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Formation of $HC{\equiv}ReH_3$ in Methane Activation by Rhenium Atoms: Observation of the Elusive Methylidyne C−H Stretching Absorption

Han-Gook Cho and Lester Andrews*

Departments of Chemistry, University of Incheon, 177 Dohwa-dong, Nam-ku, Incheon 402-749, South Korea, and University of Virginia, P. O. Box 400319, Charlottesville, Virginia 22904-4319

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Summary: $HC{\equiv}ReH_3$ is formed in the reaction of Re atoms with CH_4 in excess argon. The insertion complex is generated, and two α-hydrogen migrations follow to produce the trihydrido methylidyne complex $HC{\equiv}ReH_3$, which has a C_s structure, a C−H stretching absorption at 3102 cm^{-1}, a C≡Re stretching mode at 1049 cm^{-1}, and a very strong Re−H stretching absorption at 1804 cm^{-1}.

Since the discovery of transition-metal compounds with a carbon−metal triple bond in the 1970s,[1] carbyne complexes have been extensively studied due to their versatile chemistry and catalytic activities,[2] but only a few of them contain the simple M≡C−H moiety (M = transition metal).[3] Moreover, the C−H vibrational characteristics remain largely uninvestigated despite various efforts, partially due to very low infrared intensity and interference from other hydrogen stretching absorptions, while the C≡M stretching bands are observed and used frequently as a probe to study the ligand effects.[4,5]

Recently Hopkins et al. prepared *trans*-$W({\equiv}CH)(PMe_3)_4Cl$ with the methyl groups all deuteriated to avoid interference from the methyl hydrogen stretching absorptions and assigned the weak methylidyne C−H stretching mode near 2980 cm^{-1} with deuterium counterpart at 2240 cm^{-1}.[6] The dimensions of a related H−C≡W moiety were later measured by neutron diffraction.[7] Here, we report the preparation of the smallest high-oxidation-state complex with a C≡Re bond, namely $HC{\equiv}ReH_3$, and its IR spectrum in order to investigate the elusive methylidyne C−H stretching absorption. This simple methylidyne complex is fundamentally important, as it can be investigated by high-level theoretical calculations to understand the unique bonding and structure around the Re center. Furthermore, this trihydrido complex is a model for comparison with larger ligated monohydrido and dihydrido alkylidyne compexes.[8]

Laser-ablated Re atoms (Johnson-Matthey) were reacted with CH_4 (Matheson, UHP grade), $^{13}CH_4$, CD_4, and CH_2D_2 (Cambridge Isotopic Laboratories) in excess argon during condensation at 8 K using a closed-cycle refrigerator (Air Products HC-2). These methods have been described in detail elsewhere.[9] Reagent gas mixtures were typically 1.0−2.0% in argon. Samples were later irradiated for 20 min periods by a mercury arc lamp (175 W), with the globe removed and a combination of optical filters, and subsequently annealed to allow further reagent diffusion. Complementary density functional theory (DFT) calculations were carried out using the Gaussian 03 package,[10] B3LYP density functional,[11] and 6-311++G(3df,3pd) basis sets for C and H and SDD pseudopotential and basis set[12] for Re to provide a consistent set of vibrational frequencies for the anticipated reaction products. Zero-point energies were included in the calculation of product energies. Higher level CCSD calculations[10] were done to support the DFT results.

The C−H and C−D stretching regions in the infrared spectrum for the product of laser-ablated Re atoms with CH_4, $^{13}CH_4$, CD_4, and CH_2D_2 are shown in Figure 1. These absorptions, marked "**y**" for methylidyne, do not change on visible ($\lambda > 420$ nm) irradiation (not shown), but they increase about 40% on UV ($240 < \lambda < 380$ nm) photolysis and 10% more on the following full arc ($\lambda > 220$ nm) irradiation. The effect of sample annealing on the natural isotopic sample spectrum is illustrated: the new product absorption sharpened on annealing to 28 K, broadened on annealing to 36 K, and then reduced by half on annealing to 44 K. The allowed methane precursor fundamental bands are completely absorbing, but the overtone of the triply degenerate bending mode is observed in all of our methane experiments at 2604 and 2600 cm^{-1}. This absorption does not change on visible irradiation and decreases slightly with UV and full-arc photolysis, following the growth of the new product absorption. Similar behavior is found for the overtones of $^{13}CH_4$ and CD_4.

The product C−H stretching absorption is observed at 3101.8 cm^{-1}, and deuterium and ^{13}C counterparts are found at 2334.3 and 3090.8 cm^{-1} (H/D and $^{12}C/^{13}C$ ratios of 1.329 and 1.0036), respectively. This C−H stretching frequency is substantially higher (about 200 cm^{-1}) than those of normal saturated hydrocarbons, suggesting an adjacent multiple carbon−rhenium bond to provide higher s character to the C−H bond.[3,14] The same C−H and C−D stretching absorptions were observed within experimental error in the CH_2D_2 spectra, which indicates

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* To whom correspondence should be addressed. E-mail: lsa@virginia.edu.

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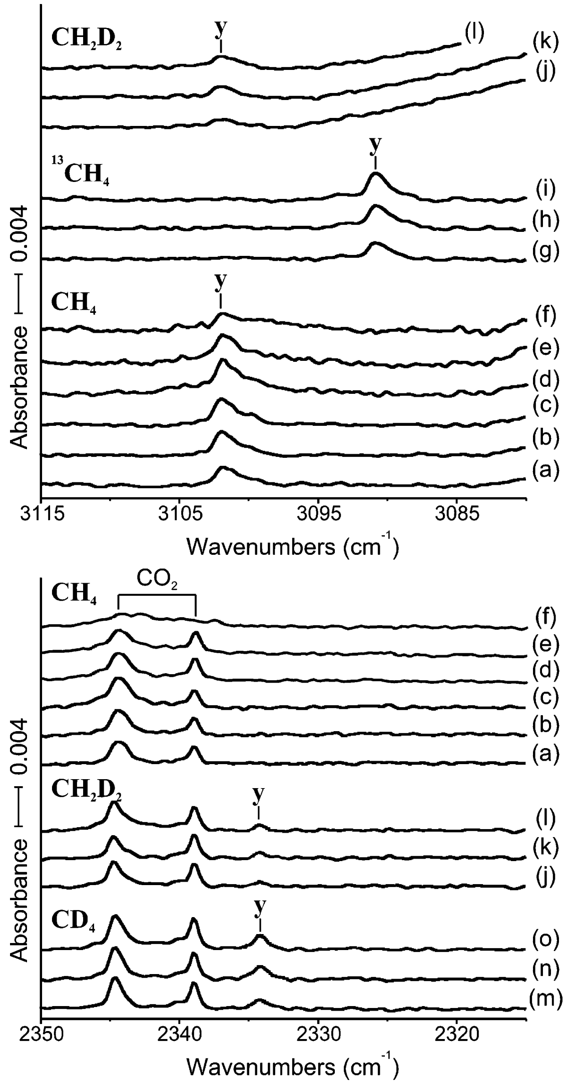

Figure 1. IR spectra in the C−H and C−D stretching regions for the Re atom reaction product with CH_4 in excess argon at 8 K: (a) for Re + 1.0% CH_4 in Ar codeposited for 1 h; (b) as in (a) after photolysis (240 < λ < 380 nm); (c) as in (a) after photolysis (λ > 220 nm); (d) as in (a) after annealing to 28 K; (e) as in (a) after annealing to 36 K; (f) as in (a) after annealing to 44 K; (g) for Re + 1.0% $^{13}CH_4$ in Ar; (h) as in (g) after photolysis (240 < λ < 380 nm); (i) as in (g) after photolysis (λ > 220 nm); (j) Re + 2.0% CH_2D_2 in Ar; (k) as in (j) after photolysis (240 < λ < 380 nm); (l) as in (j) after photolysis (λ > 220 nm); (m) for Re + 1.0% CD_4 in Ar; (n) as in (m) after photolysis (240 < λ < 380 nm); (o) as in (m) after photolysis (λ > 220 nm). The label **y** denotes the methylidyne product absorption.

that no other C−H bond is in the proximity to perturb significantly this single C−H stretching mode.

Also shown in Figure 2 are the isotopic methane product spectra in the Re−H and Re−D stretching regions. Two adjacent strong absorptions with almost equal intensities are observed at 1809.9 and 1804.0 cm^{-1}, which are split by the matrix cage. The deuterium counterparts are similarly split at 1302.5 and 1298.1 cm^{-1} (H/D ratios of 1.390 for a heavy-metal hydride), and the similarly split ^{13}C counterparts show no isotopic shift. These Re−H stretching absorptions indicate that oxidative C−H insertion by Re clearly occurs. The mixed CH_2D_2 precursor gives slightly different bands (Table 1) for this strongest absorption, which is in agreement with calculated frequencies for the strongest single Re−H(D) mode in the subject mixed-isotope (two H and two D, four possibilities) molecule.

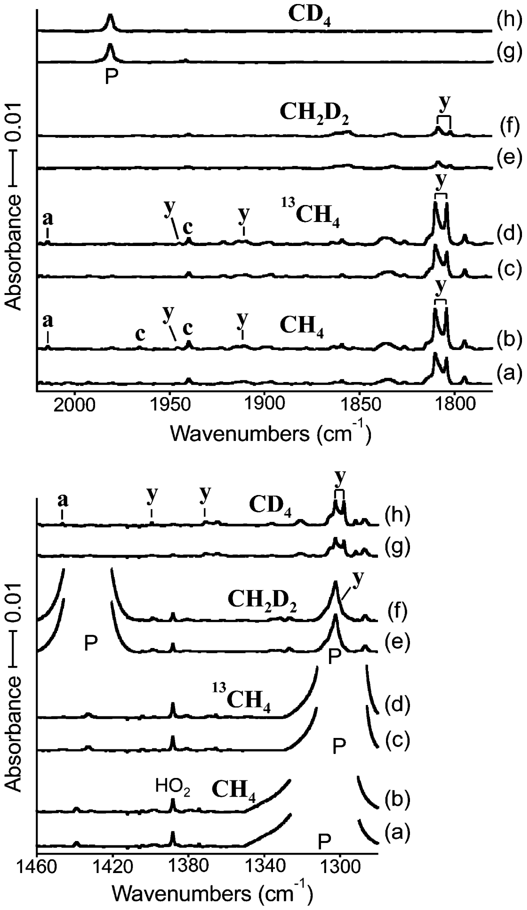

Figure 2. Re−H and Re−D stretching regions for the product of Re atom reaction with methane in excess argon at 8 K and their variation on UV (240 < λ < 380 nm) photolysis: (a) for Re + 1.0% CH_4 in Ar codeposited for 1 h; (b) as in (a) after photolysis; (c) for Re + 1.0% $^{13}CH_4$ in Ar; (d) as in (c) after photolysis; (e) Re + 2.0% CH_2D_2 in Ar; (f) as in (e) after photolysis; (g) Re + 1.0% CD_4 in Ar; (h) as in (g) after photolysis. The labels **y**, **a**, **c**, and P indicate methylidyne, aggegrate, common, and precursor absorptions, respectively.

On the basis of our previous work with methane activation by transition-metal atoms,[15] there are three possible reaction products. The monohydrido insertion product (CH_3−ReH) is predicted to be 1 kcal/mol higher than the energy of Re and CH_4 and to have a Re−H stretching mode at 2084 cm^{-1} (75 km/mol intensity), which is 228 cm^{-1} higher than the strongest calculated mode for the product assigned here (Table 1). The doublet state methylidene product (CH_2=ReH_2) is predicted to also be 1 kcal/mol higher in energy and to have 2118 cm^{-1} (57 km/mol) and 2076 cm^{-1} (154 km/mol) absorptions. The latter is 220 cm^{-1} higher than the strongest calculated mode for the present product. In addition, the isolated ReH_4, ReH, and ReH_2 molecule absorptions were previously observed at 2037.3, 1985.0, and 1646.4 cm^{-1}, respectively.[16] None of these bands was observed here, and binary rhenium hydrides are not candidates for the new product absorptions.

The third possibility, namely the methylidyne HC≡ReH_3 in the doublet ground state, is predicted theoretically to be the most stable among the plausible products: it is 7 kcal/mol lower in energy than both the insertion and methylidene complexes and

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Table 1. Observed and Calculated Frequencies of $HC\equiv ReH_3$ Isotopic Molecules in the Ground $^2A'$ Electronic State[a]

approx descripn	$HC\equiv ReH_3$ obsd	$HC\equiv ReH_3$ calc	$HC\equiv ReH_3$ int	$DC\equiv ReD_3$ obsd	$DC\equiv ReD_3$ calc	$DC\equiv ReD_3$ int	$H^{13}C\equiv ReH_3$ obsd	$H^{13}C\equiv ReH_3$ calc	$H^{13}C\equiv ReH_3$ int	$HC\equiv ReHD_2$, $DC\equiv ReH_2D$ obsd
A′ C-H str	3101.8	3264.3	36	2334.3	2430.5	25	3090.8	3252.1	35	3101.9, 2334.3
A′ ReH_2 str	1946.4	2088.8	76	1399.3	1481.4	40	1946.4	2088.8	76	
A′ Re−H str	1809.9, 1804.0	1855.7	244	1302.6, 1298.1	1318.1	121	1809.9, 1803.9	1855.7	244	1808.5, 1802.5, 1300.2
A′ C≡Re str	1048.8	1096.8	10	*b*	1041.2	7	1012.9	1061.4	9	*b*
A′ ReH_3 deform		751.4	2		549.6	0		749.5	2	
A′ HCRe bend		603.7	56		447.9	24		601.7	56	
A′ ReH_3 rock		492.3	24		368.6	18		489.3	23	
A′ ReH_2 scis		459.5	2		325.9	1		459.5	2	
A″ ReH_2 str	1910.1,1900.3	2040.3	46	1370.8,1364.6	1449.0	24	1910.1,1900.3	2040.2	46	
A″ ReH_2 twist		830.3	0		637.8	4		825.1	0	
A″ HCRe bend		695.7	109		501.6	56		694.1	108	
A″ ReH_3 rock		304.6	23		218.3	11		304.5	23	

[a] Frequencies and intensities (int) are given in cm^{-1} and km/mol, respectively. Observed values (obsd) were obtained in an argon matrix. Frequencies and intensities computed with 6-311++G(3df, 3pd) are for harmonic calculations, and the SDD core potential and basis set are used for Re. $HC\equiv ReH_3$ has a C_s structure with two equal Re−H bonds. The symmetry notations are based on the C_s structure. [b] Covered by precursor band.

6 kcal/mol below Re + CH_4. More importantly, the strongest observed absorption is in very good agreement with the calculated 1855.7 cm^{-1} frequency for the long Re−H bond stretching mode and the most intense infrared band for the methylidyne complex, as compared in Table 1. The calculated frequency is 46 cm^{-1} or 2.5% higher than the observed value, which is in the range for density functional theory and within the error limits of the harmonic approximation involved.[15−17] The frequencies calculated at the CCSD level are slightly higher, but they correlate well with the B3LYP values.

The single Re−H bond stretching mode discussed above is calculated to be by far the strongest IR absorption for $HC\equiv ReH_3$, and we expect the relative intensities calculated by density functional theory to provide an approximate guide for other modes. Figure 2 also illustrates two other weak associated product absorptions, broad features at 1946.4 and 1910.1 cm^{-1}, which show no ^{13}C shift but shift to 1399.3 and 1370.8 cm^{-1} with deuterium (H/D ratios of 1.391 and 1.393). The last two weaker Re−H stretching absorptions are consistent with the predicted symmetric and antisymmetric Re−H stretching frequencies for the ReH_2 subunit with equivalent Re−H bonds in $HC\equiv ReH_3$, as shown in Table 1 (predicted to be 6.8% and 6.3% higher). The observation of two weak and one strong Re−H stretching mode for a molecule with a ReH_3 subgroup verifies that the symmetry is lower than threefold. In fact, the two-bond stretching modes of a trigonal heavy-metal hydride are separated by less than 10 cm^{-1}.[18] Furthermore, weak absorptions are expected in this region, on the basis of the observation of a similar product in the analogous higher yield reactions with ethane at 1953.5 and 1900.1 cm^{-1} and at 1786.3, 1780.5 cm^{-1} in this laboratory. The weak band at 2014.4 cm^{-1} with a deuterium counterpart at 1446.6 cm^{-1} (labeled **a**) increases on annealing at the expense of the major product, and these bands are likely due to an aggregate species. The sharp bands at 1966.6 and 1940.3 cm^{-1} (labeled **c**) are common to other Re experiments.[16] Finally, these new absorptions are in the 1900−2000 cm^{-1} region for Re−H stretching frequencies in a representative class of rhenium dihydrido alkylidyne complexes.[2a,8b]

A weak absorption at 1048.8 cm^{-1} has its ^{13}C counterpart at 1012.9 cm^{-1} (Figure 3), but the D counterpart is unfortunately covered by the strong CD_4 absorption at 995 cm^{-1}. These weak bands are assigned to the C≡Re stretching mode. This diagnostic mode can appear only for the methylidyne product identified here. The five observed product absorptions taken together substantiate the identification of $HC\equiv ReH_3$ as the reaction product of Re with CH_4. No other major absorptions are found in the Re + CH_4 product spectra, in contrast to previous investigations of transition-metal atom reactions with methane or methyl halides, which normally reveal two or three products.[15] The formation of $HC\equiv ReH_3$ as the major product dramatically demonstrates the strong tendency of Re to favor the triple bond.[3]

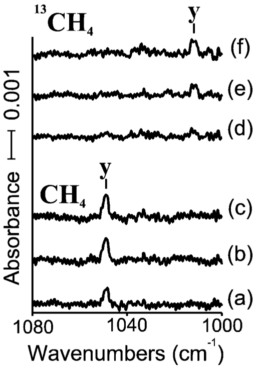

Figure 3. C≡Re stretching region for the product of Re atom reaction with CH_4 and $^{13}CH_4$ in excess argon: (a) for Re + 1.0% CH_4 in Ar codeposited for 1 h. (b) as in (a) after photolysis (240 < λ < 380 nm); (c) as in (a) after photolysis (λ > 220 nm); (d) for Re + 1.0% $^{13}CH_4$ in Ar codeposited for 1 h; (e) as in (d) after photolysis (240 < λ < 380 nm); (f) as in (d) after photolysis (λ > 220 nm). The label **y** denotes the product absorption.

The congested carbon−hydrogen stretching region often prohibits the observation of important weak absorptions in this diagnostic region. The simple precursor spectrum and the methylidyne product with no interfering ligand chromophores allow observation of the elusive C−H stretching band of the H−C≡M moiety. It is well-known that the hydrogen stretching frequency increases with the amount of s character in the C−H bond, and a C−H stretching frequency above 3000 cm^{-1} is normally regarded as evidence for the presence of an adjacent multiple bond.[14] The present C−H stretching mode is substantially higher than that found for the $(HCW)(PMe_3)_4Cl$ complex.[6]

However, the high observed C−H stretching frequency of 3101.8 cm^{-1} is substantially lower than those of acetylene (the antisymmetric stretching band is at 3284 cm^{-1} in an argon matrix and the IR-inactive symmetric stretching mode is some 90 cm^{-1} higher)[19] but is between the allowed C−H stretching modes for ethylene at 3112 and 2996 cm^{-1} in solid argon and lower than the inactive symmetric stretching modes (3019 and 3272 cm^{-1} in the gas phase).[19] The C−H bond length of 1.079 Å for $HC\equiv ReH_3$ (Figure 4) can be compared with that of 1.062 Å for acetylene and 1.082 Å for ethylene calculated at the same level of theory. The differences in electronegativity (2.5, 2.1, and 1.9 for C, H, and Re using the Pauling scale, respectively)

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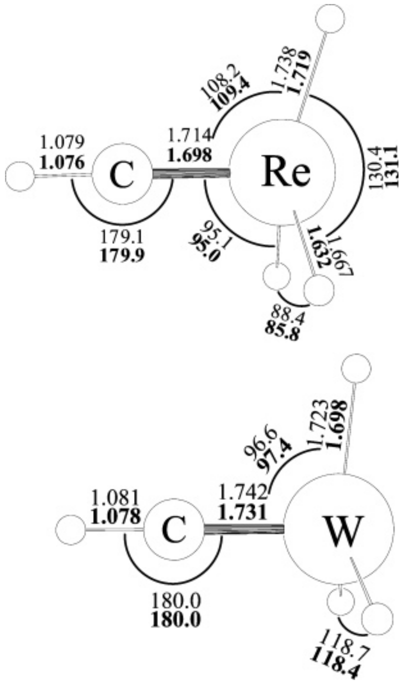

Figure 4. Structures of (top) HC≡ReH$_3$ and (bottom) HC≡WH$_3$ optimized at the B3LYP/6-311++G(3df,3pd)/SDD and CCSD/6-311++G(3df,3pd)/SDD levels. The bond lengths and angles are given in Å and deg, respectively. The B3LYP geometrical parameters are very close to the CCSD values (given in boldface type). The HC≡ReH$_3$ and HC≡WH$_3$ structures are of C_s and C_{3v} symmetry in their $^2A'$ and $^1A_1$ ground states, respectively.

lead to substantial polarization of the C≡Re bond (calculated natural charges on the C and Re atoms are −0.24 and 0.58, respectively). In addition, NBO analysis[10,20] also shows that the s character of the carbon contribution to the C−H bond is 46.6%. In other words, more s character is allocated to the polarized C≡Re bond, and as a result, the methylidyne C−H bond gains p character (53.4%) and weakens accordingly, as compared to acetylene itself.

It is also notable that the methylidyne complex is trapped while C−H insertion is believed to occur first upon the activation of methane by a Re atom, electronically excited in the laser ablation process or by ultraviolet irradiation of the strong 326 nm absorption band,[21] and α-hydrogen migration follows, as summarized in reaction 1. The increase in product

$$\mathrm{Re^* + CH_4 \rightarrow [CH_3{-}ReH]^* \rightarrow [CH_2{=}ReH_2]^* \rightarrow HC{\equiv}ReH_3} \quad (1)$$

absorptions on UV irradiation is accompanied by a decrease in methane absorption, which further supports the initial step in reaction 1. The high preference for a carbon−rhenium triple bond in the methane activation process is perhaps surprising, with the relatively small amount of energy difference between the plausible products (7 kcal/mol). Even reaction products ∼20 kcal/mol higher than the most stable one have been formed during reactions of transition-metal atoms with CH$_4$ and methyl halides or photolysis and then trapped in the solid argon matrix.[15] However, in this Re case, α-hydrogen migration is faster than relaxation of the energized intermediates in the matrix cage, and reaction 1 goes to completion.

The C_s structure calculated for doublet-state HC≡ReH$_3$ is compared with the C_{3v} structure of the previously investigated[18] singlet-state HC≡WH$_3$ complex in Figure 4. One of the hydrogen atoms bonded to the Re atom is tilted more with a longer Re−H bond (and considerably stronger absorption and lower stretching frequency) as compared to the other two. Computed atomic spin densities show that the unpaired electron is located mostly on the Re center and slightly more on the H with the longer bond to Re than on the two H atoms with shorter bonds to Re. Our observation of two weaker and one stronger Re−H stretching mode requires lower than threefold symmetry for this new molecule. Calculations with the BPW91/6-311++G(3df,3pd)/SDD and MP2/6-311++G(2d,p)/SDD methods also give similar C_s structures with one longer Re−H bond (1.735 and 1.702 Å, respectively) and two shorter Re−H bonds (1.670 and 1.639 Å, respectively). Stretching of the unique longer Re−H bond is responsible for the very strong infrared absorptions at 1809.9 and 1804.0 cm^{-1}. Our computation failed to converge with the imposition of C_{3v} symmetry. Calculations were also performed with the CCSD higher level of theory,[10] and the structural parameters are listed in boldface type in Figure 4. These are single-reference methods, and the effect of spin−orbit coupling is not included. The asymmetric structure and nonequivalent Re−H bonds in this nondegenerate ($^2A'$) electronic ground state HC≡ReH$_3$ molecule are believed to be due to first-order Jahn−Teller distortion of what would be a singly occupied e symmetry orbital in C_{3v} symmetry,[22] which is not present in the symmetrical singlet state HC≡WH$_3$ complex.

The computed H−C bond length of 1.079 Å is compared to 1.076 and 1.081 Å values for H−C≡W[4] and HC≡WH$_3$,[18] respectively, and the C−H frequency for the latter is calculated to be 29 cm^{-1} lower with half of the infrared intensity[23] found for HC≡ReH$_3$. Our calculated C≡Re bond length of 1.714 Å is slightly shorter than the C≡M bond lengths 1.755, 1.737, and 1.77(1) Å measured for the (η^5-C$_5$Me$_5$)(Br)$_3$Re≡CC(CH$_3$)$_3$,[24] H−C≡W,[4] and BrW≡CH(dmpe-d_{12})$_2$ compounds,[7] respectively.

In conclusion, HC≡ReH$_3$ is produced in methane activation by electronically excited Re atoms, and the stability of the methylidyne complex is confirmed by DFT frequency and structure calculations. In particular, the C−H stretching frequency is substantially higher than those of normal saturated hydrocarbons, due to the high s character in the C−H bond. The complex HC≡ReH$_3$ contains one longer and two shorter Re−H bonds, owing to Jahn−Teller distortion driven by an open-shell e-symmetry orbital. Finally, trihydrido complexes of Re have been proposed as intermediates in the synthesis of dihydrido complexes,[8b] but we have prepared and trapped the simple HC≡ReH$_3$ trihydrido complex from methane activation by excited atomic Re here in solid argon for the first time.

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