Infrared Spectra of the Os←NCCH$_3$, Re←NCCH$_3$, CH$_3$-ReNC, CH$_2$=Re(H)NC, CH≡Re(H)$_2$NC Complexes and their Mn Counterparts Prepared by Reactions of Laser-Ablated Os, Re and Mn Atoms with Acetonitrile in Excess Argon

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Table S1: Observed and Calculated Vibrational Frequencies of Os←NCCH$_3$ Isotopomers in the Ground $^3A_1$ State[a]

Approximate Description	Os←NCCH$_3$					Os←NCCD$_3$					Os←N^{13}C^{13}CH$_3$			
	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]
E CH$_3$ as. str.		3086.2	2	3016.6	4		2285.6	2	2233.2	2		3075.1	2	3016.9	4
E CH$_3$ as. str.		3085.4	2	3016.4	4		2285.0	2	2233.1	3		3074.3	2	3016.9	4
A$_1$ CH$_3$ as. str.	2926.0	3024.0	32	2954.5	55	2110.5	2170.1	23	2120.0	41	2922.6	3021.0	32	2954.6	54
A$_1$ CN str.	2180.8	2296.1	372	2211.2	350	2179.2	2295.2	369	2210.3	341	2131.1	2242.0	370	2212.5	349
E CH$_3$ as. bend		1469.8	10	1422.2	9		1056.1	4	1021.8	4		1468.0	10	1422.0	9
E CH$_3$ as. bend		1469.6	10	1421.7	9		1056.0	4	1021.5	4		1467.7	10	1421.9	9
A$_1$ CH$_3$ deform		1412.9	16	1363.2	20		1134.4	2	1107.3	3		1402.6	18	1362.8	20
E CH$_3$ rock		1043.7	1	998.3	1		830.0	0	789.1	0		1032.3	2	998.4	1
E CH$_3$ rock		1043.1	1	998.1	1		829.5	0	788.9	0		1031.6	2	998.4	1
A$_1$ C-C str.	973.4	989.1	73	1000.6	70	886.7	904.0	82	907.7	77	953.2	968.3	68	1000.3	69
A$_1$ Os-N str.		399.7	35	426.4	22		382.4	29	406.3	17		390.8	33	426.8	22
E OsNC bend		369.8	2	327.6	2		360.9	3	323.9	3		364.4	2	326.4	2
E OsNC bend		369.7	2	327.4	2		360.8	3	323.7	3		364.3	2	326.4	2
E CCN bend		141.6	5	121.3	6		130.7	4	111.3	4		138.9	5	121.2	6
E CCN bend		141.1	5	120.6	6		130.2	4	110.7	4		138.3	5	120.9	6

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Os. Frequencies and intensities are in cm^{-1} and km/mol. [b]Observed in an argon matrix. [c]Computed with B3LYP/6-311++G(3df, 3pd). [c]Computed with BPW91/6-311++G(3df,3pd). Os←NCCH$_3$ has a C$_{3v}$ structure. The symmetry notations are based on the C$_{3v}$ structure.

Table S2: Calculated Fundamental Frequencies of π-η^2-Os(NC)-CH$_3$ Isotopomers in the Ground ^{5}A' State[a]

Approximate Description	η^2-Os(NC)-CH$_3$				η^2-Os(NC)-CD$_3$				η^2-Os(N^{13}C)-^{13}CH$_3$			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
A' CH$_3$ as. str.	3119.1	3	3068.8	3	2312.0	1	2274.4	1	3107.6	3	3057.6	3
A" CH$_3$ as. str.	3113.1	2	3058.4	1	2304.4	1	2262.8	1	3102.1	2	3047.6	1
A' CH$_3$ s. str.	3042.2	9	2985.6	7	2183.5	4	2142.9	3	3039.1	9	2982.6	8
A' C-N str.	1870.7	22	1753.0	13	1868.8	23	1750.7	15	1824.8	22	1709.3	13
A' CH$_3$ bend	1474.1	9	1428.0	11	1112.4	13	1078.3	17	1472.2	10	1426.2	11
A" CH$_3$ bend	1469.2	13	1422.0	13	1057.4	6	1023.2	6	1467.2	13	1420.1	13
A' CH$_3$ deform	1399.1	6	1347.4	7	1058.8	5	1025.3	7	1389.0	5	1337.5	6
A' CH$_3$ rock	1065.5	60	1041.5	55	896.4	100	896.8	78	1050.2	52	1023.9	48
A" CH$_3$ rock	1044.0	1	1000.0	1	845.8	0	811.8	0	1030.9	1	987.3	1
A' C-C str.	905.6	35	893.0	26	801.4	3	775.0	1	884.2	36	873.8	28
A' N-Re str.	470.4	144	485.0	92	438.4	134	445.8	88	462.1	144	474.3	96
A" CCNOs deform	354.1	0	341.9	0	322.5	0	310.8	0	344.4	0	332.6	0
A' C-Re str.	342.6	17	367.3	46	338.1	12	365.0	41	337.8	14	364.1	42
A' CCOs bend	183.4	20	187.8	19	168.8	15	172.6	14	179.5	19	183.8	18
A" CH$_3$ tort	44.0	0	-39.9	0	35.2	0	-25.0	0	44.0	0	-40.0	0

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Os. Frequencies and intensities are in cm^{-1} and km/mol. [b]Computed with B3LYP. [c]Computed with BPW91. η^2-π-Os(NC)-CH$_3$ has a C$_s$ structure.

Table S3: Calculated Fundamental Frequencies of CH_3-OsNC Isotopomers in the Ground ^{3}A" State[a]

Approximate Description	CH$_3$-OsNC				CD$_3$-OsNC				^{13}CH$_3$-OsN^{13}C			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
A' CH$_3$ as. str.	3138.2	1	3082.6	1	2318.3	1	2276.9	1	3127.9	1	3072.5	1
A" CH$_3$ as. str.	2995.2	5	2927.8	6	2214.0	2	2163.6	3	2984.8	5	2917.6	6
A' CH$_3$ s. str.	2929.1	7	2858.0	7	2099.8	3	2048.6	4	2925.8	7	2854.8	7
A' N-C str.	2054.5	268	1929.9	160	2054.4	268	1929.8	160	2013.8	263	1891.6	157
A" CH$_3$ bend	1427.0	6	1374.4	7	1035.0	3	996.9	3	1423.9	6	1371.4	7
A' CH$_3$ bend	1387.1	6	1330.8	6	1010.0	5	970.2	6	1383.8	6	1327.6	6
A' CH$_3$ deform	1214.8	12	1164.8	10	955.0	5	918.3	2	1205.3	13	1155.5	10
A' CH$_3$ rock	730.5	25	722.5	25	584.2	13	580.5	13	722.6	26	714.3	25
A" CH$_3$ rock	593.7	1	553.8	0	443.2	1	414.1	0	590.8	1	551.0	0
A' C-Os str.	530.0	30	531.6	22	514.5	33	522.3	14	518.3	30	520.8	21
A' Os-N str.	510.3	15	518.1	5	449.3	10	449.0	11	500.6	12	507.8	4
A' OsNC ip bend	253.5	2	270.9	2	248.7	2	265.1	2	251.3	2	268.5	2
A" OsNC oop bend	221.1	0	237.2	0	220.3	0	235.5	0	218.5	0	234.4	0
A' COsN bend	97.3	3	97.6	3	89.6	3	89.6	3	94.6	3	94.9	3
A" CH$_3$ tort	49.8	1	35.8	1	37.6	1	23.3	1	49.6	1	36.0	1

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Os. Frequencies and intensities are in cm^{-1} and km/mol. [b]Computed with B3LYP. [c]Computed with BPW91. CH$_3$-OsNC has a C$_s$ structure.

Table S4: Calculated Fundamental Frequencies of $CH_2=Os(H)NC$ Isotopomers in the Ground ^1A State[a]

Approximate Description	CH$_2$=Os(H)NC				CD$_2$=Os(D)NC				^{13}CH$_2$-Os(H)N^{13}C			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
CH$_2$ as. str.	3130.2	1	3056.9	3	2319.7	0	2265.5	1	3119.2	1	3046.2	3
CH$_2$ s. str.	2923.8	15	2854.1	20	2123.0	14	2071.7	14	2917.7	15	2848.2	20
Os-H str.	2281.1	13	2254.4	7	1617.9	8	1598.8	6	2281.1	13	2254.4	7
N-C str.	2057.6	195	1940.0	100	2057.7	187	1940.2	95	2017.0	191	1901.8	97
CH$_2$ scis.	1395.8	5	1348.6	7	1108.7	2	1073.5	3	1385.4	5	1338.8	7
CH$_2$ wag	959.5	20	922.1	20	762.5	12	730.8	10	949.8	20	912.8	20
C-Os str.	868.1	6	857.8	5	745.4	4	738.6	5	846.9	6	836.6	6
COsH bend	734.2	38	722.6	35	547.7	28	555.1	21	734.2	38	722.4	35
CH$_2$ rock	656.2	10	667.1	11	522.4	14	522.6	10	647.6	10	658.5	10
Os-N str.	513.3	19	522.6	8	498.6	7	502.1	6	504.9	19	514.1	8
NOsH bend	462.0	21	476.1	18	365.5	8	381.4	6	461.5	20	475.4	17
CH$_2$ twist	329.9	5	331.4	5	263.9	2	280.3	1	329.5	5	330.9	5
OsNC ip bend	255.3	2	276.9	3	230.4	4	236.6	5	252.9	2	274.5	3
OsNC oop bend	199.6	5	207.3	5	176.5	4	179.6	4	197.0	5	204.7	4
COsN ip bend	79.2	7	84.2	6	70.2	6	74.8	6	77.2	6	82.0	6

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Os. Frequencies and intensities are in cm^{-1} and km/mol. [b]Computed with B3LYP. [c]Computed with BPW. CH$_2$=Os(H)NC has a C$_1$ structure.

Table S5: Calculated Fundamental Frequencies of $CH\equiv OsH_2NC$ Isotopomers in the Ground $^1A'$ State[a]

Approximate Description	CH≡OsH₂NC				CD≡OsD₂NC				$^{13}CH\equiv OsH_2N^{13}C$			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
A' C-H str.	3242.4	34	3179.4	31	2414.9	20	2367.9	20	3230.3	34	3167.5	30
A' OsH₂ s. str.	2312.5	9	2282.2	4	1640.6	10	1618.9	5	2312.4	10	2282.1	4
A" OsH₂ as str.	2281.3	7	2235.1	6	1617.9	5	1585.0	6	2281.2	8	2235.0	6
A' N-C str.	2090.5	545	2006.2	462	2091.2	541	2007.2	458	2049.0	539	1966.4	457
A' C-Os str.	1101.0	4	1078.6	6	1048.0	4	1026.9	6	1064.6	3	1043.0	5
A' OsCH ip bend	956.5	13	923.3	10	744.6	6	720.3	4	949.1	13	916.1	10
A" OsCH oop bend	933.5	1	893.2	2	732.2	2	696.8	2	925.5	1	886.0	2
A' OsH₂ scis.	741.8	3	720.6	2	528.1	1	513.6	1	741.8	3	720.5	2
A" OsH₂ twist	661.3	48	646.4	45	474.0	22	467.4	20	660.6	48	645.7	45
A' OsH₂ wag	614.5	65	584.3	59	466.1	19	453.1	20	613.3	66	583.1	61
A' Os-N str.	432.3	114	432.5	101	407.3	116	395.6	96	425.2	109	425.7	96
A' OsNC ip bend	159.1	0	169.9	0	155.3	0	163.7	0	157.6	0	168.5	0
A" OsH₂ rock	120.2	5	104.2	4	102.2	3	92.7	3	119.0	5	102.8	4
A' COsN bend	87.0	4	92.7	3	82.0	4	85.9	3	84.6	4	90.8	3
A" OsNC oop bend	60.9	0	59.3	1	53.5	1	53.1	1	60.5	1	58.6	1

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Os. [b]Computed with B3LYP. [c]Computed with BPW. CH≡OsH₂NC has a C_s structure.

Table S6: Observed and Calculated Vibrational Frequencies of Re←NCCH$_3$ Isotopomers in the Ground ^{6}A State[a]

Approximate Description	Re←NCCH$_3$					Re←NCCD$_3$					Re←N^{13}C^{13}CH$_3$				
	Obs[b]	BPW91[c]	Int[c]	B3LYP[d]	Int[d]	Obs[b]	BPW91[c]	Int[c]	B3LYP[d]	Int[d]	Obs[b]	BPW91[c]	Int[c]	B3LYP[d]	Int[d]
CH$_3$ as. str.		3050.4	0	3119.0	1		2258.4	1	2310.0	0		3039.5	0	3107.7	1
CH$_3$ as. str.		3048.9	1	3118.8	1		2257.5	1	2309.8	1		3037.9	1	3107.5	1
CH$_3$ s. str.		2976.5	9	3049.3	3		2136.1	15	2189.3	2		2973.5	9	3046.1	3
C-N str.	2100	2143.8	153	2362.7	13	2092	2143.0	144	2362.3	14	2049	2089.4	149	2305.9	13
CH$_3$ as. bend		1419.1	14	1474.5	11		1087.8	2	1128.6	0		1417.4	14	1472.7	11
CH$_3$ as. bend		1413.2	11	1474.2	10		1019.1	6	1059.0	5		1411.5	12	1472.4	10
CH$_3$ deform		1356.0	9	1413.8	1		1014.3	5	1058.8	5		1345.8	10	1403.3	1
CH$_3$ rock		1004.1	2	1061.7	2		816.2	2	863.3	0		992.1	2	1048.2	2
CH$_3$ rock		1002.0	3	1061.6	2		804.8	7	863.2	1		989.4	4	1048.1	2
C-C str.	covered	904.5	25	927.9	2	778	815.5	19	839.6	2	covered	884.3	23	906.2	1
CCN ip bend		361.2	0	382.2	1		331.8	0	350.9	2		352.9	0	373.2	1
CCN oop bend		325.4	4	381.7	0		308.6	3	350.4	1		319.1	3	372.7	0
Re-N str.		146.4	5	28.9	8		141.4	3	28.3	7		144.5	5	28.6	8
ReNC ip bend		65.3	10	13.2	5		61.6	9	13.1	4		64.0	10	13.1	5
ReNC oop bend		-36.0	0	4.1	2		-31.6	0	-2.7	3		-35.9	0	4.0	2

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Re. Frequencies and intensities are in cm^{-1} and km/mol. [b]Observed in an Ar matrix. [c]Computed with BPW91. [d]Computed with B3LYP. Re←NCCH$_3$ has a C$_1$ structure, which is close to the C$_s$ structure.

Table S7: Calculated Fundamental Frequencies of π-η^2-Re(NC)-CH$_3$ Isotopomers in the Ground ^{4}A" State[a]

Approximate Description	Re(NC)-CH$_3$				Re(NC)-CD$_3$				Re(N^{13}C)-^{13}CH$_3$			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
A' CH$_3$ as. str.	3122.4	7	3079.9	3	2312.4	4	2281.0	2	3111.5	7	3069.0	3
A" CH$_3$ as. str.	3084.4	4	3047.5	0	2282.5	2	2253.7	0	3074.5	4	3036.9	0
A' CH$_3$ s. str.	3027.5	17	2979.4	6	2174.6	7	2139.7	2	3024.0	17	2976.0	7
A' CCN as. str.	1625.5	14	1695.7	6	1622.9	15	1693.3	7	1582.2	15	1652.7	6
A" CH$_3$ bend	1478.9	7	1433.8	5	1065.2	3	1033.0	2	1476.7	7	1431.7	6
A' CH$_3$ bend	1469.6	11	1420.0	13	1125.7	24	1097.3	36	1467.1	11	1417.6	13
A' CH$_3$ deform	1392.7	0	1341.0	3	1051.1	5	1011.7	6	1382.8	0	1331.5	2
A' CH$_3$ rock	1105.9	84	1066.5	99	983.6	83	948.2	78	1084.4	74	1044.3	88
A" CH$_3$ rock	1002.3	0	1009.3	3	808.3	0	802.6	9	990.2	0	993.9	2
A' CCN s. str.	962.7	29	950.4	16	819.1	11	844.3	7	945.6	32	932.6	20
A' N-Re str.	616.1	30	584.8	38	595.2	25	561.7	29	611.4	29	579.2	37
A' C-Re str.	500.2	6	495.4	4	469.0	4	467.5	3	488.5	6	485.4	4
A" CCNRe deform	357.1	1	440.9	7	326.2	1	388.9	4	346.8	1	429.7	7
A' CCRe bend	245.6	11	232.8	6	224.3	9	212.1	5	240.8	11	228.1	6
A" CH$_3$ tort	21.2	1	103.8	2	19.4	2	75.2	2	21.1	1	103.8	2

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Re. Frequencies and intensities are in cm^{-1} and km/mol. [b]Computed with B3LYP. [c]Computed with BPW91. η^2-π-Re(NC)-CH$_3$ has a C$_s$ structure.

Table S8: Observed and Calculated Vibrational Frequencies of CH$_3$-ReNC Isotopomers in the Ground ^{6}A' State[a]

Approximate Description	CH$_3$-ReNC						CD$_3$-ReNC					^{13}CH$_3$-ReN^{13}C			
	obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]		B3LYP[b]	Int[b]	BPW91[c]	Int[c]		B3LYP[b]	Int[b]	BPW91[c]	Int[c]
A' CH$_3$ as. str.		3037.1	10	2992.1	8		2242.7	3	2210.1	3		3026.7	10	2981.9	8
A" CH$_3$ as. str.		3036.7	10	2990.6	8		2242.4	3	2208.0	3		3026.4	10	2980.5	8
A' CH$_3$ s. str.		2978.8	3	2924.0	3		2137.4	0	2097.8	0		2975.6	4	2921.0	3
A' NC str.	2022.9[e]	2080.5	400	1986.0	331	2020.2	2080.4	400	1986.0	331	1985.6[e]	2038.5	399	1945.9	330
A' CH$_3$ bend		1433.9	2	1385.0	3		1038.9	2	1003.5	2		1430.9	2	1382.2	3
A" CH$_3$ bend		1433.7	2	1380.5	3		1038.7	2	1000.2	3		1430.7	2	1377.7	3
A' CH$_3$ deform		1238.8	8	1189.1	4		956.7	21	920.6	15		1230.5	6	1181.0	3
A' C-Re str.		597.3	17	587.9	16		469.8	32	472.1	33		594.0	16	584.3	16
A" CH$_3$ rock		596.2	17	577.6	13		447.3	11	433.4	8		592.9	16	574.4	13
A' Re-NC str.		516.5	51	520.1	49		448.2	11	445.9	21		500.9	49	504.5	48
A' CH$_3$ rock		408.2	121	405.2	92		407.9	126	402.8	85		401.2	116	398.4	88
A" ReNC oop bend		169.2	0	167.0	1		169.0	0	166.7	1		167.5	0	165.3	0
A' ReNC ip bend		167.4	0	178.2	1		167.1	0	177.0	1		165.6	0	176.5	1
A" CH$_3$ tort		17.5	6	-29.0	2		15.7	7	15.6	3		17.2	6	-29.1	2
A' CReN bend		15.0	7	45.0	4		13.9	7	41.6	4		14.6	6	43.7	4

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Re. Frequencies and intensities are in cm^{-1} and km/mol. [b]Obseved in an argon matrix. [c]Computed with B3LYP. [d]Computed with BPW91. [e]Tentative assignment. CH$_3$-ReNC has a C$_s$ structure.

Table S9: Observed and Calculated Vibrational Frequencies of $CH_2=Re(H)NC$ Isotopomers in the Ground $^4A_1$ State[a]

Approximate Description	$CH_2=Re(H)NC$					$CD_2=Re(D)NC$					$^{13}CH_2\text{-}Re(H)N^{13}C$				
	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]
A" CH_2 as. str.		3138.1	0	3075.1	0		2330.3	0	2283.6	0		3125.8	0	3063.0	0
A' CH_2 s. str.		3044.8	1	2980.1	1		2204.3	1	2156.9	2		3039.8	1	2975.2	1
A' N-C str.		2090.9	346	2016.8	102		2087.5	421	1999.0	367		2053.5	252	2006.3	50
A' Re-H str.	1921.2	2014.5	198	1981.4	373	1378.9	1431.6	66	1418.1	58	1921 sh	2010.1	289	1951.8	422
A' CH_2 scis.		1348.1	1	1293.6	1		1056.5	3	1019.9	4		1339.3	1	1285.0	1
A' CH_2 wag		831.4	26	796.2	17		648.6	19	615.0	18		823.0	26	782.3	21
A' C-Re str.		785.3	19	777.7	26		701.3	11	696.6	11		763.5	17	762.1	21
A' Re-H ip bend	639.0	619.0	42	612.0	44		461.0	5	456.4	3	638.9	618.7	44	611.6	46
A" CH_2 rock		550.6	12	530.6	11		415.4	7	399.9	7		547.5	12	527.6	11
A' Re-NC str.		429.5	98	427.1	82		411.8	103	409.6	89		422.5	94	420.2	78
A" CH_2 twist		309.5	6	306.1	3		220.2	2	218.8	2		309.4	6	306.1	3
A" ReNC oop bend		200.7	6	178.3	2		185.7	2	174.3	3		199.5	7	176.5	2
A' CReN ip bend		171.9	3	175.7	2		168.8	3	171.0	1		170.8	3	173.9	2
A" CReN oop bend		105.3	19	93.0	3		83.7	14	87.9	3		104.3	18	90.2	3
A' ReNC ip bend		93.9	3	38.8	21		88.7	3	29.8	13		91.1	3	38.5	20

[a] Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Re. Frequencies and intensities are in cm^{-1} and km/mol. [b] Observed in an argon matrix. [c] Computed with B3LYP. [d] Computed with BPW91. $CH_2=Re(H)NC$ has a C_1 structure. [e] Tantative assignment.

Table S10: Observed and Calculated Vibrational Frequencies of CH≡ReH$_2$NC Isotopomers in the Ground ^{2}A' State[a]

Approximate Description	CH≡ReH$_2$NC					CD≡ReD$_2$NC					^{13}CH≡ReH$_2$N^{13}C				
	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]
A' C-H str.	3105.0	3250.1	36	3193.5	33	2355.0	2419.5	23	2377.7	22	covered	3238.0	35	3181.6	32
A' ReH$_2$ s. str.		2148.3	33	2115.0	25		1520.8	39	1498.4	33		2146.2	35	2114.0	30
A" ReH$_2$ as str.		2113.8	35	2090.6	23		1499.8	18	1483.0	12		2113.8	35	2090.6	23
A' C-N str.	2027.9	2090.7	553	2014.6	479	2033.5	2096.1	520	2018.4	450	1994.0	2051.2	546	1975.6	470
A' C-Re str.		1086.9	6	1069.0	6		1035.3	5	1018.1	5		1051.0	5	1033.7	6
A" ReCH oop bend		845.2	8	812.4	9		662.5	7	634.7	7		838.0	8	805.7	8
A' ReCH ip bend		810.4	2	787.1	2		625.8	3	607.1	3		805.1	2	782.1	2
A" ReH$_2$ twist	628.8[e]	631.5	51	625.3	46	447.6[e]	448.6	25	444.9	22		631.3	51	624.9	46
A' ReH$_2$ wag	600.0[e]	603.6	73	591.1	71	455.2[e]	459.4	17	453.3	13	599.6[e]	602.5	74	590.0	72
A' ReH$_2$ scis.		466.3	27	454.6	30		311.9	10	293.6	15		463.4	20	450.2	23
A' Re-NC str.		415.9	81	399.2	69		415.2	104	410.1	89		411.5	84	396.4	72
A" ReH$_2$ rock		219.0	8	238.1	6		163.8	4	179.0	3		218.8	8	238.0	6
A' CReN bend		180.8	1	185.9	2		176.5	1	182.0	2		178.4	1	183.5	1
A" ReNC ip bend		105.0	2	104.1	3		103.1	3	101.5	3		103.6	2	102.7	3
A' ReNC ip bend		90.9	4	90.3	4		87.1	4	86.2	4		88.3	3	87.8	3

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Re. Frequencies and intensities are in cm^{-1} and km/mol. [b]Observed in an argon matrix. [c]Computed with B3LYP. [d]Computed with BPW91. CH≡ReH$_2$NC has a C$_s$ structure. [e]

.Table S11: Calculated and Observed Fundamental Frequencies of CH_3-MnNC Isotopomers in the Ground $^6A_1$ State[a]

Approximate Description	CH$_3$-MnNC						CD$_3$-MnNC					^{13}CH$_3$-MnN^{13}C			
	obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]		B3LYP[b]	Int[b]	BPW91[c]	Int[c]		B3LYP[b]	Int[b]	BPW91[c]	Int[c]
E CH$_3$ as. str.		3071.0	9 x 2	3019.9	7 x 2		2269.1	2 x 2	2230.9	2		3060.4	10 x 2	3009.5	8 x 2
A$_1$ CH$_3$ s. str.		3003.6	6	2943.5	2		2154.2	0	2111.0	0		3000.6	6	2940.5	2
A$_1$ NC str.	2080.1	2119.9	377	2032.6	392	not obs	2119.9	378	2032.6	392 (2041.5)		2077.6	376	1992.0	390
E CH$_3$ bend		1441.9	0 x 2	1387.5	1 x 2		1044.4	1 x 2	1005.5	2		1438.9	0 x 2	1384.7	1 x 2
A$_1$ CH$_3$ deform		1198.8	5	1150.2	3		929.2	16	897.6	16		1190.4	4	1141.7	2
E C-Mn str.		565.3	45 x 2	528.3	34 x 2		427.6	32 x 2	398.0	23 x 2		561.9	44 x 2	525.3	33 x 2
A$_1$ C-Mn-N as. str.		546.7	149	548.7	156		520.6	154	516.5	160		537.1	148	538.6	155
A$_1$ C-Mn-N s. str.		429.7	28	427.4	33		412.6	12	412.4	14		419.6	24	417.8	28
E MnNC bend		138.1	2 x 2	122.5	0 x 2		137.5	1 x 2	122.4	0 x 2		136.9	2 x 2	121	0 x 2
E CMnN bend		56.4	17 x 2	25.1	15 x 2		53.2	17 x 2	24.1	14 x 2		55.2	16 x 2	24.6	14 x 2

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all electron basis sets are used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b]Obseved in an argon matrix. [c]Computed with B3LYP. [d]Computed with BPW91. CH$_3$-MnNC has the C$_{3v}$ structure.

Table S12: Calculated and Observed Fundamental Frequencies of Mn←NCCH$_3$ Isotopic Complexes in the Ground $^6A_1$ State[a]

Approximate Description	Mn←NCCH$_3$					Mn←NCCD$_3$					Mn←N^{13}C^{13}CH$_3$			
	Obs[b]	BPW91[c]	Int[c]	B3LYP[d]	Int[d]	Obs[b]	BPW91[c]	Int[c]	B3LYP[d]	Int[d]	Obs[b]	BPW91[c]	Int[c]	B3LYP[d]	Int[d]
CH$_3$ as. str.		3052.5	1	3119.2	0		2257.6	1	2310.1	0		3041.8	1	3108.0	0
CH$_3$ as. str.		3026.6	11	3118.8	0		2231.8	14	2309.8	0		3017.8	9	3107.5	0
CH$_3$ s. str.		2921.4	119	3049.5	3		2105.2	44	2189.4	2		2916.4	122	3046.3	3
C-N str.	2069.6	1986.4	111	2362.7	14	2063.3	1985.0	110	2362.3	14	2022.7	1939.6	104	2305.9	13
CH$_3$ as. bend		1419.4	42	1474.3	10		1018.5	16	1058.9	5		1417.5	43	1472.5	11
CH$_3$ as. bend		1415.3	8	1474.2	11		1018.6	4	1058.8	5		1413.4	8	1472.4	11
CH$_3$ deform		1343.0	1	1414.1	1		1071.2	1	1128.7	0		1333.7	2	1403.6	1
CH$_3$ rock		992.7	1	1062.0	2		790.9	0	863.5	1		981.4	1	1048.5	2
CH$_3$ rock		989.6	114	1061.5	2		787.0	160	863.2	1		979.0	105	1048.0	2
C-C str.		915.2	41	927.8	2		840.4	12	839.6	2		892.6	35	906.1	2
CCN ip bend		391.2	106	382.5	1		375.1	79	351.1	2		384.0	101	373.5	1
CCN oop bend		268.4	26	382.1	0		257.7	23	350.7	1		263.7	26	373.1	0
Mn-N str.		159.5	4	24.5	8		150.7	3	24.1	7		157.2	3	24.3	8
MnNC ip bend		75.1	1	12.5	4		63.6	1	12.4	3		74.8	1	12.4	4
MnNC oop bend		72.8	9	-11.3	3		68.8	8	-10.2	3		72.0	9	-11.3	3

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all-electron basis sets are used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b]Observed in an Ar matrix. [c]Computed with BPW91. [d]Computed with B3LYP. Mn←NCCH$_3$ has a C$_1$ structure, which is close to the C$_s$ structure.

Table S13: Calculated and Observed Fundamental Frequencies of CH_2=Mn(H)NC Isotopomers in the Ground $^4A'$ State[a]

Approximate Description	CH_2=Mn(H)NC					CD_2=Mn(D)NC					$^{13}CH_2$-Mn(H)N^{13}C			
	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]
A" CH_2 as. str.		3195.1	0	3128.7	0		2357.1	0	2325.9	0		3182.3	0	3116.1	0
A' CH_2 s. str.		3081.3	1	3011.1	2		2227.1	2	2176.6	2		3076.3	1	3006.3	2
A' N-C str.	2060.0	2112.4	436	2027.0	372	2060.0	2112.3	441	2026.6	384	2019.2	2112.4	436	2027.0	373
A' Mn-H str.		1813.2	93	1822.4	105		1295.1	50	1301.5	53		1813.2	93	1822.4	105
A' CH_2 scis.		1310.6	3	1265.1	1		993.2	2	980.0	2		1304.1	3	1257.4	1
A' CH_2 wag		778.1	7	794.0	7		619.2	13	636.6	15		770.7	7	786.6	7
A' C-Mn str.		633.8	47	690.9	24		586.8	46	621.9	15		621.4	47	675.1	24
A" CH_2 rock		522.7	10	494.6	6		396.3	9	373.6	5		519.7	10	491.8	6
A' Mn-H ip bend		507.4	70	510.3	54		364.6	35	367.0	37		506.2	75	509.9	55
A' Mn-N str.		461.4	63	467.9	72		455.1	55	463.0	49		459.3	57	467.0	70
A" CH_2 twist		290.1	51	325.4	31		215.6	31	232.6	18		290.0	51	325.2	31
A" MnH oop bend		200.6	8	204.0	19		165.2	0	176.3	6		200.5	8	203.9	19
A' MnNC ip bend		144.5	1	174.3	5		143.1	1	170.2	5		144.1	1	173.5	5
A" MnNC oop bend		114.6	7	118.9	9		101.7	8	103.5	10		114.5	7	118.8	9
A' CMnN ip bend		78.0	5	87.7	4		73.3	5	83.1	4		76.8	5	86.6	4

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all-electron basis sets are used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b]Observed in an argon matrix. [c]Computed with B3LYP. [d]Computed with BPW91. CH_2=Mn(H)NC has a C_s structure.

Table S14: Calculated Fundamental Frequencies of π-η^2-Mn(NC)-CH$_3$ Isotopomers in the Ground ^{6}A" State[a]

Approximate Description	Mn(NC)-CH$_3$				Mn(NC)-CD$_3$				Mn(N^{13}C)-^{13}CH$_3$			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
A" CH$_3$ as. str.	3110.1	2	3054.8	2	2302.0	1	2259.9	1	3099.1	2	3044.1	2
A' CH$_3$ as. str.	3104.6	8	3054.6	7	2300.0	4	2263.2	4	3093.6	8	3043.6	7
A' CH$_3$ s. str.	3028.6	25	2974.4	18	2174.1	10	2134.7	7	3025.2	25	2971.2	19
A' CCN as. str.	1920.2	52	1856.4	18	1918.4	53	1854.6	19	1874.1	51	1811.6	17
A' CH$_3$ bend	1471.6	10	1426.0	10	1104.6	7	1072.8	12	1469.7	10	1424.2	11
A" CH$_3$ bend	1467.3	13	1421.3	13	1056.4	6	1022.8	6	1465.3	13	1419.3	13
A' CH$_3$ deform	1392.9	5	1344.2	7	1057.6	5	1023.8	7	1382.9	5	1334.6	6
A' CH$_3$ rock	1046.6	57	1025.8	48	870.8	80	873.7	60	1033.1	51	1010.2	42
A" CH$_3$ rock	1039.0	0	1000.4	1	837.6	0	810.7	0	1026.3	0	987.8	1
A' CCN s. str.	902.5	19	894.1	13	805.1	2	781.9	2	879.7	19	872.8	14
A' N-Mn str.	480.5	133	475.1	111	461.7	121	451.5	108	476.4	133	470.0	113
A' C-Mn str.	366.6	4	389.5	12	352.8	2	376.5	5	359.4	3	382.9	9
A" CCNMn deform	316.9	0	322.8	0	289.4	0	293.8	0	308.1	0	314.0	0
A' CCMn bend	173.6	5	179.4	9	162.0	4	167.3	7	170.5	5	176.3	9
A" CH$_3$ tort	93.4	0	78.1	0	68.5	0	59.7	0	93.4	0	78.1	0

[a]Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the all electron basis sets are used for Mn. Frequencies and intensities are in cm^{-1} and km/mol. [b]Computed with B3LYP. [c]Computed with BPW91. η^2-π-Mn(NC)-CH$_3$ has a C$_s$ structure.