Supplementary Information

Infrared Spectra of Manganese Insertion, Vinyl, and Cyclic Complexes Prepared in Reactions of the Laser-Ablated Mn Atoms with Methane, Ethane, Ethyl Chloride, and 1,2-Dichloroethane

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Table S1: Calculated Harmonic Frequencies of the Higher Energy CH_2=MnH_2 Isotopomers in the $^4B_1$ ground state[a]

Approximate Description	CH_2=MnH_2				CD_2=MnD_2				$^{13}CH_2$=MnH_2			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
B_2 CH_2 str.	3207.1	0	3141.5	0	2385.9	1	2337.4	1	3194.0	0	3128.6	0
A_1 CH_2 str.	3083.2	1	3013.5	2	2226.8	1	2176.8	2	3078.5	1	3008.9	1
A_1 MnH_2 str.	1742.2	76	1752.9	71	1236.1	40	1243.1	38	1742.1	76	1752.8	71
B_1 MnH_2 str.	1668.4	484	1681.1	342	1202.6	244	1211.4	173	1668.3	484	1681.1	342
A_1 CH_2 scis.	1290.3	5	1248.5	1	988.7	1	987.0	0	1283.0	5	1239.5	1
B_1 CH_2 wag	681.1	3	669.3	8	531.6	0	522.3	2	675.4	3	663.8	8
A_1 MnH_2 scis.	668.1	53	681.0	10	478.6	25	489.2	7	668.1	54	678.7	6
A_1 C-Mn str.	641.6	7	725.7	18	587.1	10	642.2	11	625.3	6	710.7	21
B_2 CH_2 rock	500.5	15	465.1	13	378.1	12	351.5	9	497.7	15	462.5	13
A_2 CH_2 twist	372.8	0	402.3	0	263.7	0	284.6	0	372.8	0	402.3	0
B_2 MnH_2 wag	292.6	193	111.2	163	212.1	100	80.4	86	292.5	193	111.2	163
B_1 MnH_2 rock	217.1	61	239.7	42	160.5	34	178.6	24	216.4	60	238.8	42

[a] Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all electron basis set is used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP. [c] Computed with BPW91. CH_3-MnH has a C_{3v} structure.

Table S2: Calculated Harmonic Frequencies of MnH_2-CH_2CH_2 Isotopomers in the $^4A_2$ ground state[a]

Approximate Description	MnH_2-CH_2CH_2				MnD_2-CD_2CD_2			
	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
B_1 CH_2 str.	3184.7	7	3104.1	18	2366.7	3	2306.3	8
A_1 CH_2 str.	3098.8	1	3019.4	2	2264.5	7	2203.9	0
B_2 CH_2 str.	3089.7	8	3012.4	18	2232.2	3	2176.5	8
B_1 MnH_2 str.	1734.8	108	1741.0	33	1235.9	57	1255.4	4
A_1 MnH_2 str.	1665.5	76	1830.8	359	1311.4	62	1307.4	188
A_1 CH_2 scis.	1510.4	10	1451.1	1	1191.2	29	1235.9	17
B_2 CH_2 scis.	1445.2	4	1393.2	3	1069.1	4	1030.7	3
A_1 C-C str.	1206.5	62	1162.9	21	953.1	15	922.4	7
B_2 CH_2 wag	878.6	24	861.6	21	720.4	10	712.9	9
B_1 CH_2 twist	493.4	4	541.5	5	362.4	2	405.1	3
A_1 MnH_2 scis.	432.9	55	436.9	19	304.0	32	416.9	16

[a] Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all electron basis set is used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP. [c] Computed with BPW91. CH_3CH_2-MnH has a C_s structure.

Table S3: Calculated Harmonic Frequencies of CH_3CH-MnH_2 Isotopomers in the $^6A'$ ground state[a]

Approximate Description	$CH_3CH=MnH_2$				$CD_3CD=MnD_2$			
	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
A' CH_3 str.	3092.1	12	3044.1	8	2285.1	5	2251.8	3
A' C-H str.	3078.5	3	2995.5	5	2264.3	2	2200.2	3
A" CH_3 str.	3038.3	8	2992.9	7	2247.0	4	2213.2	3
A' CH_3 str.	2994.4	14	2942.4	14	2151.7	6	2113.9	6
A' MnH_2 str.	1724.6	98	1738.1	96	1228.3	38	1235.5	40
A" MnH_2 str.	1649.1	537	1668.7	387	1189.3	268	1202.6	194
A' CH_3 bend	1472.5	7	1424.9	8	1162.4	14	1156.0	16
A" CH_3 bend	1470.3	4	1423.2	4	1059.7	3	1025.1	3
A' C-H bend	1232.9	38	1210.7	31	1050.0	14	1028.7	11
A" CH_3 rock	971.9	10	942.7	8	774.6	8	754.1	5
A' MnH_2 scis.	664.8	74	666.6	29	469.9	19	476.4	9
A' C-Mn str.	555.1	7	603.6	10	513.7	28	540.3	15

[a] Frequencies and intensities are in cm^{-1} and km/mol computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all electron basis set is used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP. [c] Computed with BPW91. CH_3CH-MnH_2 has a C_s structure.

Table S4: Calculated Harmonic Frequencies of $ClCH_2CH_2$-MnH Isotopomers in the $^6A'$ ground state[a]

Approximate Description	$ClCH_2CH_2$-MnH				$ClCD_2CD_2$-MnH			
	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
A" C_aH_2 as str.	3131.4	8	3071.2	7	2328.3	4	2282.6	3
A' C_aH_2 s str.	3077.0	17	3014.7	14	2235.1	9	2189.4	7
A" C_bH_2 as str.	3034.7	9	2990.7	7	2245.0	3	2213.0	3
A' C_bH_3 s str.	2998.1	8	2946.5	8	2176.0	2	2138.4	3
A' Mn-H str.	1654.2	497	1651.3	399	1181.2	209	1179.7	180
A' C_aH_2 scis.	1483.0	2	1435.1	3	1145.0	112	1116.0	90
A' C_bH_2 scis.	1454.9	3	1401.7	3	1081.6	10	1044.9	8
A' C_aH_2 wag	1288.6	70	1240.2	48	977.1	129	938.9	93
A" C_aH_2 twist	1125.5	5	1081.7	4	821.3	1	791.4	1
A' C_bH_2 wag	1099.4	1	1054.3	17	872.4	10	831.7	8
A' C-C str.	1015.4	172	988.0	119	911.8	36	892.0	21
A' C-Cl str.	615.6	119	604.4	101	587.8	97	577.5	87
A" C_bH_2 rock	561.3	28	541.3	20	419.6	19	404.1	13
A' C-Mn str.	510.5	8	508.7	8	454.5	7	449.5	6

[a] Frequencies and intensities are in cm^{-1} and km/mol computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all electron basis set is used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP. [c] Computed with BPW91. Calculation results only for observable bands (frequency > 400 cm^{-1} and intensity > 5 km/mol) are shown. $ClCH_2CH_2$-MnH has a C_s structure.

Table S5: Calculated Fundamental Frequencies of CH_3CH=MnHCl Isotopomers in the $^4A'$ ground state[a]

Approximate Description	CH_3CH=MnHCl				CD_3CD=MnDCl			
	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
C_aH_3 as str.	3093.2	13	3044.3	9	2288.3	5	2252.6	4
C_b-H str.	3067.6	3	2993.0	5	2254.0	3	2206.4	3
C_aH_3 as str.	3033.8	8	2986.3	6	2241.4	4	2198.2	4
C_aH_3 s str.	2989.1	9	2936.2	8	2149.1	4	2110.4	3
Mn-H str.	1796.6	110	1806.6	111	1283.7	59	1290.4	59
C_aH_3 bend	1474.7	10	1427.4	9	1164.2	3	1149.1	7
C_aH_3 bend	1466.6	6	1418.6	7	1059.5	3	1026.5	5
C_b-H ip bend	1241.0	20	1208.9	24	1046.1	11	1020.6	7
Mn-H bend	679.2	4	678.6	1	667.3	2	641.7	4
C_b-Mn str.	558.7	43	582.6	27	532.2	30	541.0	26
Mn-H ip bend	498.0	36	517.8	31	496.7	23	506.2	5

[a] Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all electron basis set is used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP. [c] Computed with BPW91. Calculation results only for observable bands (frequency > 400 cm^{-1} and intensity > 3 km/mol) are shown. CH_3CH=MnHCl has a C_1 structure.

Table S5: Calculated Harmonic Frequencies of $ClCH_2CH_2$-MnCl Isotopomers in the $^6A'$ ground state[a]

Approximate Description	$ClCH_2CH_2$-MnCl				$ClCD_2CD_2$-MnCl			
	B3LYP[b]	Int[b]	BPW91[c]	int[c]	B3LYP[b]	Int[b]	BPW91[c]	int[c]
A" C_aH_2 str.	3134.1	6	3072.2	6	2330.3	3	2283.3	3
A' C_aH_2 str.	3079.5	14	3015.7	13	2236.8	8	2190.1	7
A" C_bH_2 str.	3046.5	5	2992.4	4	2254.4	2	2214.3	1
A' C_bH_2 str.	3008.0	5	2948.6	6	2183.3	1	2139.7	2
A' C_aH_2 wag	1294.1	50	1246.3	49	1143.8	54	1112.4	63
A" C_aH_2 rock	1294.1	11	1251.2	0	1082.9	9	1045.9	9
A" C_aH_2 twist	1127.8	5	1089.1	4	910.5	27	889.5	18
A' C_a-C_b str.	1018.8	124	998.4	120	986.6	104	948.6	93
A' C_a-Cl str.	636.2	104	619.5	105	607.8	74	593.8	72
A" C_bH_2 rock	582.7	24	562.1	18	491.1	46	485.5	57
A' C_b-Mn str.	541.3	19	539.7	23	436.9	16	420.6	12

[a] Frequencies and intensities are in cm^{-1} and km/mol computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all electron basis set is used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP. [c] Computed with BPW91. Calculation results only for observable bands (frequency > 400 cm^{-1} and intensity > 5 km/mol) are shown. $ClCH_2CH_2$-MnCl has a C_1 structure.

Table S6: Parameters from Natural Bond Order Analysis for the C-Mn and Mn-X (X = H, Cl, Br) Bonds of Insertion Products[a]

Product	<CMX[b]	r(C-M)	EBO[c]	% C	% M	r(M-X)	EBO[c]	% X (X = H, Cl, Br)	% M
CH_3-MnH	180.0	2.083	0.94	83.3 [s(23.5), p(76.4)]	16.7 [s(34.6), p(45.4), d(20.8)]	1.698	0.94	76.7 [s(99.9)]	22.3 [s(36.0), p(54.1), d(9.8)]
C_2H_5-MnH	172.4	2.091	0.92	82.7 [s(20.4), p(79.6)]	17.3 [s(32.9), p(40.3), d(26.7)]	1.701	0.94	78.0 [s(99.9)]	22.0 [s(37.4), p(51.0), d(11.5)]
$ClCH_2CH_2$-MnH	179.1	2.112	0.89	83.9 [s(18.6), p(81.3)]	16.1 [s(35.1), p(44.1), d(20.8)]	1.689	0.93	77.6 [s(99.9)]	22.4 [s(35.3), p(53.5), d(11.2)]
$ClCH_2CH_2$-MnCl	179.7	2.082	0.91	81.9 [s(18.4), p(81.4)]	18.1 [s(37.6), p(39.7), d(22.6)]	2.216	0.95	88.9 [s(24.5), p(75.1)]	11.1 [s(30.3), p(55.3), d(14.2)]
C_2H_5-MnCl	178.3	2.065	0.93	80.9 [s(19.7), p(80.1)]	19.1 [s(36.1), p(38.0), d(26.0)]	2.230	0.95	89.1 [s(24.9), p(74.8)]	10.8 [s(31.1), p(55.7), d(12.9)]
CH_3-ScH	115.5	2.169	0.99	81.2 [s(21.6), p(78.4)]	18.8 [s(26.5), p(3.4), d(70.1)]	1.823	0.99	75.0 [s(99.9)]	25.0 [s(35.3), p(9.3), d(55.4)]
CH_3-TiH	125.8	2.133	0.99	80.8 [s(22.9), p(77.1)]	19.2 [s(23.4), p(6.2), d(70.3)]	1.790	0.99	75.3 [s(99.7)]	24.6 [s(40.7), p(12.7), d(46.6)]
CH_3-VH	118.6	2.074	1.00	76.2 [s(21.2), p(78.8)]	23.8 [s(35.2), p(4.2), d(60.5)]	1.699	0.99	70.0 [s(99.7)]	30.0 [s(39.3), p(9.0), d(51.6)]
CH_3-CrH	113.3	2.039	0.99	73.0 [s(20.8), p(79.2)]	27.0 [s(35.2), p(2.7), d(62.1)]	1.654	0.99	67.5 [s(99.9)]	32.5 [s(44.8), p(6.9), d(48.3)]
CH_3-FeH	147.2	2.035	0.96	79.0 [s(21.4), p(78.6)]	21.0 [s(37.1), p(28.0), d(34.8)]	1.628	0.96	73.1 [s(99.9)]	26.9 [s(38.8), p(33.8), d(27.3)]
CH_3-CoH	141.4	1.984	0.96	76.2 [s(20.3), p(79.6)]	23.8 [s(35.7), p(25.6), d(38.7)	1.587	0.97	71.7 [s(99.9)]	28.9 [s(40.1), p(31.2), d(28.7)]
CH_3-NiH	95.7	1.845	0.97	62.3 [s(18.0), p(82.0)]	37.7 [s(41.7), p(0.5), d(57.8)]	1.436	0.96	56.7 [s(99.9)]	43.3 [s(53.1), p(2.7), d(44.3)]
CH_3-CuH	128.2	1.963	0.94	65.6 [s(16.2), p(83.7)]	34.5 [s(45.5), p(12.0), d(30.5)]	1.526	0.93	64.0 [s(99.9)]	36.0 [s(50.4), p(27.1), d(22.5)]
CH_3-CuH^-	180.0	1.988	0.93	86.0 [s(28.1), p(71.9)]	14.0 [s(49.2), p(45.2), d(5.5)]	1.565	0.94	79.5 [s(99.9)]	20.5 [s(43.2), p(53.5), d(3.3)]
CH_3-ZnH	180.0	1.954	0.97	79.7 [s(22.3), p(77.7)]	20.3 [s(52.0), p(46.2), d(1.9)]	1.543	0.96	73.1 [s(99.9)]	26.9 [s(44.9), p(53.7), d(1.40)]
CH_3-CdH	180.0	2.135	0.90	78.4 [s(19.8), p(80.1)]	21.6 [s(50.2), p(46.7), d(3.0)]	1.680	0.90	73.7 [s(99.9)]	26.3 [s(44.6), p(53.0), d(2.4)]
CH_3-HgH	180.0	2.129	0.85	75.2 [s(19.4), p(80.6)]	24.8 [s(45.7), p(47.3), d(7.0)]	1.653	0.85	69.4 [s(99.9)]	30.7 [s(41.6), p(52.6), d(5.8)]
CH_3-ReH	121.6	2.049	0.99	63.9 [s(21.1), p(78.9)]	36.1 [s(30.1), p(0.5), d(69.4)]	1.653	0.98	56.6 [s(99.8)]	43.4 [s(34.3), p(2.7), d(63.1)]
CH_3-MgBr	180.0	2.076	0.97	84.5 [s(21.7), p(78.3)]	15.5 [s(61.5), p(38.3), d(0.2)]	2.355	0.97	89.0 [s(21.7), p(77.9)]	11.0 [s(38.4), p(59.6), d(1.8)]

[a] Computed with B3LYP/6-311++G(3df,3pd). [b] C-M-X bond angle in degree. [c] Effective bond order.

Cartesian coordinates calculated (B3LYP) for the observed molecules

CH_3-MnH

C	0.000000	0.000000	-1.561110
H	0.000000	1.015384	-1.969811
H	0.879349	-0.507692	-1.969811
H	-0.879349	-0.507692	-1.969811
Mn	0.000000	0.000000	0.522253
H	0.000000	0.000000	2.219774

CH_3CH_2-MnH

C	-.515140	-2.038418	.000000
H	-.141207	-3.067071	.000000
H	-1.158789	-1.938743	.877350
H	-1.158789	-1.938743	-.877350
C	.621294	-.997934	.000000
H	1.268192	-1.165745	.869930
H	1.268192	-1.165745	-.869930
Mn	.000000	.998103	.000000
H	-.714524	2.541586	.000000

CH_2CH-MnH

C	-0.403572	-2.065170	0.000000
H	-1.473113	-1.868543	0.000000
H	-0.144391	-3.122071	0.000000
C	0.510964	-1.084988	0.000000
H	1.546412	-1.431725	0.000000
Mn	0.000000	0.912738	0.000000
H	-0.573262	2.504848	0.000000

CH_3CH_2-MnCl

C	2.137958	-1.965550	0.000000
H	3.193959	-2.250927	0.000000
H	1.684838	-2.430832	0.877801
H	1.684838	-2.430832	-0.877801
C	1.953494	-0.437112	0.000000
H	2.458732	-0.004527	0.871129
H	2.458732	-0.004527	-0.871129
Mn	0.000000	0.232455	0.000000
Cl	-2.119401	0.925074	0.000000

$MnHCl\text{-}CH_2CH_2$

Mn	0.615707	0.649286	0.000000
H	2.206934	1.152854	0.000000
Cl	-1.614375	0.917141	0.000000
C	0.615707	-2.057012	0.666648
C	0.615707	-2.057012	-0.666648
H	-0.308238	-2.013530	1.229239
H	1.536385	-2.132597	1.231299
H	-0.308238	-2.013530	-1.229239
H	1.536385	-2.132597	-1.231299

$MnCl_2\text{-}CH_2CH_2$

Mn	0.000000	0.000000	0.344488
Cl	0.000000	2.172249	0.814200
Cl	0.000000	-2.172249	0.814200
C	0.667643	0.000000	-2.263549
C	-0.667643	0.000000	-2.263549
H	1.230276	-0.924922	-2.283108
H	1.230276	0.924922	-2.283108
H	-1.230276	-0.924922	-2.283108
H	-1.230276	0.924922	-2.283108