Electronic Supplementary Information

Ligand Substitution Reactions of the $CpMn(CO)_2$(Cyclohexane) Intermediate Studied by Time-Resolved Infrared Absorption Spectroscopy

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Table S1. Pseudo-first order reaction rate constants for reaction of $CpMn(CO)_2(CyH)$ with THF.[a]

[THF], mol L^{-1}	k_{obs}, 10^6 s^{-1}				
	20 °C	**30 °C**	**40 °C**	**50 °C**	**60 °C**
0.100	0.154 (0.004)	0.253 (0.001)	0.357 (0.008)	0.575 (0.009)	0.811 (0.02)
0.101	0.192 (0.010)	0.252 (0.001)	0.359 (0.003)	0.479 (0.018)	0.654 (0.02)
0.199	0.279 (0.004)	0.405 (0.012)	0.628 (0.055)	1.04 (0.07)	1.28 (0.09)
0.200	0.273 (0.007)	0.470 (0.011)	0.743 (0.014)	1.07 (0.02)	1.61 (0.04)
0.500	0.695 (0.039)	1.02 (0.03)	1.58 (0.03)	2.38 (0.09)	3.34 (0.30)
0.500	0.668 (0.012)	1.07 (0.02)	1.61 (0.03)	2.59 (0.07)	—
0.800	1.20 (0.04)	1.60 (0.04)	2.38 (0.07)	3.69 (0.26)	5.24 (0.15)
0.800	1.07 (0.04)	1.53 (0.04)	2.58 (0.06)	3.57 (0.20)	5.32 (0.31)
1.00	1.35 (0.08)	1.86 (0.06)	2.77 (0.33)	4.25 (0.58)	6.22 (0.34)
1.00	1.32 (0.03)	1.94 (0.06)	2.71 (0.26)	4.46 (0.65)	—
1.20	1.66 (0.04)	2.24 (0.06)	3.04 (0.24)	5.36 (0.30)	—
1.205	1.62 (0.13)	2.32 (0.14)	3.15 (0.24)	5.37 (0.34)	—
1.412	1.75 (0.09)	2.56 (0.14)	3.88 (0.28)	5.96 (0.29)	—
1.60	2.09 (0.03)	3.19 (0.12)	3.69 (0.30)	—	—
1.60	1.90 (0.08)	—	3.85 (0.47)	—	—
1.80	—	3.85 (0.34)	4.37 (0.28)	—	—
1.801	—	—	4.42 (0.33)	—	—

[a] 1σ uncertainties given in parentheses.

Table S2. Pseudo-first order reaction rate constants for reaction of $CpMn(CO)_2(CyH)$ with furan.[a]

[Furan], mol L^{-1}	k_{obs}, 10^5 s^{-1}					
	15 °C	**20 °C**	**25 °C**	**35 °C**	**45 °C**	**55 °C**
0.022	0.228 (0.003)	0.310 (0.004)	0.401 (0.006)	0.572 (0.041)	—	—
0.057	0.423 (0.003)	0.595 (0.009)	0.704 (0.011)	1.27 (0.02)	2.03 (0.03)	3.10 (0.06)
0.103	0.788 (0.008)	1.00 (0.03)	1.27 (0.07)	2.09 (0.09)	3.61 (0.13)	4.62 (0.27)
0.203	1.51 (0.02)	1.72 (0.02)	2.22 (0.04)	3.55 (0.13)	6.46 (0.19)	8.63 (0.32)
0.403	2.44 (0.03)	3.12 (0.11)	3.83 (0.12)	—	10.5 (0.4)	15.6 (0.9)
0.640	3.84 (0.09)	5.57 (0.01)	6.69 (0.43)	12.3 (0.4)	17.3 (1.2)	24.7 (2.2)
0.830	4.90 (0.21)	6.57 (0.33)	9.02 (0.47)	14.6 (0.4)	21.8 (1.0)	31.7 (2.4)
1.09	6.35 (0.56)	8.55 (0.65)	10.6 (0.6)	19.8 (1.9)	25.7 (3.8)	39.1 (4.8)
1.11	6.81 (0.21)	—	12.8 (0.5)	20.7 (0.8)	27.2 (1.1)	39.4 (1.4)
1.28	8.02 (0.50)	10.9 (0.9)	13.5 (1.2)	22.7 (0.2)	34.0 (2.8)	45.8 (6.7)
1.49	10.1 (0.8)	12.2 (0.95)	15.2 (0.2)	—	—	—

[a]1σ uncertainties in parentheses.

Table S3. Pseudo-first order reaction rate constants for reaction of $CpMn(CO)_2(CyH)$ with pyrrolidine.[a]

[pyrrolidine],	k_{obs}, 10^6 s^{-1}					
mol L^{-1}	15 °C	20 °C	25 °C	35 °C	45 °C	55 °C
0.022	0.044 (0.002)	0.066 (0.002)	0.092 (0.002)	0.147 (0.004)	0.257 (0.006)	0.339 (0.009)
0.053	0.151 (0.008)	0.162 (0.014)	0.204 (0.002)	0.307 (0.005)	0.475 (0.008)	0.719 (0.008)
0.100	0.225 (0.001)	0.271 (0.016)	0.334 (0.002)	0.551 (0.003)	0.805 (0.007)	1.20 (0.01)
0.230	0.479 (0.010)	0.562 (0.008)	0.686 (0.008)	1.18 (0.03)	1.74 (0.03)	2.79 (0.01)
0.400	0.627 (0.010)	0.848 (0.015)	1.16 (0.03)	1.84 (0.06)	2.97 (0.01)	4.42 (0.02)
0.500	0.766 (0.034)	0.967 (0.034)	1.30 (0.05)	2.40 (0.09)	4.13 (0.30)	6.17 (0.04)
0.600	0.837 (0.068)	1.08 (0.05)	1.44 (0.07)	2.85 (0.02)	4.32 (0.58)	7.40 (1.31)
0.810	1.08 (0.74)	1.57 (0.15)	2.04 (0.12)	3.54 (0.19)	6.18 (0.36)	—
0.998	1.54 (2.76)	1.98 (0.27)	2.60 (0.15)	4.16 (0.39)	—	—
1.50	2.33 (0.40)	2.96 (0.53)	3.46 (0.45)	—	—	—

[a] 1σ uncertainties in parentheses.

Table S4. Pseudo-first order reaction rate constants for reaction of $CpMn(CO)_2(CyH)$ with cyclopentene.[a]

[cyclopentene],	k_{obs}, 10^6 s^{-1}					
mol L^{-1}	15 °C	20 °C	25 °C	35 °C	45 °C	55 °C
0.020	0.0131 (0.0002)	0.0215 (0.0005)	0.0249 (0.0005)	0.0431 (0.0006)	0.0747 (0.0011)	0.119 (0.002)
0.0508	0.0296 (0.0006)	0.0405 (0.0009)	0.0505 (0.0011)	0.0849 (0.0026)	0.148 (0.005)	0.236 (0.005)
0.10	0.0462 (0.0008)	0.0692 (0.0014)	0.0823 (0.0035)	0.150 (0.003)	0.234 (0.010)	0.451 (0.005)
0.30	0.174 (0.017)	0.221 (0.005)	0.281 (0.007)	0.457 (0.011)	—	—
0.50	0.247 (0.005)	0.399 (0.004)	0.469 (0.004)	0.827 (0.008)	1.35 (0.01)	2.15 (0.05)
1.00	0.476 (0.008)	0.649 (0.008)	0.791 (0.016)	1.48 (0.03)	2.21 (0.06)	3.71 (0.10)
1.50	0.694 (0.010)	0.935 (0.015)	1.24 (0.02)	2.10 (0.05)	3.34 (0.09)	5.37 (0.43)
2.00	0.976 (0.027)	1.27 (0.03)	1.73 (0.08)	2.86 (0.10)	4.80 (0.16)	7.46 (0.38)
2.50	1.04 (0.02)	1.62 (0.03)	2.25 (0.05)	3.45 (0.10)	5.65 (0.18)	—
3.00	1.37 (0.045)	1.87 (0.05)	2.51 (0.08)	—	6.70 (0.35)	—
4.00	1.92 (0.13)	—	3.48 (0.27)	—	—	—
5.00	2.23 (0.24)	—	4.34 (0.46)	—	—	—
6.00	2.36 (0.28)	—	4.98 (0.46)	—	—	—