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Structure and Vibrational Frequencies of $CH_2{=}NbH_2$, a Major Reaction Product of Methane Activation by Laser-Ablated Nb atoms

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Viable activation of methane is a long standing goal for chemists. Recent studies show that methane activation by laser-ablated transition metal atoms leads to formation of the simple insertion product CH_3-MH,[1-7] and in the case of Group 4 and 6 metals, α-H transfer also gives the methylidene dihydride complex $CH_2{=}MH_2$. Electronic structure calculations have shown agostic stabilization of these methylidene complexes through CH_2 distortion and unequal M-H bond lengths.[3-7] The activation of a second methane molecule gave new dimethylmetaldihydrides $(CH_3)_2MH_2$ in the case of Group 4, but Group 6 allowed a second α–H transfer to form the methylidynes $CH{\equiv}MH_3$. Such simple methylidene and methylidyne complexes provide a model for structures and substituent effects for the much larger high-oxidation state complexes previously synthesized.[8]

Niobium alkylidene complexes have been mostly synthesized by α–H abstraction reactions; however, attempts to provide a Nb methylidyne complex have not been successful giving related complexes instead.[8] Recently reaction of laser-ablated niobium atoms with methane has been carried out and CH_3-NbH, $CH_2{=}NbH_2$, $CH{\equiv}NbH_3^-$, and $(CH_3)_2NbH_2$ are identified in the matrix infrared spectra.[9] Questions, however, still remain in the structure of the methylidene hydride complex, $CH_2{=}NbH_2$. Spectroscopic evidences apparently show that the two Nb-H bonds are apparently equal, which are compared with the highly asymmetric MH_2 groups of Group 4 and 6 metal methylidenes.[3-7] We report here an investigation with electronic structure computations for the structure of the smallest possible niobium methylidene hydride complex ($CH_2{=}NbH_2$).

The frequencies of the product absorptions observed from reaction of Nb with methane are listed in *Table* 1.[9] The most distinctive absorptions are NbH_2 stretching bands, which are strong and appear in a relatively clean area. Deuteration leads to variations in frequency for all the absorptions, and particularly the hydrogen stretching frequencies show large isotopic shifts (H/D ratios of 1.39). On the other hand, ^{13}C substitution results in almost no change in the high frequency region, but gives sizable shifts in the low frequency region.

Without Nb hydrides[10] in the matrix spectra, the two strong Nb-H stretching absorptions with 1:2 inten-

Table 1. Frequencies of product absorptions observed from reactions of methane with Nb in excess argon[a]

Group	CH_4	CD_4	$^{13}CH_4$	CH_2D_2
i	1611.4	1159.1	1611.4	1611.0
m	1680.7	1206.0	1680.7	1680.7, **1666.4**, 1652.5
	1652.5	1189.9	1652.5	1205.5, **1198.4**, 1188.7
	805.4	736.8	784.5	
	547.1		546.6	
	480.4		480.4	
a	1542.5	1103.7	1542.2	1524.3
	1489.5	1076.1	1489.5	1506.7, 1488.2
di	1717.5	1231.5	1717.5	1717.1, 1694.5, 1686.3
	1686.3	1213.0	1686.3	1217.8, 1212.8

[a] All frequencies are taken from Ref [9] and in cm^{-1}. Stronger absorptions are bold. **i**, **m**, **a**, and **di** stand for CH_3-NbH, CH_2=NbH_2, CH≡NbH_3^-, and $(CH_3)_2NbH_2$, respectively.

sity ratio and other **m** absorptions (in *Table* 1) indicate that CH_2=NbH_2, is readily formed in reaction of Nb with CH_4. Computation results also indicate that the small Schrock carbene is in fact most stable among the plausible products.[9] CH_2D_2 provides further valuable diagnostic information for the product structure. Deuteration of one of the hydrogen atoms for the NbH_2 group effectively breaks down the coupling between the two hydrogen stretching motions.

The hydrogen stretching frequencies of CHD–NbHD in *Table* 1, which are at the middle of the symmetric and antisymmetric hydrogen stretching pairs, suggest that CH_2=NbH_2 in its doublet ground state has a C_s structure with two equal Nb-H bonds. Extensive calculations have been carried out at the levels of B3LYP, BPW91, MP2, and CCSD with 6-311++G(2d,p) and 6-311++G(3df,3pd) bases.[11] Interestingly enough, at all levels of calculation performed in this study, two stable conformations are identified for CH_2–NbH_2, the C_1 and C_s structures (*Fig.* 1). The T1 diagnostic values for the CCSD calculations are, however, fairly high (~0.06), suggesting that single-reference calculations are not enough for accurate determination of the structure.

Notice that the C_1 structure shown in *Fig.* 1, which is slightly more stable (less than 3 kcal/mol) than the C_s structure, is agostically distorted. The agostic interaction, observed as inclination of the C-H bond toward the transition metal center, is in fact quite common among high oxidation-state complexes. Clot and Eisenstein[12] and Scherer and McGrady[13]

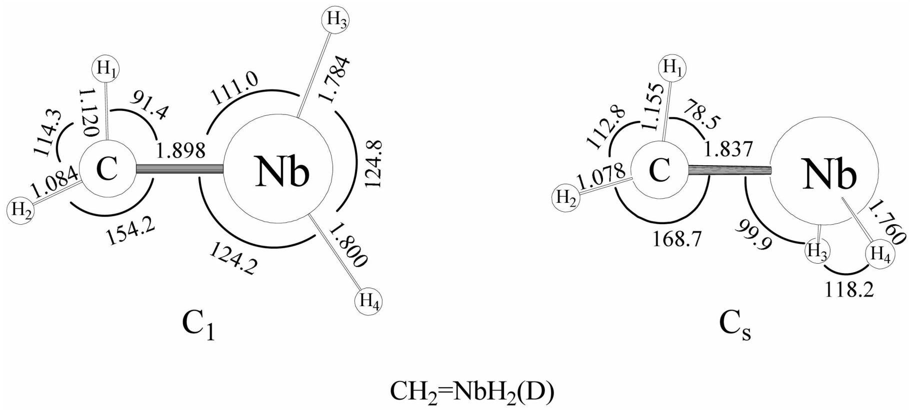

Fig. 1. Two stable (C_1 and C_s) structures of CH_2=NbH_2 in the ground doublet states. The C_1 and C_s structure shown here are calculated both at the level of CCSD/6-311++G(3df, 3pd)/SDD (for Nb). The bond lengths and angles are in Å and degrees.

Table 2. Observed and calculated fundamental frequencies of CH_2=NbH_2 isotopomers for configuration 2 (C_s) in the Ground $^2A'$ Electronic State[a]

Approximate Description	CH_2=NbH_2							CD_2=NbD_2			$^{13}CH_2$=NbH_2			CHD=NbHD		
	Freq.						Int.	Freq.		Int.	Freq.		Int.	Freq.		Int.
	Obs.	B3LYP anharm[b]	B3LYP	CCSD	BPW91	MP2		Obs.	CCSD		Obs.	CCSD		Obs.	CCSD	
ν_1 A' C-H str.		3097.8	3225.4	3272.1	3162.6	3305.2	7		2425.1	10		3260.7	6		2556.2	18
ν_2 A' C-H str.		2473.5	2599.6	2529.7	2459.6	2517.6	21		1842.4	8		2523.8	21		2394.9	11
ν_3 A' Nb-H str.	1680.7	1716.9	1771.9	1787.7	1749.9	1941.6	289	1206.0	1269.0	146	1680.7	1787.7	289	1666.4	1780.6	373
ν_4 A' CH_2 scis.		1336.8	1362.5	1448.2	1350.8	1520.1	36		1100.6	15		1441.8	37		1350.5	26
ν_5 A' C=Nb str.	805.4	828.4	853.8	889.8	852.5	1531.3	88	736.8	802.0	66	784.5	866.3	86	805.4	849.2	71
ν_6 A' NbH_2 scis.		606.8	654.6	696.3	676.3	796.4	72		515.8	24		694.8	73		594.9	67
ν_7 A' NbH_2 wag		511.9	550.7	643.1	585.7	744.6	23		473.4	29		639.6	20		565.1	16
ν_8 A' CH_2 rock	547.1	420.5	505.7	531.1	546.6	536.7	77		381.9	37	546.6	530.7	77		476.7	66
ν_9 A'' Nb-H str.	1652.5	1701.8	1761.7	1774.3	1744.2	1879.5	470	1189.9	1267.1	243	1652.5	1774.3	469	1198.4	1268.4	197
ν_{10} A'' CH_2 wag		602.5	629.3	684.4	622.0	794.5	45		537.0	22		678.5	45		547.7	20
ν_{11} A'' NbH_2 twist	480.4	404.3	457.2	458.7	469.2	549.8	66		330.7	36	480.4	457.8	65		357.1	39
ν_{12} A'' CH_2 twist		143.4	309.9	291.8	310.8	473.3	0		207.7	0		291.8	0		267.7	1

[a]Calculated with 6-311++G(3df, 3pd)/SDD (for Nb). Frequencies and intensities are in cm^{-1} and km/mol. Infrared intensities are calculated values with CCSD. [b]Anharmonic frequencies calculated with B3LYP.

recently reported that agostic stabilization has little or no dependence on C-H-M electron donation but arises from delocalization of the C=M bonding electrons. The C_1 structure varies considerably depending on the level of theory. B3LYP density functional underestimates the agostic distortion, while MP2 method and BPW91 density functional overestimate it. More rigorous CCSD method gives an intermediate result.

On the other hand, the C_s structure is quite unique with two equal Nb-H bonds. Unlike the C_1 structure, the C_s structure hardly varies regardless of the level of theory, which coincides with the experimental evidences for the two equal Nb-H bonds. It is interesting that the CH_2 group is also highly distorted (*Fig.* 1), in fact even more than in the C_1 structure. The calculated harmonic and anharmonic frequencies at various level of theory for the C_s structure are listed in *Table* 2. Among them, the BPW91 frequencies of 1749.9, 1744.2, 852.5, 546.6, and 469.2 cm^{-1} best match with the observed values of 1680.7, 1652.5, 805, 547, 480.4 cm^{-1}. The frequencies of the other methane isotopomers are also compared with the CCSD frequencies in *Table* 2, showing reasonable agreements.

The calculated vibrational characteristics, while showing reasonable agreements, also show systematic discrepancies with the experimental values. For example, the calculated symmetric and anti-symmetric Nb-H stretching frequencies are mostly too close to each other in comparison with the observed values (1680.7 and 1652.5 cm^{-1}, 28.2 cm^{-1} apart). However, unlike other methods, the MP2 frequencies are too far apart (62.1 cm^{-1}). The level of agreement between the experimental and calculated values varies markedly in the low frequency region with the calculation methods. Evidently, more accurate molecular structure of $CH_2=NbH_2$ ought to be determined while the C_s structure is better in line than the C_1 structure with the experimental results.[9]

We have shown that B3LYP, BPW91, MP2, and CCSD calculations with reasonably large bases give two possible configurations (C_1 and C_s) with similar energies for $CH_2=NbH_2$. While the C_1 configuration is consistent with those of previously studied Group 4 and 6 methylidene complexes, the C_s structure with two equal Nb-H bonds reasonably reproduces the observed frequencies and particularly the observed isotopic variations. However, the calculated vibrational characteristics also show systematic discrepancies with the observed characteristics, and they, along with the high T1 diagnostic value and the illusive two configurations, request further theoretical examinations such as multi-reference computations.

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