Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Cover Page for Supporting Information

Synthesis and Characterization of Manganese(II) Complexes Supported by Cyclopentadienyl-Phosphine Ligand

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IR spectra

Infrared Spectra was recorded on a Bruker Tensor 27 using a solution cell equipped with KBr window.

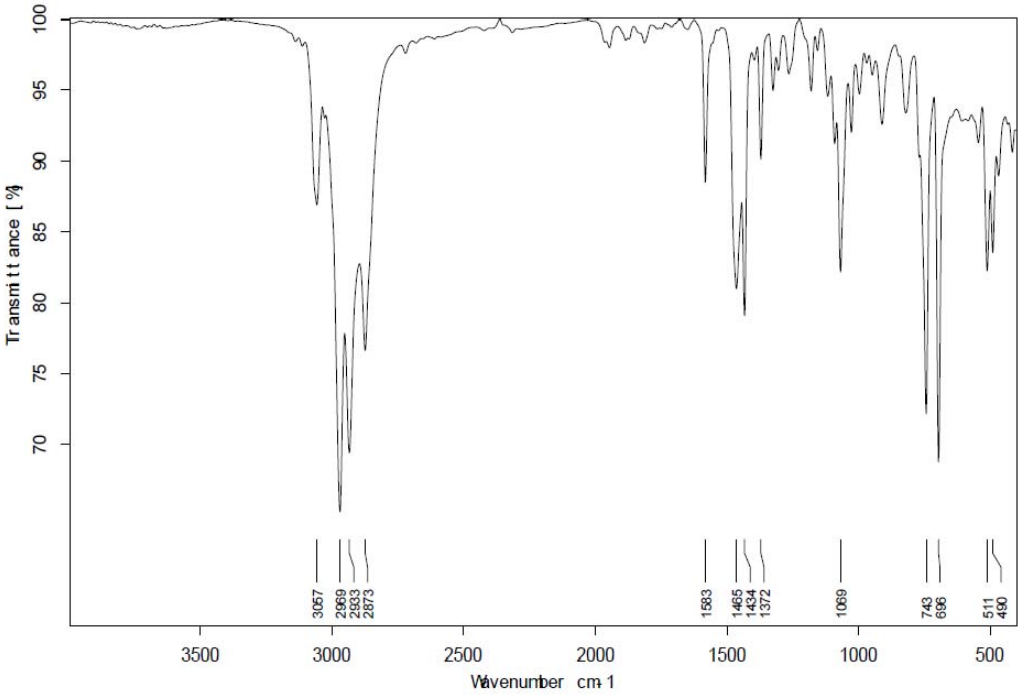

Figure S1 IR spectra of **1a** at room temperature

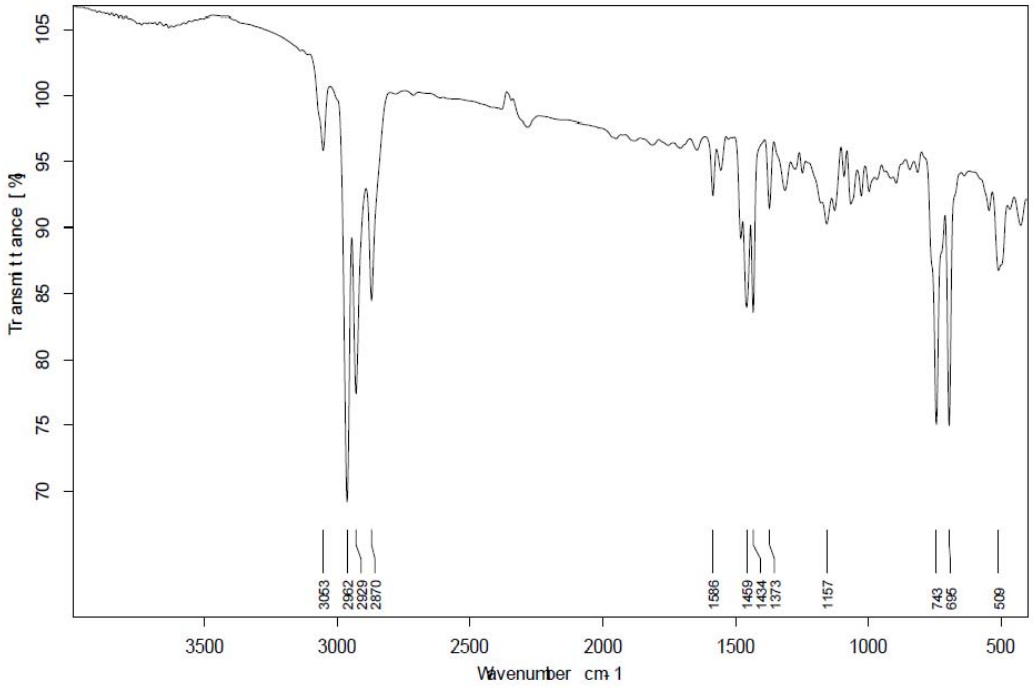

Figure S2 IR spectra of **1b** at room temperature

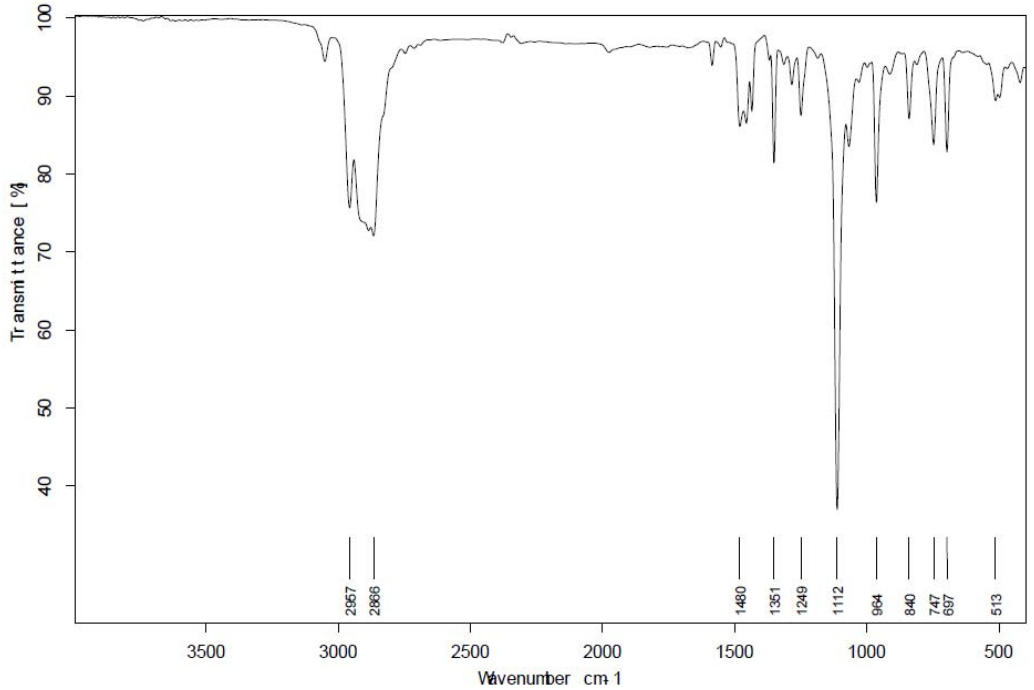

Figure S3 IR spectra of **2** at room temperature

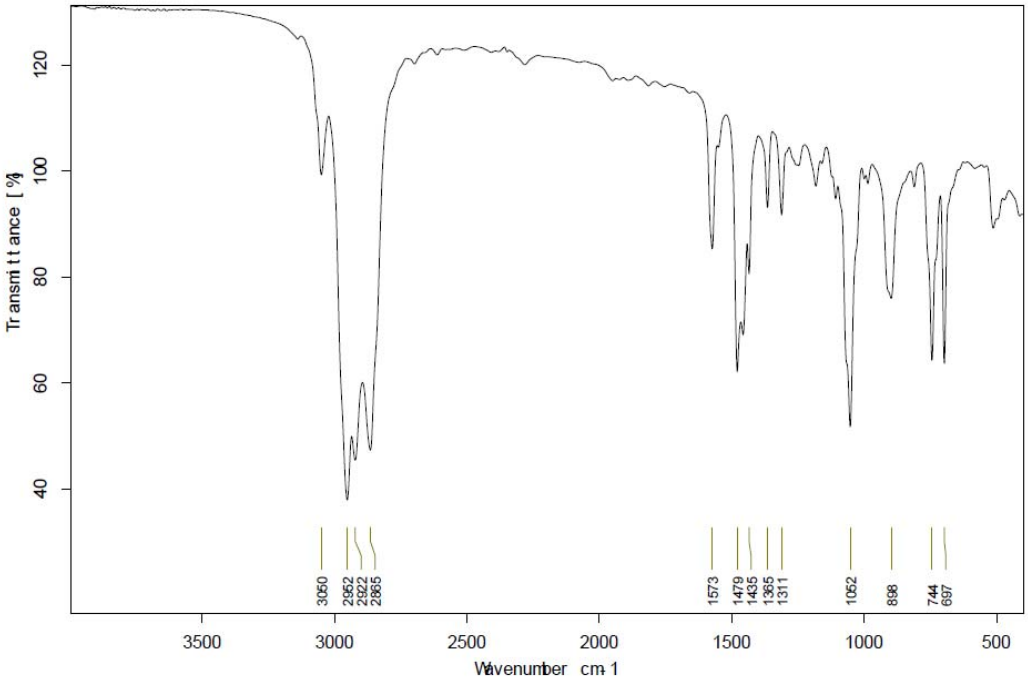

Figure S4 IR spectra of **3** at room temperature

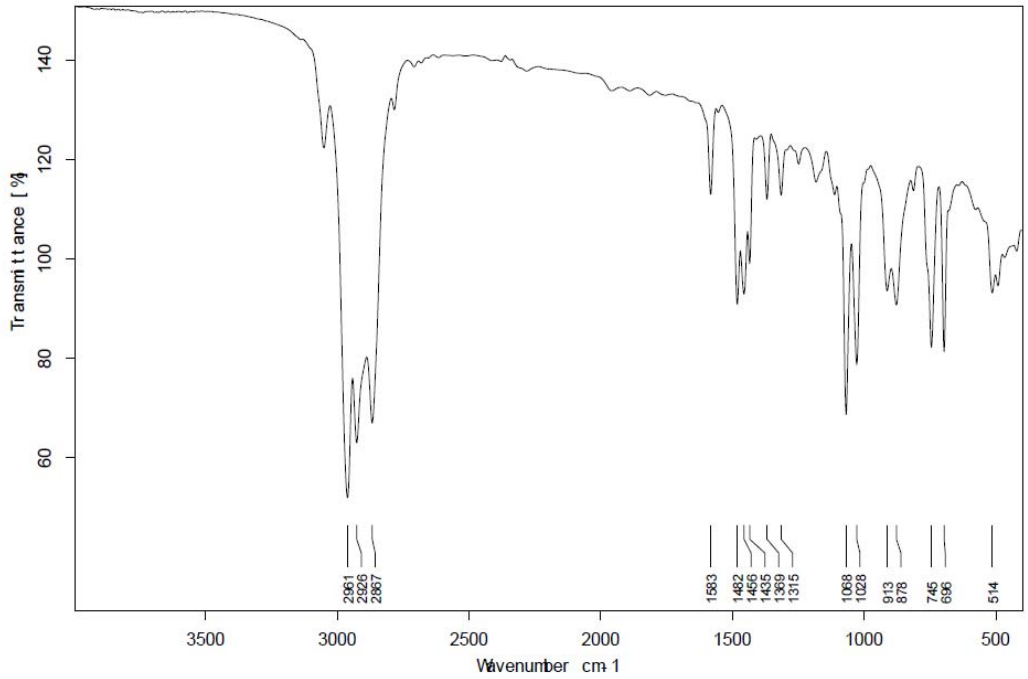

Figure S5 IR spectra of **4** at room temperature

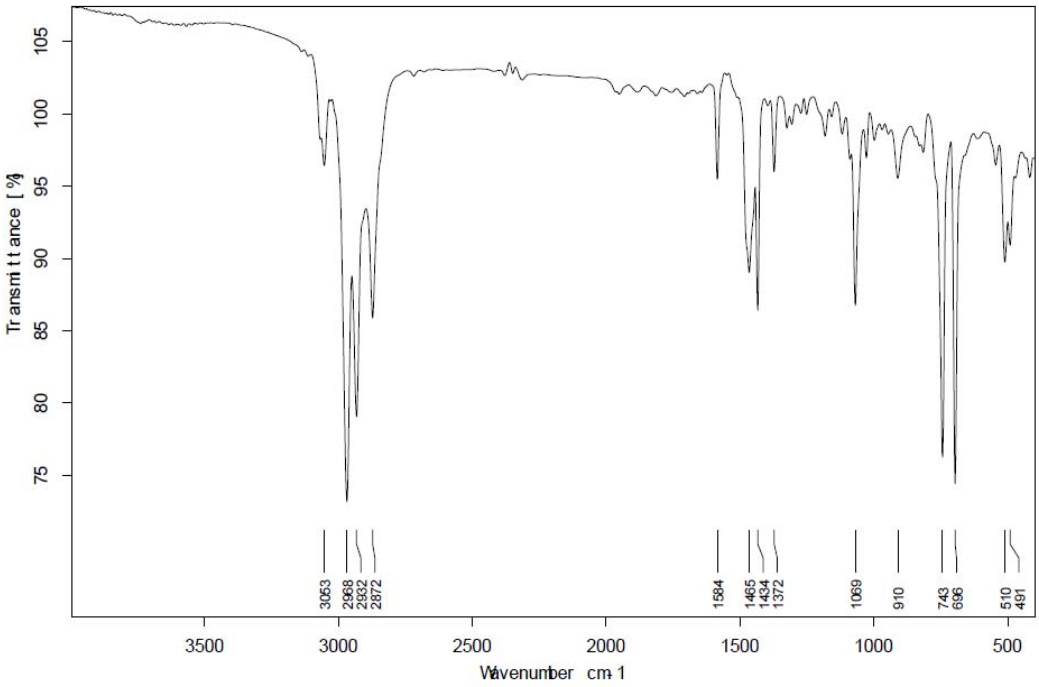

Figure S6 IR spectra of **5** at room temperature

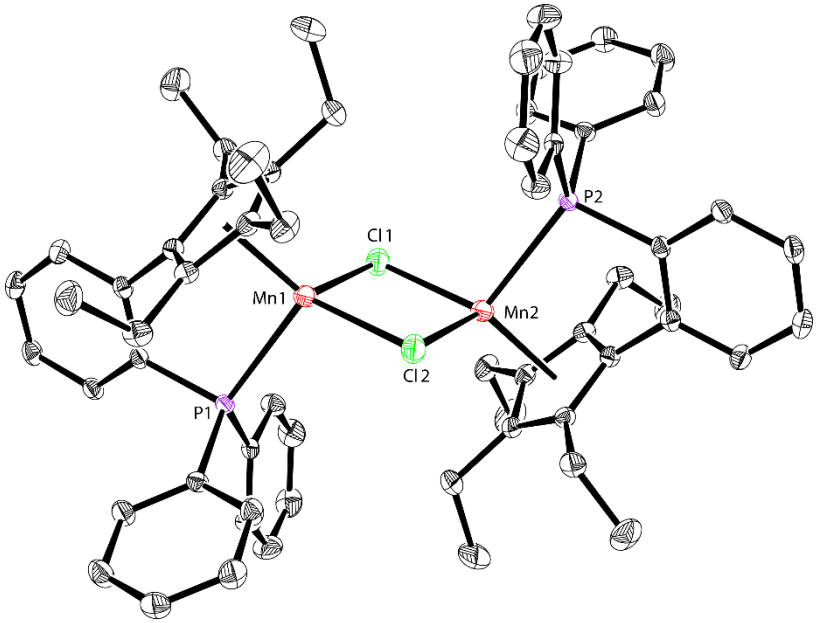

Figure S7 ORTEP drawing of **1a**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S1 Selected Bond Lengths (Å) and Angles (deg) for **1a**.

Mn(1)——Cl(1)	2.3909(7)
Mn(1)——Cl(2)	2.4603(7)
Mn(1)——P(1)	2.6066(6)
Mn(1)——Cp(1)	2.121
Cl(1)——Mn(1)——Cl(2)	94.71(3)

Table S2 X-ray crystallographic data for **1a**.

	1a
CCDC number	1870180
Empirical formula	C31H34ClMnP
Formula weight	527.94
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.7627(2)
b/Å	14.8237(2)
c/Å	15.1711(3)
α/°	90
β/°	98.826(2)
γ/°	90
Volume/Å^3	2836.24(8)
Z	4
ρ_{calc}, g/cm^3	1.236
μ/mm^{-1}	0.633
F(000)	1108.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.164 to 52.04
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$
Reflections collected	48861
Independent reflections	5540 [R_{int} = 0.0267, R_{sigma} = 0.0136]
Data/restraints/parameters	5540/0/311
Goodness-of-fit on F^2	1.051
R_1 [I>=2δ (I)]	0.0446
wR_2 [all data]	0.1318
Largest diff. peak/hole / e Å^{-3}	0.71/-0.90

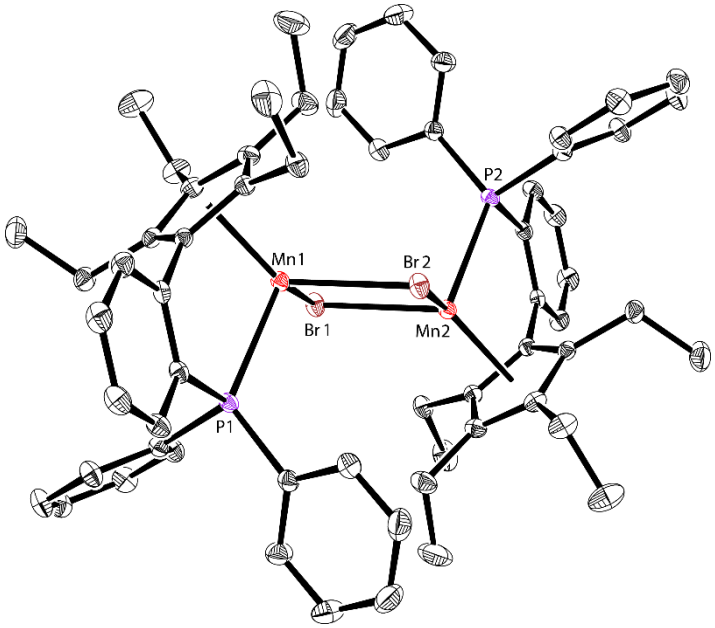

Figure S8 ORTEP drawing of **1b**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S3 Selected Bond Lengths (Å) and Angles (deg) for **1b**.

Mn(1)——Br(1)	2.5659(3)
Mn(1)——Br(2)	2.6548(3)
Mn(1)——P(1)	2.5925(5)
Mn(1)——Cp(1)	2.107
Br(1)——Mn(1)——Br(2)	93.428(3)

Table S4 X-ray crystallographic data for **1b**.

	1b
CCDC number	1870203
Empirical formula	$C_{62}H_{68}Br_2Mn_2P_2$
Formula weight	1144.80
Temperature/K	179.98(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.2781(4)
b/Å	14.9823(4)
c/Å	15.6542(5)
α/°	90
β/°	98.494(3)
γ/°	90
Volume/Å^3	2848.07(15)
Z	2
ρ_{calc}, g/cm^3	1.335
μ/mm^{-1}	1.939
F(000)	1180.0
Crystal size/mm^3	0.15 x 0.14 x 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.182 to 54.968
Index ranges	$-15 \leq h \leq 15$, $-19 \leq k \leq 19$, $-19 \leq l \leq 20$
Reflections collected	48976
Independent reflections	6515 [R_{int} = 0.0347, R_{sigma} = 0.0198]
Data/restraints/parameters	6515/0/311
Goodness-of-fit on F^2	1.057
R_1 [I>=2δ (I)]	0.0257
wR_2 [all data]	0.0667
Largest diff. peak/hole / e Å^{-3}	0.49/-0.23

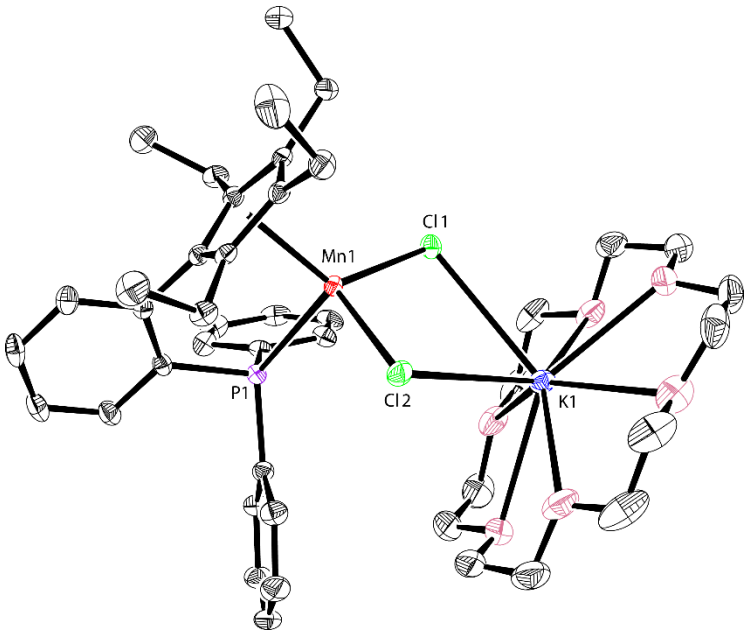

Figure S9 ORTEP drawing of **2**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S5 Selected Bond Lengths (Å) and Angles (deg) for **2**.

Mn(1)——Cl(1)	2.3997(6)
Mn(1)——Cl(2)	2.3844(7)
Mn(1)——P(1)	2.7264(6)
K(1)——Cl(2)	3.1928(8)
K(1)——Cl(2)	3.2865(8)
Mn(1)——Cp(1)	2.188
Cl(1)——Mn(1)——Cl(2)	99.83(2)
Cl(1)——K(1)——Cl(2)	65.879(16)

Table S6 X-ray crystallographic data for **2**.

	2
CCDC number	1870204
Empirical formula	$C_{90}H_{126}Cl_4K_2Mn_2O_{13}P_2$
Formula weight	1807.72
Temperature/K	179.9(3)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.8370(3)
b/Å	17.5824(4)
c/Å	21.9403(5)
α/°	90
β/°	106.277(2)
γ/°	90
Volume/Å^3	4753.55(19)
Z	2
ρ_{calc}, g/cm^3	1.263
μ/mm^{-1}	0.556
F(000)	1912.0
Crystal size/mm^3	0.12 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.052 to 52.044
Index ranges	$-15 \leq h \leq 15$, $-21 \leq k \leq 21$, $-27 \leq l \leq 27$
Reflections collected	77334
Independent reflections	18552 [R_{int} = 0.0250, R_{sigma} = 0.0216]
Data/restraints/parameters	18552/1/1028
Goodness-of-fit on F^2	1.018
R_1 [I>=2δ (I)]	0.0231
wR_2 [all data]	0.0583
Largest diff. peak/hole / e Å^{-3}	0.42/-0.23
Flack parameter	-0.007(3)

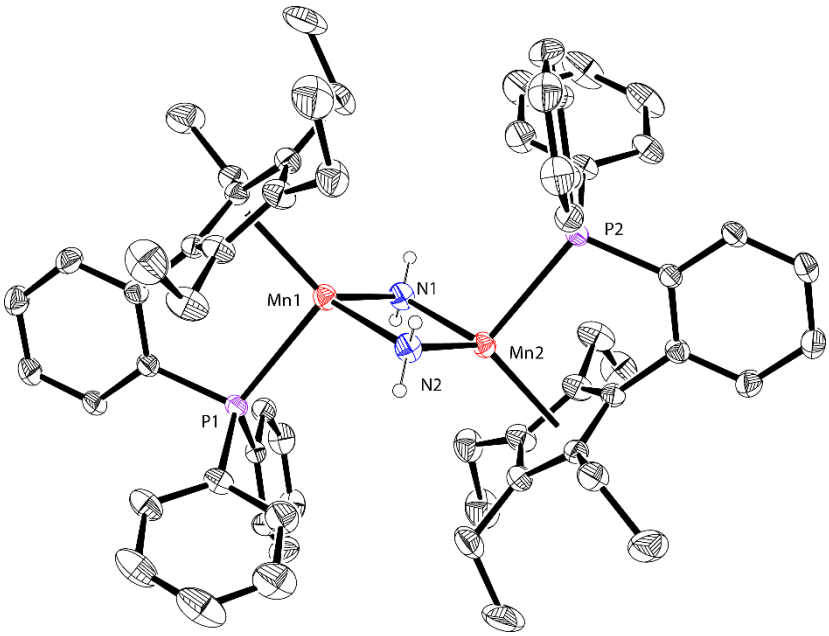

Figure S10 ORTEP drawing of **3**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms, except that on nitrogen atoms N1 and N2, are omitted for clarity.

Table S7 Selected Bond Lengths (Å) and Angles (deg) for **3**.

Mn(1)——N(1)	2.1299(19)
Mn(1)——N(2)	2.096(2)
Mn(1)——P(1)	2.6525(6)
Mn(1)——Cp(1)	2.201
N(1)——Mn(1)——N(2)	88.79(8)

Table S8 X-ray crystallographic data for **3**.

	3
CCDC number	1870205
Empirical formula	$C_{31}H_{36}MnNP$
Formula weight	508.52
Temperature/K	179.99(11)
Crystal system	triclinic
Space group	P-1
a/Å	10.0194(3)
b/Å	12.4401(4)
c/Å	13.4146(4)
α/°	116.797(3)
β/°	96.699(3)
γ/°	106.485(3)
Volume/Å^3	1371.44(8)
Z	2
ρ_{calc}, g/cm^3	1.231
μ/mm^{-1}	0.558
F(000)	538.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.848 to 54.97
Index ranges	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
Reflections collected	35623
Independent reflections	6266 [R_{int} = 0.0325, R_{sigma} = 0.0225]
Data/restraints/parameters	6266/0/319
Goodness-of-fit on F^2	1.061
R_1 [I>=2δ (I)]	0.0493
wR_2 [all data]	0.1480
Largest diff. peak/hole / e Å^{-3}	1.24/-0.47

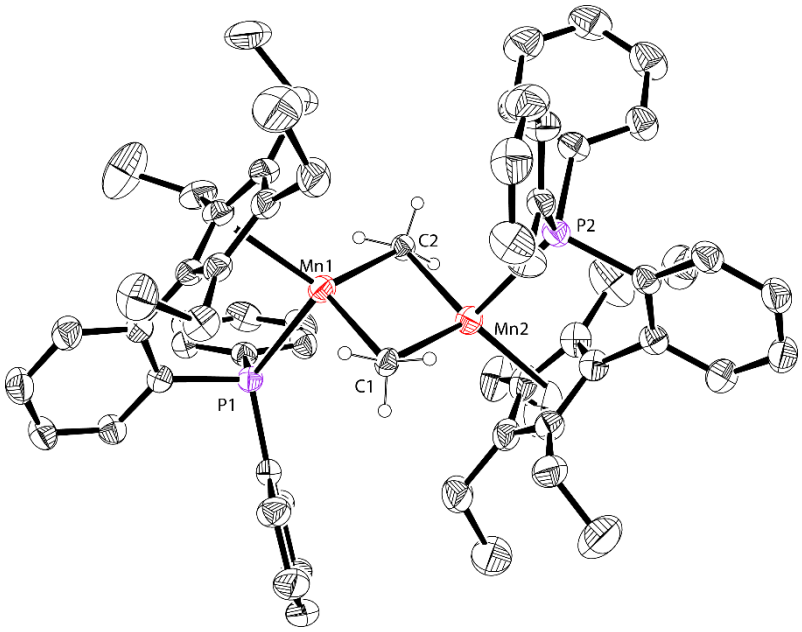

Figure S11 ORTEP drawing of **4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms, except that on carbon atoms C1 and C2, are omitted for clarity.

Table S9 Selected Bond Lengths (Å) and Angles (deg) for **4**.

Mn(1)——C(1)	2.2249(18)
Mn(1)——C(2)	2.308(2)
Mn(1)——P(1)	2.7056(6)
Mn(1)——Cp(1)	2.226
C(1)——Mn(1)——C(2)	104.24(7)

Table S10 X-ray crystallographic data for **4**.

	4
CCDC number	1870206
Empirical formula	$C_{64}H_{74}Mn_2P_2$
Formula weight	1015.05
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.9695(6)
b/Å	13.7409(8)
c/Å	19.5247(8)
α/°	70.409(4)
β/°	88.912(4)
γ/°	62.015(5)
Volume/Å^3	2854.5(3)
Z	2
ρ_{calc}, g/cm^3	1.181
μ/mm^{-1}	0.535
F(000)	1076.0
Crystal size/mm^3	0.2 x 0.2 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.982 to 52.044
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-24 \leq l \leq 24$
Reflections collected	51743
Independent reflections	11156 [R_{int} = 0.0275, R_{sigma} = 0.0221]
Data/restraints/parameters	11156/20/656
Goodness-of-fit on F^2	1.033
R_1 [I>=2δ (I)]	0.0417
wR_2 [all data]	0.1215
Largest diff. peak/hole / e Å^{-3}	0.61/-0.30

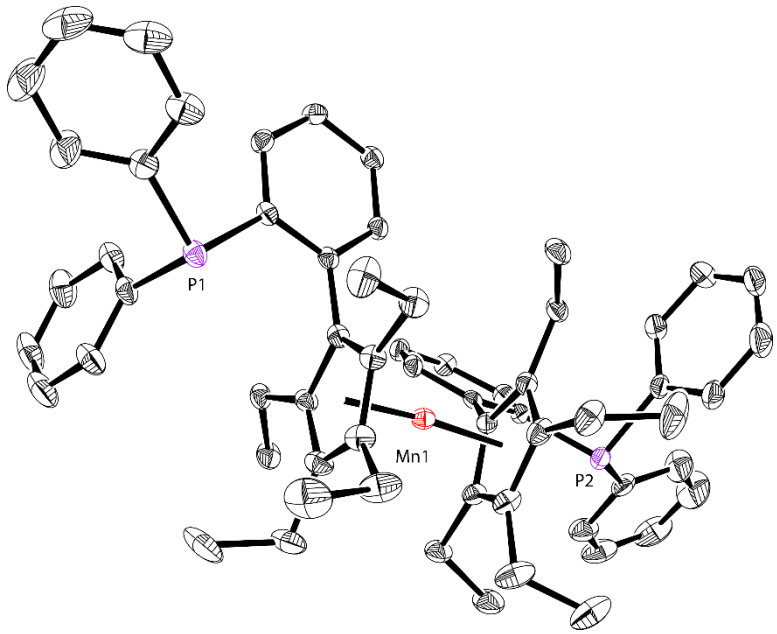

Figure S12 ORTEP drawing of **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table S11 Selected Bond Lengths (Å) and Angles (deg) for **5**.

Mn(1)——Cp(1)	1.771

Table S12 X-ray crystallographic data for **5**.

	5
CCDC number	1870207
Empirical formula	$C_{62}H_{68}MnP_2$
Formula weight	930.04
Temperature/K	293(2)
Crystal system	tetragonal
Space group	$P\text{-}42_1c$
a/Å	13.5013(2)
b/Å	13.5013(2)
c/Å	27.8106(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5069.5(2)
Z	4
ρ_{calc}, g/cm^3	1.219
μ/mm^{-1}	0.363
F(000)	1980.0
Crystal size/mm^3	0.1 x 0.1 x 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.906 to 52.044
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$, $-34 \leq l \leq 34$
Reflections collected	72701
Independent reflections	4987 [R_{int} = 0.0482, R_{sigma} = 0.0179]
Data/restraints/parameters	4987/0/298
Goodness-of-fit on F^2	1.074
R_1 [I>=2δ (I)]	0.0368
wR_2 [all data]	0.0978
Largest diff. peak/hole / e Å^{-3}	0.50/-0.39
Flack parameter	-0.008(5)