SUPPLEMENTARY DATA

A solid-state ^{55}Mn NMR spectroscopy and DFT investigation of manganese pentacarbonyl compounds

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Table S1. Principal components of the ^{55}Mn CS tensors measured from powder samples.

		δ_{11} / ppm	δ_{22} / ppm	δ_{33} / ppm
$ClMn(CO)_5$		-512.7	-594.6	-1772.7
$BrMn(CO)_5$		-666.1	-752.8	-1821.1
$IMn(CO)_5$		-1017.5	-1065.0	-1967.5
$Hg[Mn(CO)_5]_2$		-2199.7	-2199.7	-2449.7
$CH_3Mn(CO)_5$		-2195.0	-2195.0	-2375.0
$PhCH_2Mn(CO)_5$		-1873.0	-1999.0	-2293.0
$Ph_3SnMn(CO)_5$[a]		-2393.5	-2603.1	-2608.5
$Ph_2ClSnMn(CO)_5$	site 1	-2397.7	-2414.7	-2567.7
	site 2	-2364.0	-2382.0	-2544.0

a) From Ref. 1.

Table S2. Non-relativistic DFT calculated ^{55}Mn NMR parameters for optimized and experimental geometries.[a]

	σ_{11}/ppm	σ_{22}/ppm	σ_{33}/ppm	σ_{iso}/ppm	δ_{iso} / ppm	Ω / ppm	κ	C_Q / MHz	η_Q
MnO_4^-[b]	-	-	-	-3492	0	-	-	-	-
$FMn(CO)_5$[c]	-2635	-2635	-1268	-2180	-1312	1367	1.00	-3.5	0.00
$ClMn(CO)_5$[d]	-2237	-2224	-1379	-1947	-1545	858	0.97	-6.6	0.57
$ClMn(CO)_5$[c]	-2146	-2146	-1189	-1827	-1665	956	1.00	10.6	0.00
$BrMn(CO)_5$[c]	-1966	-1966	-1151	-1694	-1798	814	1.00	14.6	0.00
$IMn(CO)_5$[d]	-1946	-1940	-1323	-1584	-1908	624	0.98	7.1	0.02
$IMn(CO)_5$[c]	-1664	-1664	-1109	-1479	-2013	555	1.00	13.2	0.00
$Cl_3SnMn(CO)_5$[d] site 1	-1535	-1402	-1157	-1365	-2127	377	0.30	46.8	0.30
site 2	-1489	-1371	-1248	-1369	-2123	241	0.04	-18.3	0.38
$PhCH_2Mn(CO)_5$[c,e]	-1549	-1483	-1063	-1365	-2127	486	0.70	-19.1	0.10
$Hg[Mn(CO)_5]_2$[d]	-1255	-1235	-1031	-1173	-2319	224	0.80	21.9	0.10
$CH_3Mn(CO)_5$[c,e]	-1239	-1237	-1021	-1166	-2326	218	1.00	-28.2	0.00
$HMn(CO)_5$[f]	-1038	-997	-906	-980	-2512	132	0.39	-50.7	0.43
$HMn(CO)_5$[c]	-1047	-931	-931	-970	-2522	116	-1.00	-47.9	0.00
$HMn(CO)_5$[g]	-942	-942	-852	-912	-2580	90	1.00	-19.4	0.00
$Ph_3SnMn(CO)_5$[d]	-714	-626	-590	-643	-2677	124	-0.41	19.9	0.81

a) The magnetic shielding parameters are defined as follows:[2] $\sigma_{11} \le \sigma_{22} \le \sigma_{33}$, $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, $\Omega = \sigma_{33} - \sigma_{11}$, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$, $\delta_{sample} = \sigma_{ref}(calc) - \sigma_{sample}(calc)$. The EFG parameters are incorporated in $C_Q = eQV_{ZZ}/h$ and $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$ where $|V_{XX}| \le |V_{YY}| \le |V_{ZZ}|$, e is the electron charge and h is the Planck constant.

b) Optimized to T_d symmetry ($r_{(Mn-O)}$ = 1.621 Å)
c) Structures were optimized to C_{4v} symmetry, except where noted.
d) Experimental single-crystal X-ray diffraction structure.
e) Due to ligand, optimized geometry deviates from C_{4v} symmetry.
f) Experimental single-crystal neutron diffraction structure.[3]
g) Experimental gas-phase structure from microwave spectroscopy.[4]

Table S3. Scalar + spin-orbit relativistic DFT calculated ^{55}Mn NMR parameters for experimental geometries.

	σ_{11}/ppm	σ_{22}/ppm	σ_{33}/ppm	σ_{iso}/ppm	δ_{iso} / ppm	Ω / ppm	κ	C_Q / MHz	η_Q
MnO_4^{-}[b]	-	-	-	-3401	0	-	-	-	-
MnO_4^{-}[c]	-3275	-3231	-3190	-3232	-169	85	-0.05	-5.46	0.246
$ClMn(CO)_5$[d]	-2151	-2139	-1301	-1864	-1537	850	0.97	-6.29	0.539
$IMn(CO)_5$[d]	-1827	-1821	-1242	-1630	-1771	585	0.98	7.79	0.015
$Cl_3SnMn(CO)_5$[d] site 1	-1627	-1332	-1229	-1396	-2005	398	-0.49	44.22	0.450
site 2	-1586	-1455	-1178	-1406	-1995	408	0.36	-22.86	0.608
$Hg[Mn(CO)_5]_2$[d]	-1477	-1463	-965	-1302	-2099	512	0.95	-18.66	0.173
$Mn_2(CO)_{10}$[d]	-1198	-1189	-985	-1124	-2277	213	0.92	-6.79	0.436
η^5-$CpMn(CO)_3$[d]	-1281	-1234	-714	-1077	-2324	567	0.83	66.32	0.068
$HMn(CO)_5$[e]	-966	-926	-836	-910	-2492	130	0.38	-52.15	0.433
$HMn(CO)_5$[f]	-872	-872	-785	-843	-2558	87	1.00	-19.79	0.000
$Ph_3SnMn(CO)_5$[d]	-682	-583	-540	-602	-2799	142	-0.40	23.41	0.780

a) The magnetic shielding parameters are defined as follows:[2] $\sigma_{11} \le \sigma_{22} \le \sigma_{33}$, $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, $\Omega = \sigma_{33} - \sigma_{11}$, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$, $\delta_{sample} = \sigma_{ref}(calc) - \sigma_{sample}(calc)$. The EFG parameters are incorporated in $C_Q = eQV_{ZZ}/h$ and $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$ where $|V_{XX}| \le |V_{YY}| \le |V_{ZZ}|$, e is the electron charge and h is the Planck constant.

b) Optimized to T_d symmetry ($r_{(Mn-O)}$ = 1.621 Å)

c) Experimental X-ray diffraction structure.

d) Experimental single-crystal X-ray diffraction structure.

e) Experimental single-crystal neutron diffraction structure.[3]

f) Experimental gas-phase structure from microwave spectroscopy.[4]

References

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