

[CH₃-MoF], [CH₂=MoHF], and [CH≡MoH₂F] Formed by Reaction of Laser-Ablated Molybdenum Atoms with Methyl Fluoride: Persistent Photoreversible Interconversion through α -Hydrogen Migration and Agostic Interaction

Han-Gook Cho^[a] and Lester Andrews^{*[b]}

Abstract: Simple molybdenum methyl, carbene, and carbyne complexes, [CH₃-MoF], [CH₂=MoHF], and [CH≡MoH₂F], were formed by the reaction of laser-ablated molybdenum atoms with methyl fluoride and isolated in an argon matrix. These molecules provide a persistent photoreversible system through α -hydrogen migration between the carbon and metal atoms: The methyl and carbene complexes are produced by applying UV irradiation

(240–380 nm) while the carbyne complex is depleted, and the process reverses on irradiation with visible light ($\lambda > 420$ nm). An absorption at 589.3 cm⁻¹ is attributed to the Mo–F stretching mode of [CH₃-MoF], which

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is in fact the most stable of the plausible products. Density functional theory calculations show that one of the α -hydrogen atoms of the carbene complex is considerably bent toward the metal atom (\angle HCMo = 84.5°), which provides evidence of a strong agostic interaction in the triplet ground state. The calculated C≡Mo bond length in the carbyne is in the range of triple-bond values in methylidyne complexes.

Introduction

Simple methylidene complexes, [CH₂=MHF], have been synthesized recently by reacting laser-ablated Group 4 transition-metal atoms with CH₃F.^[1–3] These complexes exhibit distortion of the CH₂ group and agostic bonding. Since the first preparation of high-oxidation-state transition-metal complexes, a large number of substituted alkylidenes ([R¹R²C=M]) and alkylidynes ([RC≡M]) have been investigated.^[4] These compounds are typically prepared by intramolecular α -hydrogen transfer from a bis(alkyl) precursor and are important for catalytic activities in metathesis reactions of alkenes and alkynes.^[5,6]

Stable alkylidene complexes of Group 4 metals are relatively rare, but such Group 6 metal complexes are abundant,

and the higher valence capacity allows the formation of substituted alkylidyne complexes not possible with Group 4 metals.^[4] Accordingly we have reacted excited Mo atoms with CH₃F to initiate the formation of simple methylidene and methylidyne complexes that are related by intramolecular α -hydrogen transfer. Here, these complexes are first identified through comparison of their matrix IR spectra and density functional theory (DFT) frequency calculations.

Experimental Section

The laser-ablation matrix infrared experiment has been described previously.^[7–9] Briefly, laser-ablated molybdenum atoms (Goodfellow) were reacted with CH₃F (Matheson), CD₃F (synthesized from CD₃Br and HgF₂),^[10] and ¹³CH₃F (Cambridge Isotopic Laboratories) in excess argon (MG Industries) during condensation on a CsI window at 7 K. Infrared spectra were recorded at 0.5 cm⁻¹ resolution on a Nicolet 550 spectrometer with type B HgCdTe detector. Samples were irradiated by a mercury arc lamp (175 W, globe removed) for 20 min periods, were then annealed, and more spectra were recorded.

Computational methods: Complementary DFT calculations were carried out by using the Gaussian 98 package,^[11] with B3LYP density functional, 6-311++G(2d, p) and 6-311++G(3df, 3pd) basis sets for C, H, and F, and SDD effective core potential and basis set for Mo (14 valence electrons) to provide vibrational frequencies for anticipated reaction prod-

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ucts. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by means of vibrational analysis. All the vibrational frequencies were calculated analytically.

Results and Discussion

Infrared spectra in the regions of 1770–1870 cm^{-1} and 500–850 cm^{-1} for laser-ablated Mo atoms co-deposited with Ar/ CH_3F at 7 K and their variation upon photolysis and annealing are illustrated in Figure 1. In the region of 1770–1870 cm^{-1} , major product absorptions are found at 1797.7 and 1844.8 cm^{-1} (labeled II and III, respectively). Visible, broad-band irradiation with an Hg lamp and a filter ($\lambda > 420$ nm), following the co-deposition, leads to a considerable decrease in the absorption at 1797.7 cm^{-1} and an increase in the absorption at 1844.8 cm^{-1} . However, UV irradiation (240–380 nm) causes a dramatic increase in the absorption at 1797.7 cm^{-1} and a decrease in the absorption at 1844.8 cm^{-1} . In the subsequent irradiations with visible ($\lambda > 420$ nm) and UV light (240–380 nm), the variation in absorption intensity repeats persistently.

Similar dramatic variations in absorption intensity during photolysis are also observed in the region of 500–850 cm^{-1} , accompanied by variations in the 1770–1870 cm^{-1} region, as shown in Figure 1. In particular, the strong absorptions at 642.5 and 675.4 cm^{-1} (labeled II) weaken considerably on visible photolysis, while the neighboring absorptions at 557.4, 571.6, and 715.8 cm^{-1} (marked III) increase significantly. On the other hand, the following UV photolysis

leads to a reverse result. The remarkable variations in absorption intensity are observed repeatedly in the following cycles of irradiation with visible and UV light with a gradual increase in the total absorption intensity. The variations in absorption intensity suggest that two major products are formed in the reaction of vaporized Mo atoms with methyl fluoride, the increase in intensity of one product in the process of photolysis is accompanied by the decrease in intensity of the other and vice versa.

The weak absorption at 589.3 cm^{-1} (labeled I) exhibits intensity behavior on irradiation cycles almost like that of group II, but UV irradiation only restores or reproduces part of this absorption whereas the group II absorptions become even stronger. A weak 441.4 cm^{-1} band (not shown) is associated with the 589.3 cm^{-1} absorption.

As shown in Figures 2 and 3, whereas ^{13}C substitution leads to negligible shifts in frequency of the product absorptions at 1797.7 and 1844.8 cm^{-1} , deuteration results in large shifts in the two major absorptions to 1292.1 cm^{-1} and two bands at 1322.1 and 1330.5 cm^{-1} (H/D isotopic ratios of 1.391:1, 1.395:1, or 1.387:1), indicating that they are Mo–H stretching absorptions of the reaction products. In earlier studies, the hydrogen stretching absorptions of molybdenum hydrides were observed in the same frequency region.^[12] This indicates that Mo–H bonds are formed readily in the reaction of Mo atoms with methyl fluoride, and that the two major $[\text{R}-\text{MoH}_x]$ products are interconvertible by using visible and ultraviolet irradiation.

The product absorptions are sorted into three groups on the basis of their behavior upon irradiation, annealing, and variation in precursor concentration, as listed in Table 1, and compared with the predicted product vibrational characteristics shown in Tables 2, 3, and 4. The group I and II absorptions are relatively stronger in the original spectrum after the co-deposition of methyl fluoride and Mo atoms, but decrease in intensity to less than a half upon visible irradiation. Group I is restored to its original intensity, but group II absorption intensities increase by more than three times upon UV irradiation. The Mo–H stretching absorptions at 1797.7, 1797.7, and 1291.1 cm^{-1} in Figures 1, 2, and 3, respectively, belong to group II. In the process of annealing, these bands sharpen and weaken gradually.

The group III absorptions are relatively weak in the original spectrum after co-deposition, but increase by more than twice

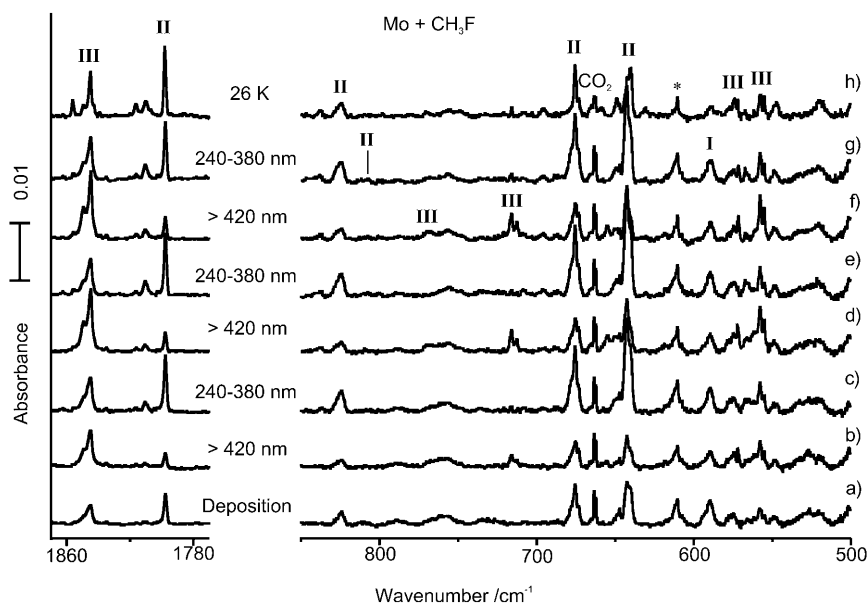


Figure 1. IR spectra in the 1870–1770 and 850–500 cm^{-1} regions for laser-ablated Mo atoms co-deposited with CH_3F at 7 K. a) Mo + 0.5% CH_3F in Ar co-deposited for 1 h, b) after broad-band irradiation with a filter ($\lambda > 420$ nm) for 20 min, c) after broad-band irradiation with a UV-transmitting filter (240 $< \lambda < 380$ nm), d) after $\lambda > 420$ nm irradiation, e) after 240–380 nm irradiation, f) after $\lambda > 420$ nm irradiation, g) after 240–380 nm irradiation, and h) after annealing to 26 K. I, II, or III stands for the product band group. The * absorption is unidentified.

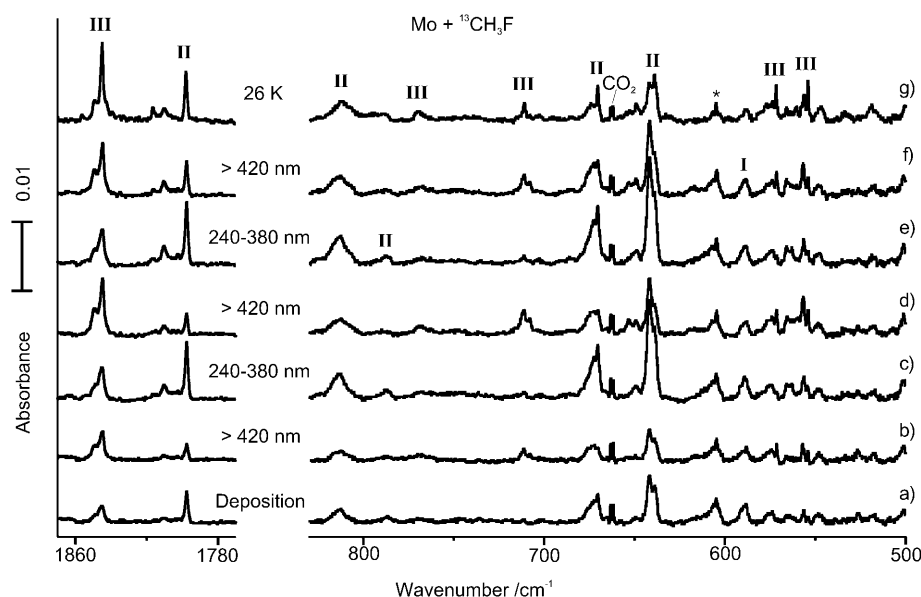


Figure 2. IR spectra in the 1860–1780 and 850–500 cm^{-1} regions for laser-ablated Mo atoms co-deposited with $^{13}\text{CH}_3\text{F}$ at 7 K. a) Mo + 0.5% $^{13}\text{CH}_3\text{F}$ in Ar co-deposited for 1 h, b) after broad-band irradiation with a filter ($\lambda > 420$ nm) for 20 min, c) after broad-band irradiation with a UV-transmitting filter ($240 < \lambda < 380$ nm), d) after $\lambda > 420$ nm irradiation, e) after 240–380 nm irradiation, f) after $\lambda > 420$ nm irradiation, and g) after annealing to 26 K. I, II, or III stands for the product band group. The * absorption is unidentified.

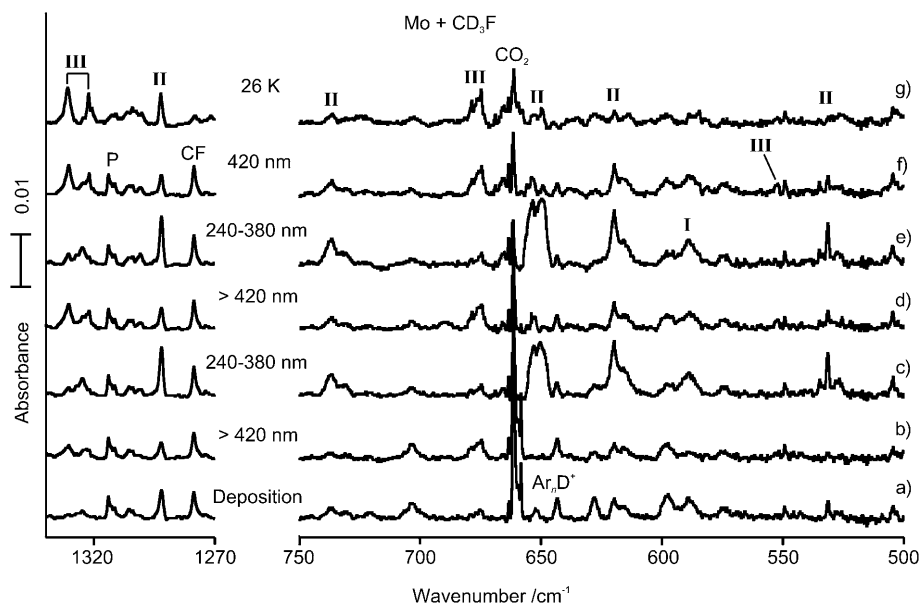


Figure 3. IR spectra in the 1340–1270 and 759–500 cm^{-1} regions for laser-ablated Mo atoms co-deposited with CD_3F at 7 K. a) Mo + 0.5% CD_3F in Ar co-deposited for 1 h, b) after broad-band irradiation with a filter ($\lambda > 420$ nm) for 20 min, c) after broad-band irradiation with a UV-transmitting filter ($240 < \lambda < 380$ nm), d) after $\lambda > 420$ nm irradiation, e) after 240–380 nm irradiation, f) after $\lambda > 420$ nm irradiation, and g) after annealing to 26 K. I, II, or III stands for the product band group. P indicates precursor absorption.

in intensity upon visible irradiation. They increase and decrease repeatedly upon irradiation with visible and UV light, in reverse to group II. Group III absorptions first increase slightly in annealing, but later sharpen and weaken gradually. The Mo–H stretching absorptions at 1844.8 cm^{-1} in Figure 1 and the corresponding group III absorptions in

stretching mode; unfortunately, this band was not observed in the $^{13}\text{CH}_3\text{F}$ experiment.

Group II: The IR spectra in Figures 1, 2, and 3 show that the compound responsible for group II is formed originally in a relatively large amount in the reaction of methyl fluo-

Figures 2 and 3 belong to this group. The Mo–H stretching absorptions of groups II and III are 47.1 cm^{-1} apart, and the distinct vibrational characteristics and behavior upon photolysis and annealing of groups II and III indicate that they are two different photoreversible Mo–H species.

Absorptions of H_2CF , HCF , and CF radicals, fragments of methyl fluoride, result from photolysis by the laser-ablation plume.^[13,14] These absorptions are common to previous investigations with methyl fluoride.^[1–3]

Group I: Following our investigations with Group 4 metal atoms and CH_3F , we expected metal insertion into the C–F bond to form the methyl molybdenum fluoride [$\text{CH}_3\text{–MoF}$]. Accordingly we performed B3LYP calculations on this molecule in quintet and triplet states and found that the quintet state is lower in energy by 19 kcal mol^{-1} . For comparison, the quintet [$\text{CH}_2\text{F–MoH}$] isomer is 50 kcal mol^{-1} higher in energy. The computed [$\text{CH}_3\text{–MoF}$] structure is illustrated in Figure 4. The two strongest infrared absorbing modes are predicted to be at 628.8 cm^{-1} (148 km mol^{-1} ; mostly Mo–F stretching mode) and 448.6 cm^{-1} (23 km mol^{-1} ; mostly C–Mo stretching mode) (Table 2). The 589.3 cm^{-1} absorption shows no ^{13}C shift and a 0.3 cm^{-1} D shift, which is appropriate for the strong absorption computed at 628.8 cm^{-1} with no ^{13}C shift and a 0.2 cm^{-1} D displacement. The weak 441.4 cm^{-1} absorption is tentatively assigned to the C–Mo

Table 1. Frequencies of product absorptions observed from reactions of methyl fluoride with Mo in excess argon.^[a]

Group	CH ₃ F	CD ₃ F	¹³ CH ₃ F	Description
I	589.3	589.0	589.3	Mo–F str
	441.4			C–Mo str
II	1797.7 , 1810.4	1292.1 , 1300.8	1797.7 , 1810.4	Mo–H str
	824.0	737.2	813.9	C=Mo str
	801.0	620.0	787.2	CMoH bend
	673.1, 675.4	531.2	670.6 , 672.7	CH ₂ wag
	640.3, 642.5	656.0, 654.3	639.2, 642.0	Mo–F str
III	1844.8 , 1849.7	1330.5	1844.7 , 1849.5	MoH ₂ str
		1322.1		MoH ₂ str
	769.0	675.0	769.0	MoH ₂ bend
	712.7, 715.8	552.2	708.4, 711.4	MoH ₂ wag
	571.6 , 574.3		571.6 , 574.7	MoH ₂ twist
	555.0, 557.4		554.1, 556.9	MoCH bend

[a] All frequencies are in cm⁻¹. Stronger absorptions are bold. Description gives major coordinate. Abbreviations used: str, stretching; bend, bending; wag, wagging; twist, twisting.

Table 2. Observed and calculated fundamental frequencies of CH₃–MoF in the ground electronic state (⁵A').^[a]

Approximate description	[CH ₃ –MoF]			[CD ₃ –MoF]			[¹³ CH ₃ –MoF]		
	obsd	calcd	<i>I</i>	obsd	calcd	<i>I</i>	obsd	calcd	<i>I</i>
ν_1 A' CH ₃ str		3094.1	3		2290.7	1		3082.9	3
ν_2 A' CH ₃ str		3051.3	9		2240.5	4		3043.5	9
ν_3 A' CH ₃ str		2931.0	11		2111.4	3		2925.8	11
ν_4 A' CH ₃ def		1440.6	2		1046.7	2		1437.2	2
ν_5 A' CH ₃ sciss		1400.2	2		1016.9	2		1397.0	1
ν_6 A' CH ₂ sciss		1186.4	5		927.7	4		1177.3	5
ν_7 A' Mo–F str	589.3	628.8	148	589.0	628.6	146	589.3	628.8	148
ν_8 A'' MoCH bend		594.3	15		504.7	20		585.3	15
ν_9 A'' CH ₃ rock		588.2	15		438.1	9		584.9	13
ν_{10} A' C–Mo str	441.4	448.6	23		371.5	11	— ^[b]	440.0	23
ν_{11} A'' CH ₂ rock		153.8	0		111.7	0		153.7	0
ν_{12} A'' CMoF bend		119.5	5		107.5	5		118.3	5

[a] B3LYP/6-311++G(3df, 3pd)/SDD level. Frequencies and intensities (*I*) are in cm⁻¹ and kmol⁻¹, respectively. Infrared intensities are calculated values. Abbreviations used: str, stretching; bend, bending; def, deformation; sciss, scissoring; rock, rocking. [b] Not observed in lower yield ¹³CH₃F experiment.

ride with Mo atoms in comparison with group III, but the amount decreases on visible irradiation and increases markedly on UV irradiation. In order to help the assignment of the experimental spectrum, we computed the triplet [CHF=MoH₂] and [CH₂=MoHF] isomers, and found that the latter is 56 kcal mol⁻¹ lower in energy. The group II frequencies are compared in Table 3 with frequencies computed for the

triplet methyldene complex [CH₂=MoHF] using the B3LYP functional and both 6-311++G(2d,p) and 6-311++G-(3df,3pd) basis sets, and agreement is quite good for the four strongest infrared absorptions. Note that some frequencies are predicted more accurately with the medium basis set and some with the larger basis set. We also used the BPW91 functional, and these similar frequencies are also listed in Table 3.

The strong 1797.7 cm⁻¹ absorption shifts to 1292.1 cm⁻¹ on deuteration (H/D ratio 1.391:1), which is appropriate for the Mo–H stretching mode. The scale factor (obsd/calcd = 1797.7/1890.1 = 0.951) is comparable to values for other Mo–H species.^[15,16] The 824.0 cm⁻¹ absorption shifts to 813.9 cm⁻¹ with ¹³CH₃F and to 737.2 cm⁻¹ with CD₃F, which are compatible with shifts for the calculated 843.4 cm⁻¹ mode. The very weak 801.0 cm⁻¹ band shifts by 13.8 cm⁻¹ with ¹³CH₃F and 181.0 cm⁻¹ with CD₃F and the harmonic

computed C–Mo–H bending mode at 810.0 cm⁻¹ shifts by 9.0 and 221.8 cm⁻¹. The strong 675.4 cm⁻¹ absorption shifts by 4.8 cm⁻¹ with ¹³CH₃F and 144.2 cm⁻¹ with CD₃F. The predicted 700.5 cm⁻¹ CH₂ out-of-plane wagging mode shifts by 5.7 and 153.8 cm⁻¹ in the harmonic approximation. The strong 642.5 cm⁻¹ band shifts down 0.5 cm⁻¹ with ¹³CH₃F and up 11.8 cm⁻¹ with CD₃F, and the mostly Mo–F stretching mode computed at 644.0 cm⁻¹ has a 0.7 cm⁻¹ redshift and a 18.4 cm⁻¹ blueshift. Clearly mixing is involved between nearby in-plane modes, which causes the uncommon deuterium blueshift. This arises because the in-plane vibrational modes are mixed internal coordinates: The 801.0 and 642.5 cm⁻¹ bands for [CH₂=MoHF] are mostly C–Mo–H bending and Mo–F stretching modes, respectively, but on deuteration the C–Mo–D bending mode shifts below the Mo–F stretching mode. Thus, the [CD₂=MoDF] modes mix differently and cause a blueshift and intensification for the

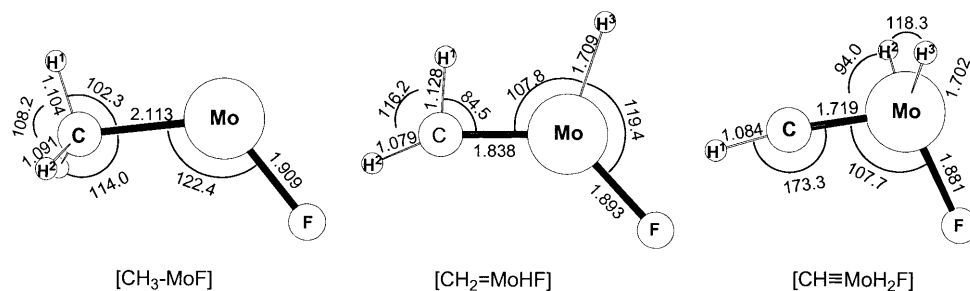


Figure 4. Structures computed for [CH₃–MoF], [CH₂=MoHF], and [CH≡MoH₂F] at the B3LYP/6-311++G(3df, 3pd)/SDD level of theory. Bond distances are in angstroms and bond angles in degrees.

Table 3. Observed and calculated fundamental frequencies of CH₂=MoHF isotopomers in the ground ³A'' electronic state.^[a]

Approximate description	[CH ₂ =MoHF]					[CD ₂ =MoDF]			[¹³ CH ₂ =MoHF]		
	obsd	calcd ^[b]	calcd ^[c]	calcd	<i>I</i>	obsd	calcd	<i>I</i>	obsd	calcd	<i>I</i>
ν_1 A' C–H str		3168.8	(3227.4)	3233.6	7		2397.0	7		3222.4	7
ν_2 A' C–H str		2647.8	(2775.7)	2759.2	5		2007.5	4		2753.0	5
ν_3 A' Mo–H str	1797.7	1873.7	(1893.0)	1890.1	160	1292.1	1344.4	83	1797.7	1890.1	160
ν_4 A' CH ₂ bend		1343.0	(1356.8)	1368.5	23		1066.8	17		1360.1	24
ν_5 A' C=Mo str	824.0	851.7	(835.4)	843.4	78	737.2	739.7	51	813.9	827.5	86
ν_6 A' CMoH bend	801.0	808.8	(803.4)	810.0	13	620.0	598.2	13	787.2	801.1	4
ν_7 A' Mo–F str	642.5	640.9	(634.5)	644.0	113	654.3	662.4	125	642.0	643.3	112
ν_8 A' CH ₂ rock		534.6	(503.2)	525.7	16		397.2	7		522.7	15
ν_9 A' CMoF bend		200.6	(191.9)	195.9	2		179.2	2		194.2	2
ν_{10} A' CH ₂ wag	675.4	679.1	(680.1)	700.5	69	531.2	546.7	46	670.6	694.8	68
ν_{11} A' CH o-o-p bend		442.1	(455.9)	449.0	14		327.8	5		449.0	14
ν_{12} A' MoH o-o-p bend		95.1	(107.3)	94.1	44		71.8	25		93.8	44

[a] B3LYP/6-311++G(3df, 3pd)/SDD level. Frequencies and intensities (*I*) are in cm⁻¹ and kmol⁻¹, respectively. Infrared intensities are calculated values. Abbreviations used: str, stretching; bend, bending; wag, wagging; rock, rocking; o-o-p, out-of-plane. [b] Frequencies computed using BPW91/6-311++GH(3df,3pd)/SDD. [c] Frequencies computed using B3LYP/6-311++G(2d,p)/SDD.

654.3 cm⁻¹ absorption. The overall fit between the five calculated [CH₂=MoHF] and observed group II absorptions and the isotopic counterparts supports our identification of the methyldene complex [CH₂=MoHF].

The [CH₂=MoHF] structure for the planar triplet-state complex illustrated in Figure 4 shows distortion of the CH₂ subgroup and an agostic bonding interaction to stabilize the C=Mo double bond. The agostic H-C-M angle for the Mo methyldene, 86.3°, is considerably smaller than the 96.3° value for the Zr methyldene computed at the same 6-311++G(2d,p)/SDD level of theory.^[3] (This angle decreases to 84.5° with the large basis set, Figure 4.) The BPW91 calculation gave virtually the same structure. Hence, we conclude that [CH₂=MoHF] exhibits a stronger agostic interaction than [CH₂=ZrHF]. The former complex is planar at the metal center whereas the latter is non-planar. These methyldene complexes become distorted in order to stabilize the C=M double bond.^[17–19]

Notice that the agostic hydrogen is *trans* to fluorine in [CH₂=MoHF]. A calculation starting with a *cis*-agostic-hydrogen structure converged to the *trans* form. A single-point calculation for the *cis* structure gave a value 0.7 kcal mol⁻¹ higher in energy than that for the *trans* ground-state energy.

Two other comparisons are of interest. The [CH₂=MoHF] methyldene complex we have characterized in solid argon has a calculated 1.838 Å C=Mo bond length. This bond length may be compared to our computed 1.870 Å value for the simple hydrogen derivative [CH₂=MoH₂] and to X-ray diffraction values ranging from 1.827 to 1.878 Å for several heavily ligated and substituted methyldene complexes discussed by Schrock.^[4] The Mo–H stretching frequency in [CH₂=MoHF] (1797.7 cm⁻¹) is slightly higher than values recently observed for [CH₂=MoH₂] in solid argon (1791.6 and 1759.6 cm⁻¹).^[16]

Group III: The group III absorptions are favored on visible irradiation, and they appear to be formed by rearrangement of [CH₂=MoHF]. Note that the sharp 1844.8 cm⁻¹ band gives way, on deuteration, to two bands at 1322.1 and

1330.5 cm⁻¹. Calculations performed for the [CH≡MoH₂F] molecule revealed the singlet structure shown in Figure 4 and two Mo–H stretching modes within 2 cm⁻¹ (our bandwidth) and two Mo–D stretching modes separated by 9.6 cm⁻¹ with the higher frequency antisymmetric stretching mode stronger by half again. Our 1322.1 and 1330.5 cm⁻¹ group III bands for the deuterated product separated by 8.4 cm⁻¹ are in excellent agreement. Thus, the 1844.8 cm⁻¹ absorption is due to both antisymmetric and symmetric Mo–H₂ stretching modes of [CH≡MoH₂F], and the scale factor (1844.8/1940.1 = 0.951) is the same as that found for [CH₂=MoHF]. The 1330.5 cm⁻¹ band is then due to the antisymmetric Mo–D₂ stretching mode and the 1322.1 cm⁻¹ band to the symmetric Mo–D₂ stretching motion of [CD≡MoD₂F].

The four next strongest [CH≡MoH₂F] modes have been assigned following the computed frequencies (Table 4). The 769.0 cm⁻¹ band shows no ¹³C shift but shifts to 675.0 cm⁻¹ with deuterium substitution, which follows the computed 797.3 cm⁻¹ MoH₂ bending mode. The 715.8 cm⁻¹ absorption shifts 4.4 cm⁻¹ with ¹³C and 163.6 cm⁻¹ with deuterium: The computed MoH₂ wagging mode at 748.2 cm⁻¹ has a 4.8 cm⁻¹ ¹³C shift and a 161.6 cm⁻¹ deuterium shift. The sharp 557.4 cm⁻¹ band shifts 0.5 cm⁻¹ with ¹³C and the 571.6 cm⁻¹ band shows no ¹³C shift, which are both in agreement with the computed Mo–C–H bending mode at 584.6 cm⁻¹ and MoH₂ deformation mode at 599.9 cm⁻¹. Unfortunately, the weak C≡Mo stretching mode computed at 1052 cm⁻¹ is masked by CH₃F precursor absorption. In summary, the excellent agreement between the six computed [CH≡MoH₂F] modes and isotopic variants and the observed group III bands confirms our assignments to [CH≡MoH₂F].

The singlet for the [CH≡MoH₂F] methyldyne is computed to be 5 kcal mol⁻¹ higher in energy than the triplet for the [CH₂=MoHF] methyldene, which is 5 kcal mol⁻¹ higher than the quintet for the [CH₃–MoF] methyl insertion product, and these structure and bonding isomers are interconverted through α-hydrogen transfers on irradiation. Finally, the singlet for the [CF≡MoH₃] isomer is found to have C_{3v},

Table 4. Observed and calculated fundamental frequencies of CH≡MoH₂F isotopomers in the ground ¹A' electronic state.^[a]

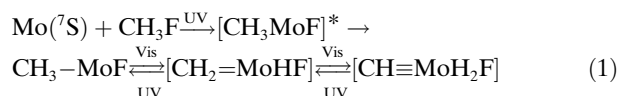
Approximate description	[CH≡MoH ₂ F]			[CD≡MoD ₂ F]			[¹³ CH≡MoH ₂ F]			
	obsd	calcd ^[b]	calcd	<i>I</i>	obsd	calcd	<i>I</i>	obsd	calcd	<i>I</i>
ν_1 A' C–H str		(3201.2)	3212.7	14		2387.4	12		3200.3	14
ν_2 A' MoH ₂ str	1844.8	(1944.9)	1940.1	132	1322.1	1376.5	68	1844.7	1940.1	132
ν_3 A' C≡Mo str		(1052.5)	1052.3	16		1005.8	13		1019.8	16
ν_4 A' MoH ₂ bend	769.0	(794.3)	797.3	89	675.0	681.5	140	769.0	797.1	91
ν_5 A' MoH ₂ wag	715.8	(726.9)	748.2	56	552.2	589.6	4	711.4	743.4	53
ν_6 A' Mo–F str		(646.5)	656.3	36		540.3	17		655.5	25
ν_7 A' MoCH bend	557.4	(563.9)	584.6	101		426.6	39	556.9	583.8	101
ν_8 A' CMoF bend		(260.5)	261.2	5		242.5	5		257.4	5
ν_9 A'' MoH ₂ str	1844.8	(1945.5)	1942.0	204	1330.5	1386.1	108	1844.7	1942.0	204
ν_{10} A'' CH o-o-p bend		(823.4)	841.8	1		669.2	2		833.6	1
ν_{11} A'' MoH ₂ def	571.6	(584.9)	599.9	76		430.2	40	571.6	599.8	76
ν_{12} A'' MoH ₂ rock		(423.4)	423.6	0		317.8	0		423.5	0

[a] B3LYP/6-311++G(3df, 3pd)/SDD level. Frequencies and intensities (*I*) are in cm⁻¹ and km mol⁻¹, respectively. Infrared intensities are calculated values. Abbreviations used: str, stretching; bend, bending; wag, wagging; def, deformation; rock, rocking; o-o-p, out-of-plane. [b] Frequencies computed using 6-311++G(2d, p) basis set.

symmetry, 46 kcal mol⁻¹ higher in energy than [CH≡MoH₂F], and a {C≡MoH₃} subunit similar to that computed for [CH≡MoH₃].^[16]

Three additional comparisons are noteworthy. The [CH≡MoH₂F] methylidyne complex we have observed here has a computed 1.719 Å C≡Mo bond length. This may be compared to the 1.714 Å value computed^[16] for the simple hydrogen compound [CH≡MoH₃], the 1.743 and 1.754 Å measurements for [(AdO)₃Mo≡CR] complexes, and the 1.762 Å bond length determined for [(R¹R²N)₃Mo≡CPPh]⁻.^[20,21] In addition, the strong Mo–H frequency (1844.8 cm⁻¹) for [CH≡MoH₂F] is slightly higher than that for [CH≡MoH₃] (1830.0 cm⁻¹).^[16] Finally, Table 5 compares geometrical parameters and Mulliken charges computed for the three structures. We note that the positive charge on the metal center increases with oxidation state of the metal. This contracts the 4d orbitals and facilitates bonding to carbon.

Reaction mechanisms: Laser-ablated Mo atoms are excited and overcome any energy barrier for insertion to form [CH₃–MoF]. Larger amounts of [CH₂–MoHF] and [CH≡MoH₂F] result from successive α-hydrogen-transfer^[22] reactions in the energized [CH₃MoF]* and [CH₂MoHF]* intermediates first formed. Even though CH₃F has three C–H bonds to compete with one C–F bond for insertion by Mo, the [CH₂F–MoH] product is 56 kcal mol⁻¹ higher in energy, and Mo inserts exclusively into the C–F bond. We employed photochemistry to evolve and group the three major product absorptions from the activation of CH₃F by Mo atoms, shown in Equation (1).



Visible irradiation of the initial sample containing all three products halves the absorption intensity of groups I and II and doubles that of III. Thus, by two successive α-hydrogen transfers, [CH₂–MoHF] and [CH≡MoH₂F] are formed from [CH₃–MoF]. Subsequent ultraviolet irradiation reverses the process, but the amount of [CH₂–MoHF] is tripled and that of [CH₃–MoF] is only doubled as the amount of [CH≡MoH₂F] is decreased slightly, so one hydrogen on Mo is returned to carbon more rapidly than two. The relative energies

Table 5. Geometrical parameters and physical constants of [CH₃–MoF], [CH₂–MoHF], and [CH≡MoH₂F].^[a]

Parameters	[CH ₃ –MoF]	[CH ₂ –MoHF]	[CH≡MoH ₂ F]
<i>r</i> (C–H ¹)	1.106	1.127	1.085
<i>r</i> (C–H ²)	1.093	1.081	–
<i>r</i> (C–Mo)	2.113	1.845	1.725
<i>r</i> (Mo–H ³)	–	1.710	1.701
<i>r</i> (Mo–F)	1.914	1.896	1.884
<i>r</i> (Mo…H)	2.586	2.098	2.805
∠H ¹ CH ²	108.2	116.5	–
∠H ² CH ³	109.5	–	118.3
∠CMoF	122.5	132.2	107.9
∠CMoH ³	–	108.6	93.9
∠H ³ MoF	–	119.2	117.6
∠H ¹ CMo	102.3	86.3	173.0
∠H ² CMo	114.1	157.2	–
Φ(H ¹ CMoH ²)	116.6	0.0	–120.6
Φ(H ¹ CMoF)	180.0	180.0	0.0
symmetry	C _s	C _s	C _s
<i>q</i> (C) ^[b]	–0.94	–0.87	–0.73
<i>q</i> (H ¹) ^[b]	0.12	0.15	0.09
<i>q</i> (H ²) ^[b]	0.14	0.09	–0.09
<i>q</i> (H ³) ^[b]	0.14	–0.13	–0.09
<i>q</i> (Mo) ^[b]	1.02	1.21	1.27
<i>q</i> (F) ^[b]	–0.49	–0.45	–0.46
μ ^[c]	2.93	2.20	1.29
state ^[d]	⁵ A'	³ A''	¹ A'
Δ <i>E</i> ^[e]	58.1	52.8	48.3

[a] Bond lengths and angles are in Å and degree, respectively. Calculated using the 6-311++G(2d, p) basis set. [b] Mulliken atomic charge. [c] Molecular dipole moment in D. [d] Electronic state. [e] Binding energies in kcal mol⁻¹.

of the [CH₃–MoF], [CH₂–MoHF], and [CH≡MoH₂F] bonding isomers are important here, but the relative rates of relaxation of an excited state and α-hydrogen transfer to an isomer excited state are also important: both contribute to the photochemical product yield observed here. The ultraviolet irradiation contains the ⁷S→⁷P resonance absorption of Mo in solid argon,^[23] and this excitation can promote the insertion reaction to form more [CH₃–MoF]. The final UV

irradiation, Figure 1g, does deplete $[\text{CH}\equiv\text{MoH}_2\text{F}]$ and reproduce $[\text{CH}_2=\text{MoHF}]$ and $[\text{CH}_3-\text{MoF}]$. The matrix infrared spectra clearly show that these α -hydrogen transfers are persistent and completely reversible.

Conclusion

Simple molybdenum methyl, carbene, and carbyne complexes, $[\text{CH}_3-\text{MoF}]$, $[\text{CH}_2=\text{MoHF}]$, and $[\text{CH}\equiv\text{MoH}_2\text{F}]$, were formed by reaction of laser-ablated molybdenum atoms with methyl fluoride and isolated in an argon matrix. These molecules provide a persistent photoreversible system through α -hydrogen migration between the carbon and metal atoms; the methyl and carbene complexes are produced by irradiation with UV light (240–380 nm) while the carbyne complex is depleted, and the process reverses on irradiation with visible light ($\lambda > 420$ nm). An absorption at 589.3 cm^{-1} is attributed to the Mo–F stretching mode of $[\text{CH}_3-\text{MoF}]$, which is in fact most stable among the plausible products. DFT frequency calculations provide an accurate model for these new compounds, and structure calculations show that one of the α -hydrogen atoms of the carbene complex is considerably bent toward the metal atom ($\angle\text{HCMo} = 84.5^\circ$), which provides evidence of a strong agostic interaction in the triplet ground state. The calculated $\text{C}\equiv\text{Mo}$ bond length in the carbyne is in the range of triple-bond values in larger ligated methylidyne complexes.

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- [1] H.-G. Cho, L. Andrews, *J. Phys. Chem. A* **2004**, *108*, 6294.
- [2] H.-G. Cho, L. Andrews, *J. Am. Chem. Soc.* **2004**, *126*, 10485.
- [3] H.-G. Cho, L. Andrews, *Organometallics* **2004**, *23*, 4357.
- [4] R. R. Schrock, *Chem. Rev.* **2002**, *102*, 145.
- [5] M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565.

- [6] E. Tran, P. Legzdins, *J. Am. Chem. Soc.* **1997**, *119*, 5071.
- [7] L. Andrews, A. Citra, *Chem. Rev.* **2002**, *102*, 885, and references therein.
- [8] L. Andrews, X. Wang, *J. Am. Chem. Soc.* **2003**, *125*, 11751.
- [9] X. Wang, L. Andrews, *J. Phys. Chem. A* **2003**, *107*, 570.
- [10] L. Andrews, J. M. Dyke, N. Jonathan, N. Keddar, A. Morris, A. Ridha, *J. Phys. Chem.* **1984**, *88*, 2364.
- [11] Gaussian 98 (Revision A.11.4), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2002**.
- [12] Z. L. Xiao, R. H. Hauge, J. L. Margrave, *J. Phys. Chem.* **1992**, *96*, 636 (Mo + H₂).
- [13] M. E. Jacox, D. E. Milligan, *J. Chem. Phys.* **1969**, *50*, 3252.
- [14] J. I. Raymond, L. Andrews, *J. Phys. Chem.* **1971**, *75*, 3235.
- [15] I. Bytheway, M. W. Wong, *Chem. Phys. Lett.* **1998**, *282*, 219.
- [16] H.-G. Cho, L. Andrews, *J. Am. Chem. Soc.* **2005**, *127*, 8226.
- [17] W. Scherer, G. S. McGrady, *Angew. Chem.* **2004**, *116*, 1816; *Angew. Chem. Int. Ed.* **2004**, *43*, 1782.
- [18] a) O. Eisenstein, Y. Jean, *J. Am. Chem. Soc.* **1985**, *107*, 1177; b) E. Clot, O. Eisenstein, in "Agostic Interactions from a Computational Perspective", *Structure and Bonding, Computational Inorganic Chemistry* (Eds.: N. Kaltzoyannis, J. E. McGrady), Springer, Heidelberg, **2004**, pp. 1–36.
- [19] G. Ujaque, A. C. Cooper, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1998**, *120*, 361.
- [20] Y. C. Tsai, P. L. Diaconescu, C. C. Cummins, *Organometallics* **2000**, *19*, 5260.
- [21] T. Agapie, P. L. Diaconescu, C. C. Cummins, *J. Am. Chem. Soc.* **2002**, *124*, 2412.
- [22] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, **2001**, p. 190.
- [23] M. J. Pellin, D. M. Gruen, T. Fisher, T. Foosnaes, *J. Chem. Phys.* **1983**, *79*, 5871.

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