Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Data

Activation of the Manganese(I) Tricarbonyl Core by Selective Variation of Bidentate Ligands (L,L'-Bid = N,N'and N,O Donor Atom Sets) in fac-$[Mn(CO)_3(L,L'\text{-}Bid)(CH_3OH)]^n$ complexes.

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Appendix

Table 1. Observed hydrogen interactions in the molecular structure of *fac*-$[Mn(CO)_3(Bipy)(H_2O)].CF_3SO_3$ (**1**).

D-H...A	D(D-H) (Å)	D(H…A) (Å)	D(D…A) (Å)	D-H…A (°)
O04-H1A...O09[a]	0.84(3)	1.77(3)	2.566(6)	157(4)
O04-H1B...O09[b]	0.88(3)	2.33(4)	2.976(9)	131(3)
O04-H1B...O05[b]	0.88(3)	2.05(4)	2.896(4)	160(4)
C014-H14...O08	0.9300	2.5400	3.461(6)	174.00
C017-H17...O08	0.9300	2.4600	3.385(5)	176.00
C018-H18...O02[c]	0.9300	2.5600	3.221(4)	128.00
C019-H19...O03[d]	0.9300	2.550	3.362(4)	146.00

Symmetry operators: a = -x,-y,-z; b = x, 1+y, z; c = 0.5+, 0.5–y, -0.5+z; d = 1–x, 1–y, -z.

Figure 1. Illustration of hydrogen interactions in *fac*-$[Mn(CO)_3(Bipy)(H_2O)].CF_3SO_3$ (**1**). Hydrogen atoms not part of hydrogen interactions omitted for clarity.

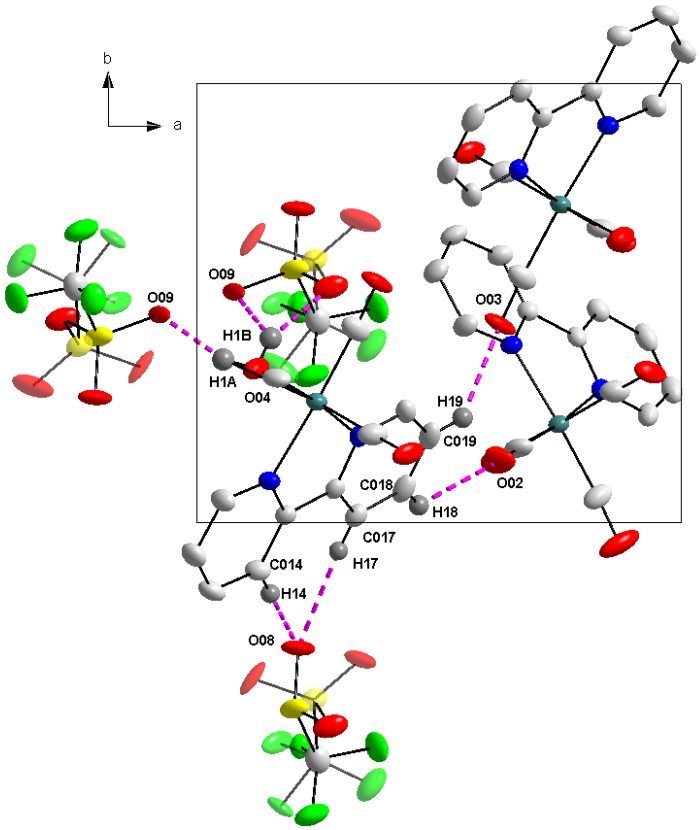

Figure 2. π-Stacking in the molecular structure of *fac*-[$Mn(CO)_3(Bipy)(H_2O)$].CF_3SO_3 (**1**). Hydrogen atoms and anions omitted for clarity.

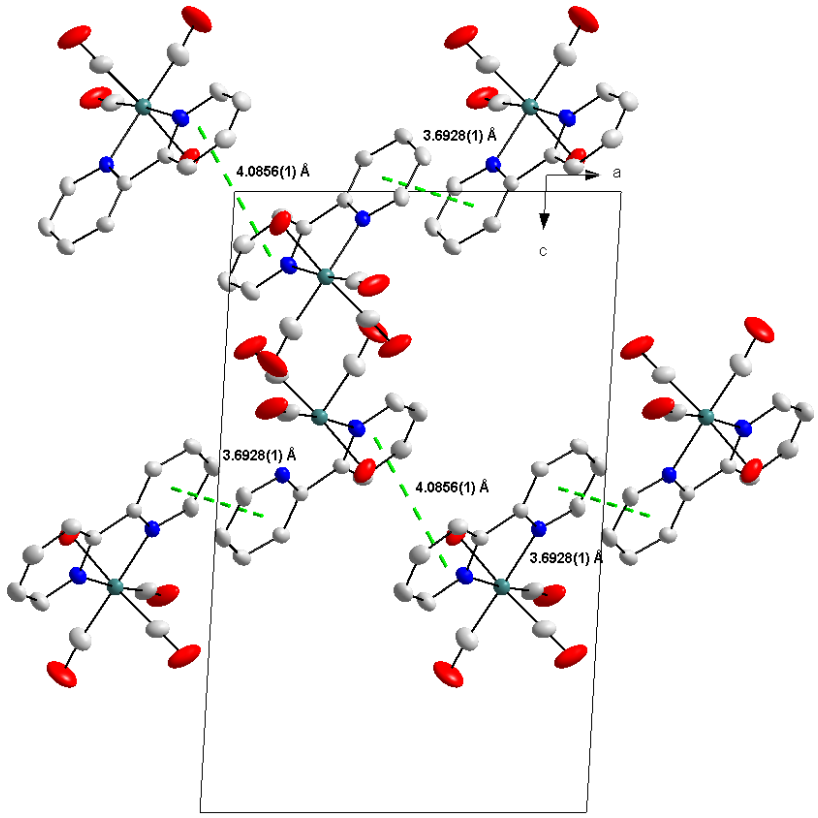

Table 2. Observed hydrogen interactions in the molecular structure of *fac*-[$Mn(CO)_3(Phen)(H_2O)$].CF_3SO_3 (**6**).

D-H…A	D(D-H) (Å)	D(H…A) (Å)	D(D…A) (Å)	D-H…A (°)
O04-H1A...O07	0.86(3)	1.89(3)	2.709(3)	159(3)
O04-H1B...O06[a]	0.86(3)	1.93(3)	2.745(3)	160(3)
C020-H020...O02[b]	0.9300	2.5600	3.203(3)	127.00
C017-H017...O05[c]	0.9300	2.5100	3.305(3)	144.00
C011-H011...F1[d]	0.9300	2.4600	3.205(3)	137.00
C013-H013...F2[e]	0.9300	2.3900	3.143(3)	138.00

Symmetry operators: a = 1-x, 1-y, 1-z; b = -0.5+x, 0.5-y, 0.5+z; c = 1-x, -y, 1-z; d = 1.5-x, -0.5+y, 0.5-z; e = x, -1+y, z.

Figure 3. Illustration of hydrogen interactions in *fac*-[$Mn(CO)_3(Phen)(H_2O)$].CF_3SO_3 (**6**). Hydrogen atoms not part of hydrogen interactions omitted for clarity.

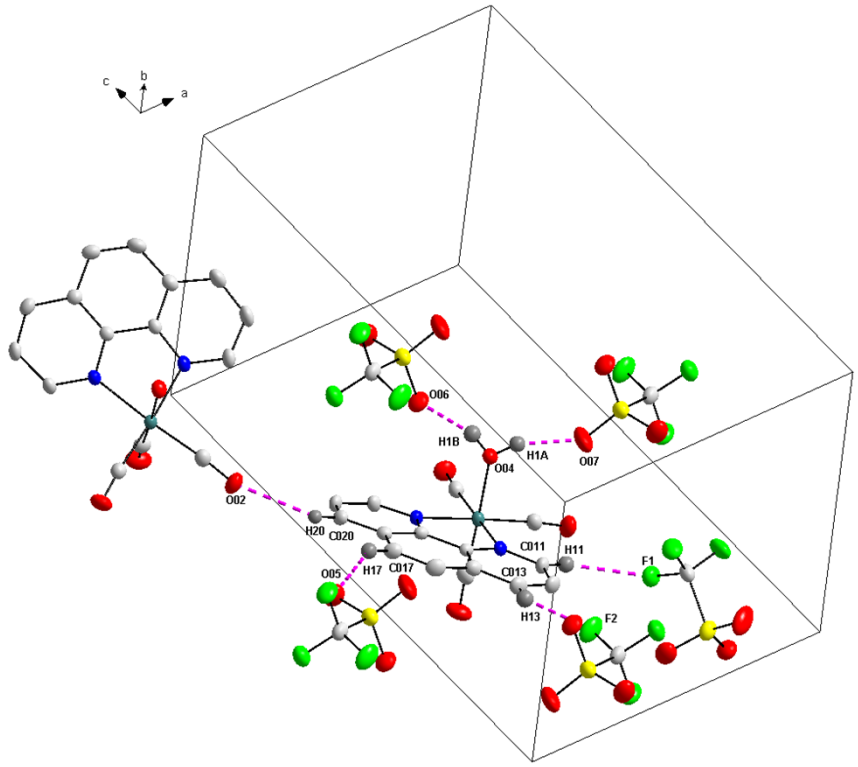

Figure 4. π-Stacking in the molecular structure of *fac*-[$Mn(CO)_3(Phen)(H_2O)$].CF_3SO_3 (**6**). Hydrogen atoms and anions omitted for clarity

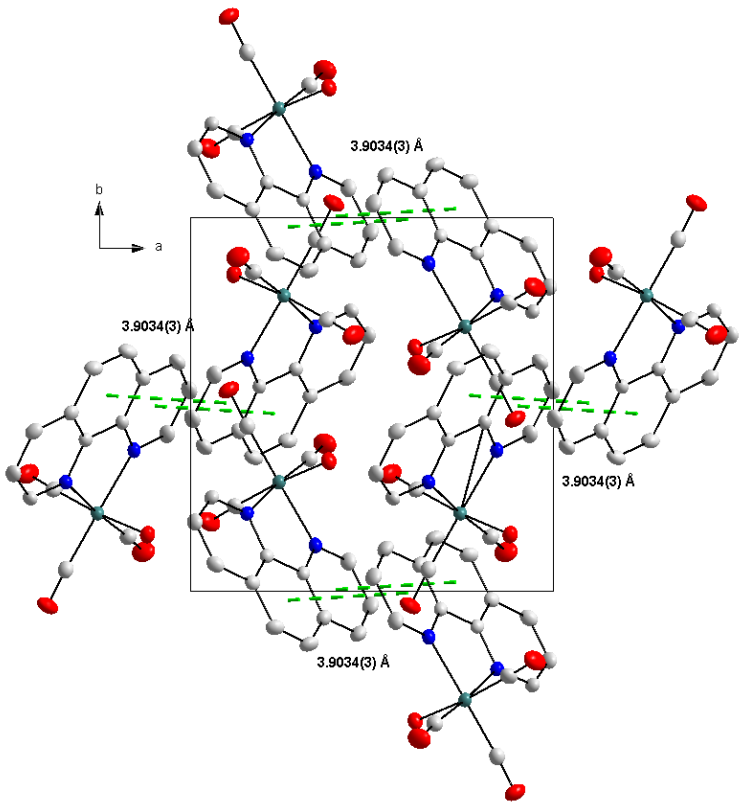

Table 3. The effect of different entering ligands on *fac*-$[Mn(CO)_3(Bipy)(CH_3OH)]^+$ at 25.0 °C. [Mn] =5 × 10^{-4} M, λ (pyridine) = 370 nm , λ (thiourea) = 365 nm , λ (Bromide) = 445 nm.

	10^3 k_{obs} (s^{-1})		
[ligand]	**Br^-**	**Py**	**TU**
0.01 M	12.5±0.4	0.0384±0.0007	1.13±0.04
0.02 M	17.1±0.6	0.0738±0.0005	2.27±0.05
0.04 M	21.5±0.4	0.116±0.004	4.33±0.01
0.05 M	23.2±0.8	0.153±0.003	5.34±0.06
0.075 M	30.3±0.3	0.233±0.006	7.56±0.06
0.1 M	41.1±0.2	0.301±0.002	9.76±0.02

Table 4. The effect of Br^- as entering ligands on *fac*-$[Mn(CO)_3(Phen)(CH_3OH)]^+$ at 15.0 °C, 25.0 °C, 35.0 °C and 45.0 °C. [Mn] =5 × 10^{-4} M, λ = 370 nm.

	10^1 k_{obs} (s^{-1})			
[Br^-]	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.01 M	0.12±0.01	0.283±0.003	0.625±0.004	1.84±0.03
0.02 M	0.14±0.03	0.317±0.005	0.78±0.01	2.24±0.06
0.04 M	0.1771±0.0008	0.43±0.01	1.00±0.07	2.81±0.03
0.05 M	0.204±0.006	0.450±0.006	1.19±0.04	3.13±0.07
0.075 M	0.26± 0.02	0.6008±0.0009	1.46±0.05	3.9±0.1
0.1 M	0.29±0.01	0.725± 0.004	1.79±0.07	4.5±0.2

Table 5. The effect of Py as entering ligands on *fac*-$[Mn(CO)_3(Phen)(CH_3OH)]^+$ at 15.0 °C, 25.0 °C, 35.0 °C and 45.0 °C. [Mn] = 5 × 10^{-4} M, λ = 370 nm.

	10^4 k_{obs} (s^{-1})			
[Py]	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.01 M	0.126±0.003	0.409±0.006	1.04±0.05	3.50±0.05
0.02 M	0.232±0.005	0.641±0.005	1.79±0.04	5.33±0.06
0.04 M	0.395±0.007	1.03±0.02	2.88±0.05	9.79±0.02
0.05 M	0.453±0.003	1.37±0.01	3.56±0.03	12.8±0.5
0.075 M	0.678±0.002	1.98±0.04	5.20±0.09	17.3±0.4
0.1 M	0.806±0.008	2.53±0.03	6.70±0.03	22±2

Table 6. The effect of TU as entering ligands on *fac*-$[Mn(CO)_3(Phen)(CH_3OH)]^+$ at 15.0 °C, 25.0 °C, 35.0 °C and 45.0 °C. [Mn] = 5 × 10^{-4} M, λ = 375 nm.

	10^2 k_{obs} (s^{-1})			
[TU]	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.01 M	0.143±0.004	0.314±0.004	0.483±0.005	0.846±0.005
0.02 M	0.163±0.002	0.362±0.008	0.656±0.002	1.07±0.02
0.04 M	0.220±0.007	0.53±0.01	0.912±0.002	1.79±0.02
0.05 M	0.254±0.003	0.597±0.007	0.987±0.007	2.00±0.08
0.075 M	0.321±0.004	0.803±0.005	1.47±0.04	2.52±0.04
0.1 M	0.360±0.004	0.961±0.001	1.74±0.05	3.28±0.03

Table 7. The effect of Br^- as entering ligands on *fac*-$[Mn(CO)_3(Pico)(CH_3OH)]$ at 15.0 °C, 25.0 °C, 35.0 °C and 45.0 °C. [Mn] = 3 x 10^{-3} M, λ = 415 nm.

	10^1 k_{obs} (s^{-1})			
[Br^-]	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.01 M	0.0898±0.0003	0.0898±0.0008	0.58±0.01	2.03±0.05
0.02 M	0.103±0.005	0.103±0.004	0.71±0.02	2.21±0.04
0.04 M	0.138±0.002	0.138±0.004	0.89±0.01	2.86±0.02
0.05 M	0.154±0.006	0.154±0.003	1.01±0.03	3.28±0.02
0.075 M	0.211±0.005	0.211±0.007	1.31±0.05	3.92± 0.03
0.1 M	0.244±0.006	0.244±0.002	1.61±0.04	4.55±0.04

Table 8. The effect of Py as entering ligands on *fac*-$[Mn(CO)_3(Pico)(CH_3OH)]$ at 15.0 °C, 25.0 °C, 35.0 °C and 45.0 °C. [Mn] = 3 x 10^{-3} M, λ = 365 nm.

	10^1 k_{obs} (s^{-1})			
[Py]	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.01 M	0.0397±0.0003	0.102±0.002	0.407±0.005	1.43±0.03
0.02 M	0.0784±0.0008	0.180±0.009	0.654±0.002	1.98±0.02
0.04 M	0.146±0.002	0.284±0.003	1.28±0.02	3.53±0.05
0.05 M	0.195±0.001	0.371±0.005	1.55±0.05	3.99±0.07
0.075 M	0.281±0.006	0.636±0.003	2.5± 0.2	4.85±0.07
0.1 M	0.383±0.005	0.851±0.002	3.36±0.03	5.45±0.05

Table 9. The effect of TU as entering ligands on *fac*-[$Mn(CO)_3(Pico)(CH_3OH)$] at 15.0 °C, 25.0 °C, 35.0 °C and 45.0 °C. [Mn] = 3 x 10^{-3} M, λ = 385 nm.

	$10^1 k_{obs}$ (s^{-1})			
[TU]	**15.0 °C**	**25.0 °C**	**35.0 °C**	**45.0 °C**
0.01 M	0.281±0.003	0.700±0.005	1.78±0.05	3.8±0.1
0.02 M	0.462±0.004	1.09±0.04	2.54±0.03	5.4±0.2
0.04 M	0.813±0.007	1.97±0.07	4.20±0.02	8.7±0.1
0.05 M	0.981±0.007	2.80±0.03	5.85±0.05	10.6±0.3
0.075 M	1.42±0.02	3.47±0.04	7.5± 0.8	15.5±0.2
0.1 M	1.91±0.06	4.57±0.05	9.6±0.4	19±3

Table 10. The effect of Py and TU as entering ligands on *fac*-[$Mn(CO)_3(2,4\text{-}QuinH)(CH_3OH)$] at 25.0 °C. [Mn] = 2 x 10^{-4} M, λ (pyridine) = 380 nm, λ (thiourea) = 395 nm.

	$10^1 k_{obs}$ (s^{-1})	
[ligand]	**Py**	**TU**
0.01 M	0.71±0.02	3.14±0.06
0.02 M	1.17±0.05	4.66±0.04
0.04 M	2.36± 0.03	6.7±0.1
0.05 M	2.57±0.03	7.1±0.1
0.075 M	3.94±0.01	9.2±0.2
0.1 M	4.67±0.05	10.1±0.1