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Infrared Spectra of CH_2=Zr(H)NC, CH_3-ZrNC, and η_2-Zr(NC)-CH_3 Produced by Reactions of Laser-Ablated Zr Atoms with Acetonitrile

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Abstract

The zirconium methylidene isocyanide, methyl isocyanide, and η_2-nitrile-π-complex are observed in the matrix IR spectra from reactions of laser-ablated Zr atoms and acetonitrile isotopomers. The methylidene CH_2=Zr(H)NC has a C_1 agostic structure in line with simple early transition-metal methylidenes recently produced from reactions with small alkanes and methyl halides, and the extent of agostic distortion is also comparable. Formation of the isocyanide complexes from acetonitrile is interesting but not surprising according to previous studies of metal reactions with nitrile containing compounds, and their stabilities over the cyanide species are reproduced by DFT calculations. Observation of the relatively rare nitrile π-complex and its photo-dissociation suggests that the reaction proceeds in the order of Zr←$NCCH_3$, η_2-Zr(NC)-CH_3, CH_3-ZrNC, and CH_2=Zr(H)NC. The intermediate transition-state structures are also examined.

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Table S1: Calculated Fundamental Frequencies of CH_2=Zr(H)CN Isotopomers in the Ground ^{1}A State[a]

Approximate Description	CH_2=Zr(H)CN				CD_2=Zr(D)CN				$^{13}CH_2$=Zr(H)^{13}CN			
	BPW91[b]	Int[b]	B3LYP[c]	Int[c]	BPW91[b]	Int[b]	B3LYP[c]	Int[c]	BPW91[b]	Int[b]	B3LYP[c]	Int[c]
CH_2 as. str.	3133.5	3	3185.2	2	2317.8	5	2355.9	5	3122.9	2	3174.5	2
CH_2 as. str.	2667.5	2	2825.4	5	1942.3	1	2057.0	2	2661.3	2	2818.8	5
CN str.	2142.8	59	2234.2	68	2142.8	60	2234.2	68	2095.9	53	2185.3	60
Zr-H str.	1636.4	311	1655.0	388	1164.3	162	1177.7	202	1636.4	311	1655.0	388
CH_2 scis.	1315.5	24	1336.0	22	1004.4	17	1031.2	22	1309.0	24	1328.1	21
C-Zr str.	781.8	73	771.5	88	706.8	54	691.2	60	760.8	72	751.8	88
CH_2 wag	647.3	105	692.3	146	506.2	98	541.7	106	642.2	96	686.4	142
C-H ip bend	628.0	85	635.8	63	477.7	46	478.6	57	624.8	89	633.4	60
CH_2 twist	466.0	16	446.4	25	391.9	41	371.9	55	464.2	16	446.0	25
CH_2 rock	431.7	53	396.2	22	341.4	12	322.5	4	431.0	51	392.0	19
Zr-CN str.	392.3	49	371.0	58	310.6	23	302.3	15	386.4	50	366.3	58
C-H oop bend	299.5	26	283.9	52	257.4	7	238.3	15	294.8	27	279.6	55
ZrCN oop bend	163.0	2	160.5	1	157.7	2	160.2	1	159.3	2	156.1	1
ZrCN ip bend	152.0	16	149.9	40	131.1	11	126.7	25	149.2	15	147.8	38
CZrC bend	77.6	18	68.6	42	70.0	16	60.4	37	76.1	17	67.5	41

[a]Frequencies and intensities are in cm^{-1} and km/mol. [b]Frequencies computed with BPW91/6-311++G(3df,3pd). [c]Frequencies and intensities computed with B3LYP/6-311++G(3df, 3pd). CH_2=Zr(H)CN has a C_1 structure.

Table S2: Calculated Fundamental Frequencies of CH_3-ZrCN Isotopomers in the Ground ^{3}A" State[a]

Approximate Description	CH_3-ZrCN				CD_3-ZrCN				$^{13}CH_3$-ZrCN			
	BPW91[b]	Int[b]	B3LYP[c]	Int[c]	BPW91[b]	Int[b]	B3LYP[c]	Int[c]	BPW91[b]	Int[b]	B3LYP[c]	Int[c]
A' CH_3 as. str.	3049.7	1	3090.7	2	2252.3	1	2282.5	1	3039.5	1	3080.4	1
A" CH_3 as. str.	2976.9	3	3023.7	5	2198.9	1	2233.5	1	2966.7	4	3013.3	5
A' CH_3 s. str.	2905.2	4	2960.4	4	2088.8	2	2124.0	1	2901.9	4	2957.0	4
A' CN str.	2107.5	6	2212.0	14	2107.6	6	2212.0	14	2061.7	5	2163.8	11
A" CH_3 bend	1362.9	7	1415.0	5	989.4	4	1027.1	4	1359.8	7	1411.8	5
A' CH_3 bend	1352.5	1	1404.6	1	982.1	1	1019.8	1	1349.4	1	1401.4	1
A' CH_3 deform	1096.6	9	1149.2	9	869.8	21	906.5	21	1086.8	8	1139.4	7
A' C-Zr str.	513.3	40	516.2	44	452.0	32	454.4	38	501.9	38	505.1	41
A' Zr-CN str.	404.7	53	413.5	71	391.8	47	393.9	66	399.0	54	407.7	71
A" CH_3 rock	330.0	3	360.6	5	247.1	2	269.4	3	328.3	3	358.8	5
A' CH_3 rock	349.7	1	358.2	7	291.4	1	300.8	1	345.1	1	353.3	7
A' ZrCN ip bend	212.1	1	213.3	1	202.4	1	205.6	2	206.3	1	207.3	1
A" ZrCN oop bend	207.0	0	200.2	0	204.9	0	198.7	0	201.2	0	194.6	0
A" CH_3 tort	113.0	0	110.3	0	82.1	0	80.0	0	113.0	0	110.2	0
A' CZrC bend	75.2	3	79.2	4	68.9	3	72.5	4	74.2	3	78.1	4

[a]Frequencies and intensities are in cm^{-1} and km/mol. [b]Frequencies computed with BPW91/6-311++G(3df,3pd). [c]Frequencies and intensities computed with B3LYP/6-311++G(3df, 3pd). CH_3-ZrCN has a C_s structure, and the symmetry notations are based on the C_s structure.

Table S3: Calculated Fundamental Frequencies of Zr←$NCCH_3$ Isotopomers in the Ground $^3A_1$ State[a]

Approximate Description	Zr←$NCCH_3$				Zr←$NCCD_3$				Zr←$N^{13}C^{13}CH_3$			
	BPW91[b]	Int[b]	B3LYP[c]	Int[c]	BPW91[b]	Int[b]	B3LYP[c]	Int[c]	BPW91[b]	Int[b]	B3LYP[c]	Int[c]
E CH_3 as. str.	3007.5	5	3073.7	3	2225.6	3	2276.4	2	2996.8	5	3062.6	3
E CH_3 as. str.	2989.6	7	3073.7	3	2209.1	6	2276.4	2	2980.2	7	3062.6	3
A_1 CH_3 as. str.	2923.3	137	3014.2	57	2101.3	58	2164.0	0	2919.2	136	3011.2	57
A_1 CN str.	1947.4	583	2137.2	580	1945.2	604	2134.3	618	1896.4	584	2082.3	569
E CH_3 as. bend	1417.7	17	1463.1	9	1019.5	7	1051.5	4	1415.9	18	1461.3	9
E CH_3 as. bend	1410.2	7	1463.1	9	1013.8	3	1051.5	4	1408.6	7	1461.3	9
A_1 CH_3 deform	1353.3	41	1408.4	29	1080.7	1	1124.0	0	1343.4	50	1397.9	33
E CH_3 rock	994.1	2	1031.7	2	785.2	1	820.3	1	983.8	2	1020.4	2
E CH_3 rock	970.2	9	1031.7	2	751.6	82	820.3	1	960.1	12	1020.4	2
A_1 C-C str.	909.3	151	929.8	87	840.0	89	845.6	97	890.9	142	910.1	81
E CCN bend	365.6	0	316.1	1	354.8	0	305.9	2	359.8	0	310.6	1
E CCN bend	247.8	5	316.1	1	245.4	6	305.9	2	249.9	4	310.6	1
A_1 Zr-N str.	217.4	67	293.7	48	215.6	62	285.6	44	212.3	71	288.8	46
E ZrNC bend	68.4	3	112.6	2	63.2	2	104.9	1	69.3	3	110.8	2
E ZrNC bend	48.8	50	112.6	2	45.4	42	104.9	1	47.0	50	110.8	2

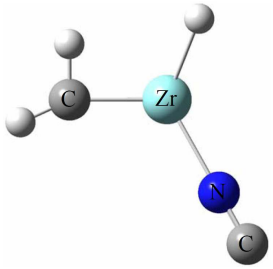
[a]Frequencies and intensities are in cm^{-1} and km/mol. [b]Frequencies computed with BPW91/6-311++G(3df,3pd). [c]Frequencies and intensities computed with B3LYP/6-311++G(3df, 3pd). Zr←$NCCH_3$ has a C_{3v} structure with B3LYP/6-311++G(3df, 3pd), whereas it has a C_s structure close to the C_{3v} structure with BPW91/6-311++G(3df,3pd). The symmetry notations are based on the C_{3v} structure.

Table S4: Observed and Calculated Fundamental Frequencies of $HC\equiv C\text{-}NH_2$ Isotopomers in the Ground $^1A'$ State[a]

Approximate Description	$HC\equiv C\text{-}NH_2$					$DC\equiv C\text{-}ND_2$					$H^{13}C\equiv{}^{13}C\text{-}NH_2$				
	Obs[b]	BPW91[c]	Int[d]	B3LYP[d]	Int[d]	Obs[b]	BPW91[c]	Int[d]	B3LYP[d]	Int[d]	Obs[b]	BPW91[c]	Int[d]	B3LYP[d]	Int[d]
A" NH_2 as. str.	3460.2	3533.9	32	3624.2	42	2633.1	2609.1	16	2677.2	20	3460.0	3533.9	32	3624.2	42
A' NH_2 s. str.		3454.7	4	3540.0	14		2493.7	12	2555.7	19		3454.4	7	3539.9	15
A' C-H str.	3377.7	3422.5	90	3480.5	98	2669.7	2658.2	125	2710.1	138	3366.4	3405.1	82	3462.3	89
A' CCN as. str.	2124.3	2181.6	129	2237.5	139	covered	2045.5	74	2091.9	76	covered	2104.4	123	2158.3	133
A' NH_2 scis.		1590.6	24	1636.3	26		1203.8	25	1237.5	28		1590.4	23	1636.0	26
A" NH_2 rock		1161.2	0	1191.1	0		908.4	1	934.6	1		1156.7	0	1186.4	0
A' CCN s. str.		1068.9	15	1086.8	19		982.9	11	1001.0	13		1052.9	14	1070.6	18
A" C-H bend		650.3	40	699.3	41		504.5	19	547.0	20		645.6	40	693.8	41
A' NH_2 wag	554.3	585.5	172	568.2	129	487.8	494.5	50	499.9	36	552.3	583.9	177	565.3	136
A' C-H bend	457.7	466.8	94	482.1	178		382.9	71	352.2	90	451.7	460.9	93	480.0	170
A' CCN bend		362.8	25	429.1	8		299.9	39	382.0	47		354.0	21	416.2	7
A" CCN bend		354.6	9	369.3	8		318.0	9	329.0	9		344.3	8	358.8	7

[a]Frequencies and intensities are in cm^{-1} and km/mol. [b]Observed in an argon matrix. [c]Frequencies computed with BPW91/6-311++G(3df,3pd).

[d]Frequencies and intensities computed with B3LYP/6-311++G(3df, 3pd). $HC\equiv C\text{-}NH_2$ has a C_s structure, and the symmetry notations are based on the C_s structure.



TOC

Laser-ablated Zr atoms react with acetonitrile, and the products are identified from isotopic shifts and correlation with the DFT calculated frequencies. CH_2=Zr(H)NC, CH_3-ZrNC, and η_2-Zr-NC-CH_3 are identified in the product spectra. The methylidene complex exhibits an agostic structure.