2)
C(25)-C(26)	1.523(3)
O(1A)-C(1A)	1.416(8)
O(1A)-C(3A)	1.425(7)
C(1A)-C(2A)	1.517(8)
C(3A)-C(4A)	1.507(9)

C(3)-Mn(1)-C(2)	96.47(8)
C(3)-Mn(1)-C(4)	94.35(8)
C(2)-Mn(1)-C(4)	88.94(8)
C(3)-Mn(1)-C(1)	95.99(8)
C(2)-Mn(1)-C(1)	90.41(8)
C(4)-Mn(1)-C(1)	169.65(8)
C(3)-Mn(1)-P(1)	100.50(6)
C(2)-Mn(1)-P(1)	162.80(6)
C(4)-Mn(1)-P(1)	86.98(5)
C(1)-Mn(1)-P(1)	90.62(6)
C(3)-Mn(1)-Mn(2)	172.01(6)
C(2)-Mn(1)-Mn(2)	90.37(6)
C(4)-Mn(1)-Mn(2)	81.62(5)
C(1)-Mn(1)-Mn(2)	88.06(6)
P(1)-Mn(1)-Mn(2)	72.502(15)
C(8)-Mn(2)-C(7)	91.87(8)
C(8)-Mn(2)-C(6)	85.11(8)
C(7)-Mn(2)-C(6)	90.27(8)
C(8)-Mn(2)-C(5)	88.01(8)
C(7)-Mn(2)-C(5)	91.60(8)

C(6)-Mn(2)-C(5)	172.93(7)
C(8)-Mn(2)-N(3)	168.08(7)
C(7)-Mn(2)-N(3)	99.01(6)
C(6)-Mn(2)-N(3)	89.98(6)
C(5)-Mn(2)-N(3)	96.46(6)
C(8)-Mn(2)-Mn(1)	84.64(5)
C(7)-Mn(2)-Mn(1)	175.00(6)
C(6)-Mn(2)-Mn(1)	92.99(5)
C(5)-Mn(2)-Mn(1)	84.72(5)
N(3)-Mn(2)-Mn(1)	84.78(4)
N(2)-P(1)-N(1)	106.69(7)
N(2)-P(1)-Mn(1)	125.49(5)
N(1)-P(1)-Mn(1)	127.71(5)
C(22)-N(1)-C(25)	116.02(12)
C(22)-N(1)-P(1)	118.04(10)
C(25)-N(1)-P(1)	125.79(11)
N(3)-N(2)-P(1)	110.77(10)
C(9)-N(3)-N(2)	113.45(13)
C(9)-N(3)-Mn(2)	132.24(11)
N(2)-N(3)-Mn(2)	114.21(9)
O(1)-C(1)-Mn(1)	179.6(2)
O(2)-C(2)-Mn(1)	178.31(17)
O(3)-C(3)-Mn(1)	179.23(18)
O(4)-C(4)-Mn(1)	177.93(14)
O(5)-C(5)-Mn(2)	172.89(16)
O(6)-C(6)-Mn(2)	173.48(15)
O(7)-C(7)-Mn(2)	175.98(16)
O(8)-C(8)-Mn(2)	177.45(16)
N(3)-C(9)-C(10)	122.77(14)
N(3)-C(9)-C(16)	120.84(14)
C(10)-C(9)-C(16)	116.38(13)
C(15)-C(10)-C(11)	118.74(15)
C(15)-C(10)-C(9)	119.18(14)
C(11)-C(10)-C(9)	122.06(14)
C(12)-C(11)-C(10)	120.27(16)

C(11)-C(12)-C(13)	120.65(17)
C(14)-C(13)-C(12)	119.39(17)
C(13)-C(14)-C(15)	120.62(16)
C(14)-C(15)-C(10)	120.29(16)
C(17)-C(16)-C(21)	119.55(16)
C(17)-C(16)-C(9)	118.99(15)
C(21)-C(16)-C(9)	121.26(15)
C(18)-C(17)-C(16)	120.23(17)
C(19)-C(18)-C(17)	120.14(18)
C(20)-C(19)-C(18)	120.00(18)
C(19)-C(20)-C(21)	120.40(17)
C(20)-C(21)-C(16)	119.65(17)
N(1)-C(22)-C(23)	111.63(13)
N(1)-C(22)-C(24)	110.98(14)
C(23)-C(22)-C(24)	112.93(16)
N(1)-C(25)-C(27)	111.63(13)
N(1)-C(25)-C(26)	112.50(14)
C(27)-C(25)-C(26)	112.77(14)
C(1A)-O(1A)-C(3A)	112.2(4)
O(1A)-C(1A)-C(2A)	108.3(5)
O(1A)-C(3A)-C(4A)	109.0(4)

Symmetry transformations used to generate equivalent atoms:

Table 19. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[Mn_2(CO)_8(\mu\text{-}\{P(N^iPr_2)=N\text{-}N(=CPh_2)\}]$ (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn(1)	16(1)	15(1)	21(1)	2(1)	5(1)	1(1)
Mn(2)	17(1)	14(1)	20(1)	-1(1)	6(1)	0(1)
P(1)	15(1)	14(1)	18(1)	0(1)	4(1)	-1(1)
O(1)	35(1)	46(1)	60(1)	-7(1)	29(1)	1(1)
O(2)	44(1)	22(1)	51(1)	11(1)	17(1)	8(1)
O(3)	32(1)	45(1)	24(1)	0(1)	0(1)	-6(1)
O(4)	27(1)	33(1)	28(1)	-2(1)	13(1)	-3(1)
O(5)	39(1)	26(1)	44(1)	7(1)	21(1)	-3(1)
O(6)	35(1)	28(1)	33(1)	4(1)	20(1)	1(1)
O(7)	29(1)	43(1)	34(1)	-18(1)	7(1)	-4(1)
O(8)	32(1)	23(1)	46(1)	-3(1)	15(1)	8(1)
N(1)	16(1)	16(1)	21(1)	1(1)	2(1)	-1(1)
N(2)	15(1)	15(1)	22(1)	0(1)	5(1)	-2(1)
N(3)	16(1)	15(1)	17(1)	0(1)	4(1)	-1(1)
C(1)	25(1)	21(1)	35(1)	0(1)	10(1)	3(1)
C(2)	25(1)	22(1)	31(1)	3(1)	9(1)	3(1)
C(3)	22(1)	25(1)	25(1)	6(1)	6(1)	2(1)
C(4)	23(1)	17(1)	20(1)	2(1)	4(1)	-1(1)
C(5)	24(1)	20(1)	27(1)	-2(1)	10(1)	1(1)
C(6)	21(1)	17(1)	24(1)	-2(1)	7(1)	2(1)
C(7)	22(1)	23(1)	29(1)	-3(1)	11(1)	2(1)
C(8)	25(1)	18(1)	26(1)	-1(1)	7(1)	-1(1)
C(9)	15(1)	18(1)	17(1)	2(1)	3(1)	0(1)
C(10)	16(1)	18(1)	24(1)	0(1)	9(1)	0(1)
C(11)	19(1)	28(1)	27(1)	-3(1)	6(1)	3(1)
C(12)	26(1)	30(1)	34(1)	-12(1)	12(1)	-2(1)
C(13)	27(1)	21(1)	42(1)	-1(1)	20(1)	3(1)
C(14)	23(1)	26(1)	33(1)	6(1)	9(1)	8(1)
C(15)	18(1)	25(1)	25(1)	0(1)	6(1)	1(1)
C(16)	14(1)	18(1)	25(1)	0(1)	5(1)	1(1)

C(17)	25(1)	28(1)	29(1)	3(1)	9(1)	-3(1)
C(18)	29(1)	30(1)	46(1)	8(1)	15(1)	-6(1)
C(19)	24(1)	25(1)	56(1)	-1(1)	9(1)	-8(1)
C(20)	24(1)	26(1)	38(1)	-7(1)	1(1)	-5(1)
C(21)	23(1)	23(1)	28(1)	-2(1)	5(1)	-2(1)
C(22)	16(1)	19(1)	24(1)	0(1)	3(1)	-2(1)
C(23)	19(1)	48(1)	36(1)	11(1)	9(1)	-3(1)
C(24)	28(1)	32(1)	38(1)	-13(1)	-1(1)	-2(1)
C(25)	21(1)	15(1)	27(1)	4(1)	4(1)	-2(1)
C(26)	31(1)	17(1)	33(1)	0(1)	9(1)	3(1)
C(27)	25(1)	24(1)	25(1)	6(1)	7(1)	-1(1)
O(1A)	26(1)	30(2)	36(1)	-1(1)	7(1)	3(1)
C(1A)	26(4)	52(5)	37(3)	3(3)	9(3)	-6(3)
C(2A)	42(3)	41(3)	56(3)	-10(2)	23(2)	-9(2)
C(3A)	24(3)	41(4)	33(2)	7(2)	9(3)	8(3)
C(4A)	38(2)	37(2)	49(2)	-2(2)	17(2)	4(2)

Table 20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $[Mn_2(CO)_8(\mu\text{-}\{P(N^iPr_2)=N\text{-}N(=CPh_2)\}]$ (**5**).

	x	y	z	U(eq)
H(11)	1841	4819	3187	31
H(12)	1101	5814	3480	35
H(13)	-615	6255	2212	34
H(14)	-1616	5682	661	34
H(15)	-923	4669	375	28
H(17)	401	3245	2789	33
H(18)	-1000	2410	2423	42
H(19)	-2141	2137	680	44
H(20)	-1867	2690	-701	39
H(21)	-447	3521	-348	31
H(22)	6382	4627	3289	25
H(23C)	6666	5636	1977	42
H(23B)	6678	4875	1732	42
H(23A)	7714	5183	2731	42
H(24C)	5808	5482	4206	44
H(24B)	6327	5990	3599	44
H(24A)	7194	5472	4391	44
H(25)	4953	5956	1841	26
H(26C)	3748	5979	2888	33
H(26B)	2668	5702	1892	33
H(26A)	3225	6399	1828	33
H(27C)	3062	5236	358	31
H(27B)	4362	5298	316	31
H(27A)	3539	5929	157	31
H(1A2)	1092	5470	5159	47
H(1A1)	597	5360	6086	47
H(2A3)	-865	6159	5366	54
H(2A2)	-482	6241	4371	54
H(2A1)	399	6471	5514	54

H(3A2)	362	4240	5489	40
H(3A1)	667	4397	4467	40
H(4A3)	-1229	4053	3360	49
H(4A2)	-1607	3943	4352	49
H(4A1)	-626	3483	4185	49