

Supplementary Information

belonging to the manuscript

A Structural Study of $[\text{CpM}(\text{CO})_3\text{H}]$ ($\text{M} = \text{Cr}, \text{Mo}$ and W) by Single Crystal X-Ray Diffraction and DFT Calculations: Sterically Crowded Yet Surprisingly Flexible Molecules

Richard P. L. Burchell, Peter Sirsch, Andreas Decken and G. Sean McGrady

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S2 – $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{H}]$ **2**

S3 – $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}]$ **3**

S3 – $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$ **4**

S4 – $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3]$ **5**

- **Geometrical parameters for the optimised geometries of 4 and 5**

S5 – $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$ **4**

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- **Selected vibrational modes for 1-3 (S7)**

• Cartesian coordinates for the optimised geometries of 1-5:

$[(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}]$ (1):

24	-0.144818000	0.061960000	0.000000000
6	-0.928375000	-2.044058000	0.000000000
6	-0.116089000	-1.854691000	1.149057000
6	1.199759000	-1.545423000	0.713301000
6	1.199759000	-1.545423000	-0.713301000
6	-0.116089000	-1.854691000	-1.149057000
1	-1.979325000	-2.287761000	0.000000000
1	-0.442379000	-1.936214000	2.174547000
1	2.050848000	-1.360920000	1.350325000
1	2.050848000	-1.360920000	-1.350325000
1	-0.442379000	-1.936214000	-2.174547000
6	-0.745206000	0.963650000	1.501428000
6	1.226734000	1.328568000	0.000000000
6	-0.745206000	0.963650000	-1.501428000
8	-1.159257000	1.483512000	2.438875000
8	2.077995000	2.097960000	0.000000000
8	-1.159257000	1.483512000	-2.438875000
1	-1.689553000	0.405615000	0.000000000

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{H}]$ (2):

42	-0.142565000	0.054232000	0.000000000
6	-0.939599000	-2.224010000	0.000000000
6	-0.123469000	-2.050924000	1.150978000
6	1.199736000	-1.768717000	0.715244000
6	1.199736000	-1.768717000	-0.715244000
6	-0.123469000	-2.050924000	-1.150978000
1	-1.993125000	-2.458114000	0.000000000
1	-0.449952000	-2.138221000	2.176208000
1	2.058801000	-1.622558000	1.352007000
1	2.058801000	-1.622558000	-1.352007000
1	-0.449952000	-2.138221000	-2.176208000
6	-0.722931000	1.116143000	1.587634000
6	1.326946000	1.426602000	0.000000000
6	-0.722931000	1.116143000	-1.587634000
8	-1.084547000	1.676888000	2.522721000
8	2.169766000	2.206431000	0.000000000
8	-1.084547000	1.676888000	-2.522721000
1	-1.806349000	0.446686000	0.000000000

$[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{H}]$ (3):

74	-0.121605000	0.037989000	0.000000000
6	-0.883551000	-2.242479000	0.000000000
6	-0.073077000	-2.048635000	1.152032000
6	1.246571000	-1.737683000	0.716153000
6	1.246571000	-1.737683000	-0.716153000
6	-0.073077000	-2.048635000	-1.152032000
1	-1.933325000	-2.492166000	0.000000000
1	-0.398808000	-2.141557000	2.176751000
1	2.101902000	-1.575093000	1.353497000
1	2.101902000	-1.575093000	-1.353497000
1	-0.398808000	-2.141557000	-2.176751000
6	-0.683479000	1.091996000	1.591589000
6	1.320650000	1.422456000	0.000000000
6	-0.683479000	1.091996000	-1.591589000
8	-1.029173000	1.645496000	2.539957000
8	2.162397000	2.208244000	0.000000000
8	-1.029173000	1.645496000	-2.539957000
1	-1.809313000	0.372416000	0.000000000

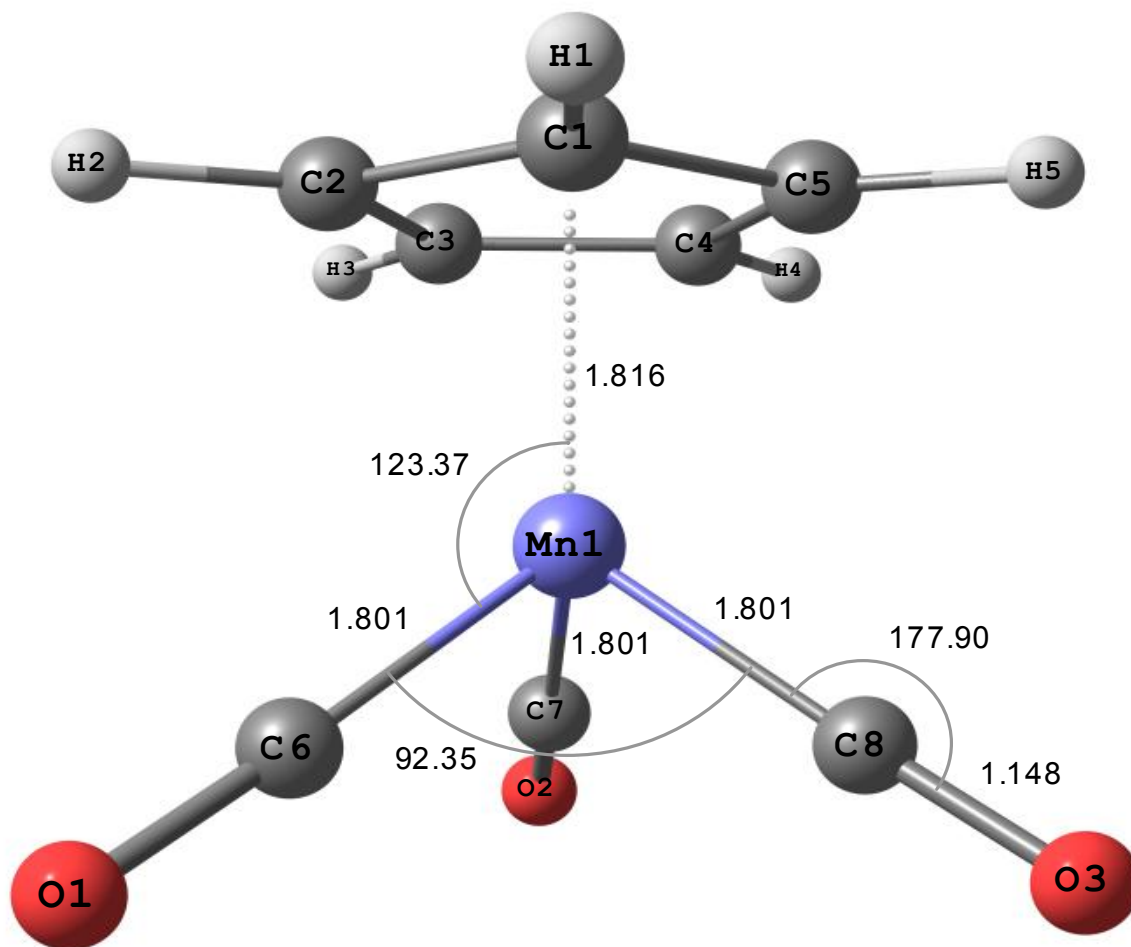
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3]$ (4):

25	0.075700000	0.001469000	-0.000551000
6	-1.729514000	-1.218413000	0.123754000
6	-1.743113000	-0.489765000	-1.102791000
6	-1.748683000	0.892928000	-0.800635000
6	-1.743858000	1.032783000	0.623335000
6	-1.737939000	-0.268736000	1.184065000
1	-1.731459000	-2.291724000	0.228480000
1	-1.739295000	-0.919058000	-2.093070000
1	-1.757569000	1.698841000	-1.517915000
1	-1.752814000	1.961448000	1.172088000
1	-1.727024000	-0.500558000	2.238319000
6	1.068748000	-0.953465000	-1.161078000
6	1.051346000	1.494802000	-0.251100000
6	1.077512000	-0.521899000	1.401985000
8	1.664756000	-1.578698000	-1.917265000
8	1.635641000	2.469567000	-0.414039000
8	1.680687000	-0.865254000	2.316389000

$[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3]$ (5):

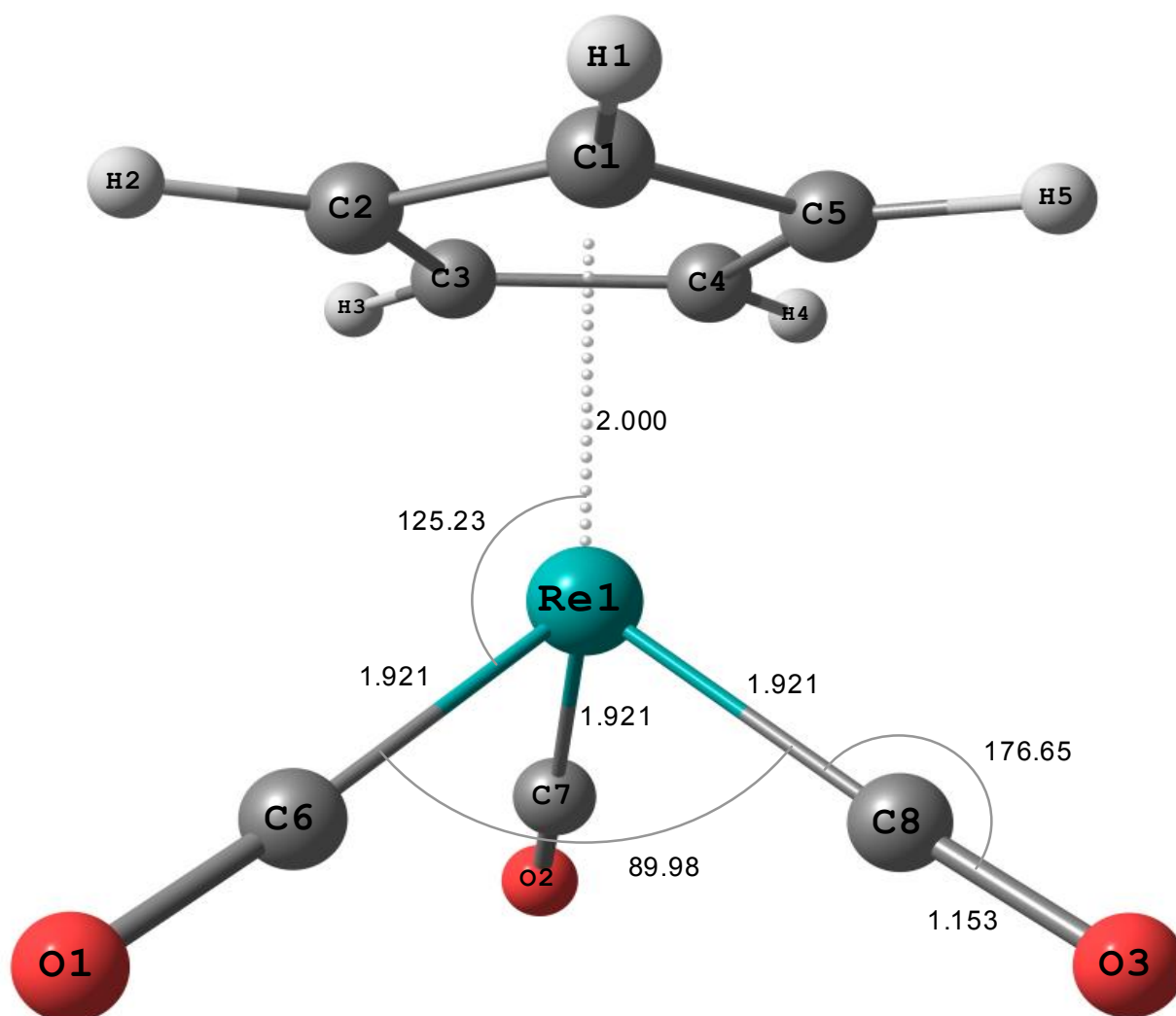
75	-0.060065000	0.000388000	0.000325000
6	1.936534000	-1.221693000	0.092875000
6	1.938305000	-0.289090000	1.177581000
6	1.943866000	1.024619000	0.640991000
6	1.944269000	0.916710000	-0.789668000
6	1.937597000	-0.465775000	-1.118170000
1	1.965437000	-2.296574000	0.175004000
1	1.945536000	-0.542489000	2.226762000
1	1.966627000	1.942320000	1.207918000
1	1.973093000	1.736648000	-1.490017000
1	1.943035000	-0.875666000	-2.116808000
6	-1.171078000	-0.767757000	1.365823000
6	-1.154047000	1.578815000	-0.018471000
6	-1.168807000	-0.797645000	-1.349852000
8	-1.783346000	-1.248126000	2.216842000
8	-1.754358000	2.563440000	-0.029947000
8	-1.778384000	-1.298115000	-2.191133000

• Geometrical parameters for CpMn(CO)_3 (4) (distances in Å; angles in deg)



Unit:	Distance [Å]	Unit:	Angle [deg]
Mn1–C6	1.801	X–Mn1–C6	123.4
Mn1–C7	1.801	X–Mn1–C7	123.2
Mn1–C8	1.801	X–Mn1–C8	123.5
Mn1–X	1.816	C6–Mn1–C7	92.9
C6–O1	1.148	C6–Mn1–C8	92.4
C7–O2	1.148	C7–Mn1–C8	92.7
C8–O3	1.148	C6–Mn1–X–C8	-120.3

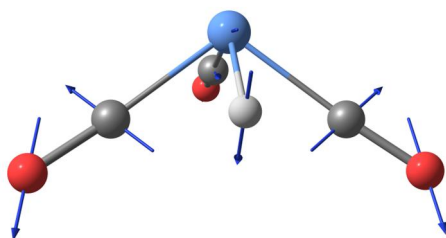
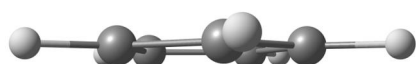
• Geometrical parameters for CpRe(CO)_3 (**5**) (distances in Å; angles in deg)



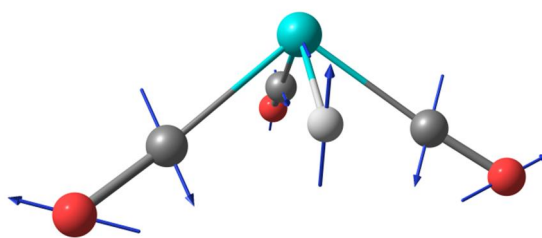
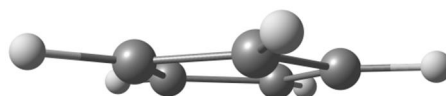
Unit:	Distance [Å]	Unit:	Angle [deg]
Re1–C6	1.921	X–Re1–C6	125.2
Re1–C7	1.921	X–Re1–C7	124.9
Re1–C8	1.921	X–Re1–C8	125.2
Re1–X	2.000	C6–Re1–C7	90.4
C6–O1	1.153	C6–Re1–C8	90.0
C7–O2	1.153	C7–Re1–C8	90.3
C8–O3	1.153	C6–Re1–X–C8	119.8

Selected vibrational modes for $\text{CpCr(CO)}_3\text{H}$ (1), $\text{CpMo(CO)}_3\text{H}$ (2), and $\text{CpW(CO)}_3\text{H}$ (3), showing the concerted movement of the MH and M(CO)_2 moieties

1 (@446 cm^{-1})



2 (@526 cm^{-1})



3 (@530 cm^{-1})

