

Figure S1. IR spectra in the regions of 915-895, and 520-490 cm⁻¹ for laser-ablated La atoms co-deposited with CD₃F in excess argon at 8 K. (a) La + 0.2% CD₃Cl in Ar co-deposited for 1 h. (b) After broad-band photolysis with a filter ($\lambda > 420$ nm). (c) After broad-band photolysis with a filter ($240 < \lambda < 380$ nm). (d) After annealing to 28 K. (e) After annealing to 32 K. **i** and **m** denote the product absorption groups. **P** indicates absorption by precursor.

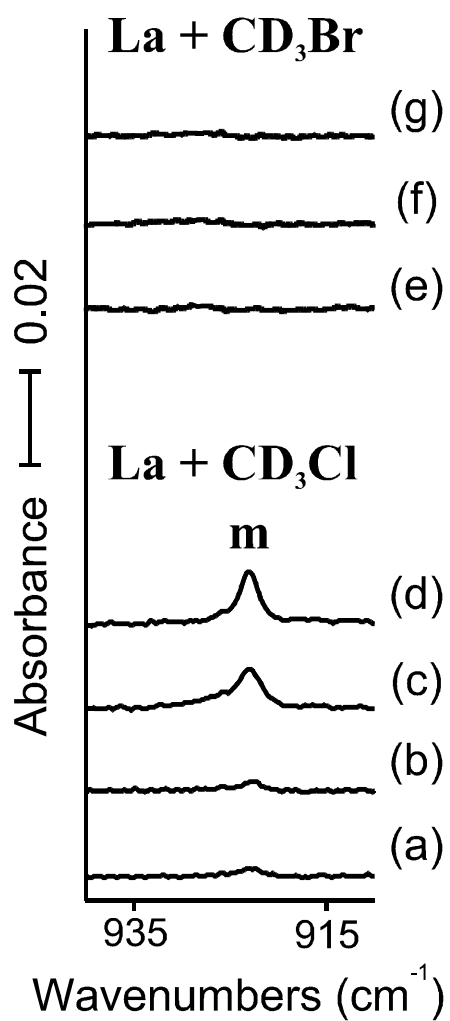


Figure S2. IR spectra in the regions of 940-910 cm⁻¹ for laser-ablated La atoms co-deposited with CD₃Cl (a-d) and CD₃Br (e-g) in excess argon at 8 K and their variation. (a) La + 0.2% CD₃Cl in Ar co-deposited for 1 h. (b) After broad-band photolysis with a filter ($\lambda > 420$ nm). (c) After broad-band photolysis with a filter ($240 < \lambda < 380$ nm). (d) After annealing to 28 K. (e) La + 0.2% CD₃Br in Ar co-deposited for 1 h. (f) After broad-band photolysis with a filter ($\lambda > 420$ nm). (g) After broad-band photolysis with a filter ($240 < \lambda < 380$ nm). **m** denotes the product absorption group.

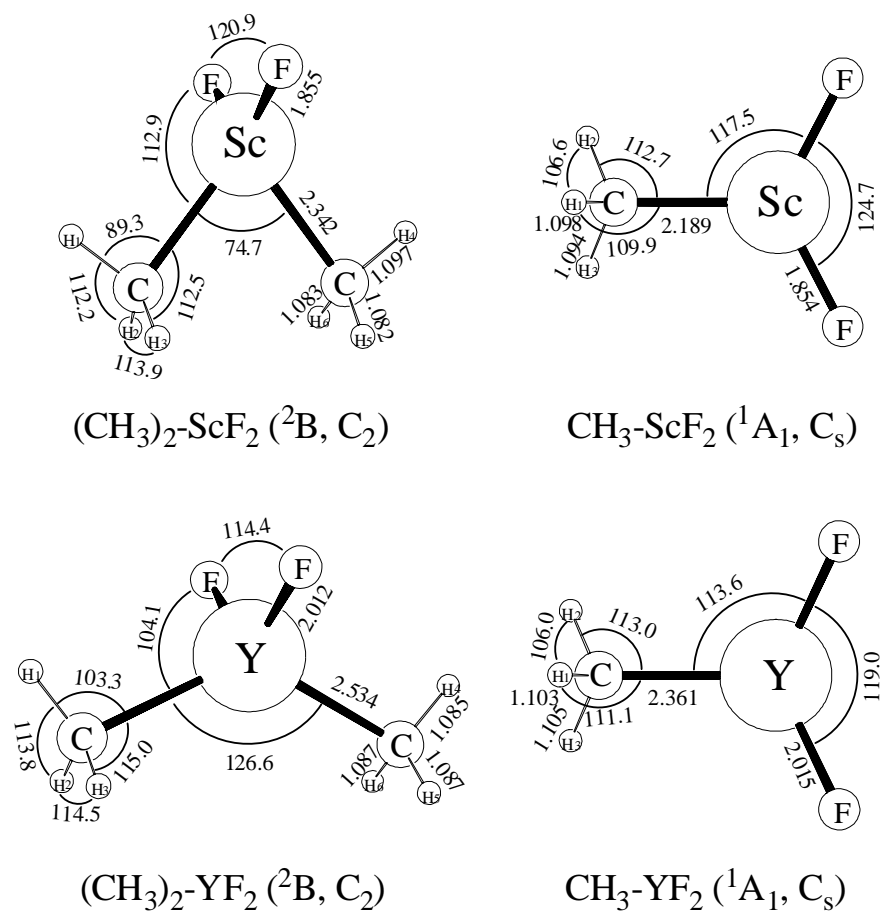


Figure S3. The optimized molecular structures of $(\text{CH}_3)_2\text{MF}_2$ and $\text{CH}_3\text{-MF}_2$ calculated using B3LYP and the 6-311++G(3df,3pd) basis set. The all electron basis is used for Sc, whereas the SDD pseudopotential and basis are used for Y. The bond lengths and angles are in Å and degree. The electronic states and molecular symmetry are shown below the structure. They might be responsible for the observed **h** absorptions.

Table S1: Harmonic Frequencies of CH₃-ScF and CH₃-YF in the Ground ²A' Electronic States

Calculated with the B3LYP and BPW91 Density Functionals^a

Approximate Description	CH ₃ -ScF				CH ₃ -YF			
	B3LYP		BPW91		B3LYP		BPW91	
	Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.
A' CH ₃ str.	3079.8	9	3039.8	7	3067.7	12	3027.6	10
A' CH ₃ str.	2974.8	6	2920.9	4	2963.9	11	2912.9	9
A' CH ₃ bend	1419.9	0	1369.4	0	1422.2	0	1374.1	0
A' CH ₃ deform	1139.0	11	1089.9	11	1141.7	15	1097.0	13
A' Sc-X str.	667.8	171	663.2	148	592.4	110	588.9	100
A' C-Sc str.	510.3	65	505.8	58	465.9	38	462.3	38
A' CH ₃ rock	414.8	21	399.9	17	397.6	15	389.6	12
A' CScX bend	133.2	6	136.7	4	113.8	6	115.7	5
A'' CH ₃ str.	3038.7	7	2992.4	7	3022.9	8	2980.2	7
A'' CH ₃ bend	1430.1	10	1381.8	13	1431.9	10	1385.5	11
A'' CH ₃ rock	379.7	7	351.3	3	358.8	2	340.6	1
A'' CH ₃ distort	4.2	1	10.7	1	2.5	0	15.0	0

^aFrequencies and intensities computed with B3LYP or BPW91/6-311++G(3df, 3pd), and all electron basis is used for Sc. Frequencies and intensities are in cm⁻¹ and km/mol. Both CH₃-ScF and CH₃-YF have also a C_s (planar) structure. The symmetry notations are based on the C_s structure.

Table S2: Harmonic Frequencies of CH₂-ScHF and CH₂-YHF in the Doublet Ground Electronic States Calculated with the B3LYP and BPW91 Density Functionals^a

Approximate Description	CH ₂ -ScHF				CH ₂ -YHF			
	B3LYP		BPW91		B3LYP		BPW91	
	Freq.	Int.	Freq.	Int.	Freq.	Int.	Freq.	Int.
A' CH str.	3109.8	13	3052.5	14	3094.6	19	3040.2	19
A' CH str.	3033.0	8	2970.6	10	3023.9	18	2965.0	20
A' Sc-H str.	1551.3	511	1512.8	482	1445.5	494	1421.4	472
A' CH ₂ scis.	1369.2	2	1323.8	2	1375.1	3	1329.5	2
A' Sc-X str.	699.3	326	687.2	301	595.9	254	589.0	233
A' C-Sc str.	572.1	99	559.2	86	587.3	82	561.8	70
A' CScH bend	492.6	19	484.4	18	455.8	20	447.8	22
A' CH ₂ rock	375.0	9	361.6	7	356.0	20	352.1	16
A' CScX bend	145.1	2	144.4	2	143.1	116	162.5	71
A'' CH ₂ wag	609.6	82	575.7	76	507.3	131	499.8	121
A'' CH ₂ twist	209.6	36	199.2	32	196.4	47	190.1	131
A'' ScH OOP bend	99.7	290	73.8	284	83.2	163	98.4	85

^aFrequencies and intensities computed with B3LYP or BPW91/6-311++G(3df, 3pd), and all electron basis is used for Sc. Frequencies and intensities are in cm⁻¹ and km/mol. CH₂-ScHF has a C_s (planar) structure, but CH₂-YHF has a C₁ structure. The symmetry notations are based on the C_s structure.

Table S3: Geometrical Parameters and Physical Constants Calculated for CH₃-MX from reactions of Group 3 metals with Methyl Halide^a

Parameters	CH ₃ -ScF	CH ₃ -ScCl	CH ₃ -ScBr	CH ₃ -YF	CH ₃ -YCl	CH ₃ -YBr	CH ₃ -LaF	CH ₃ -LaCl	CH ₃ -LaBr
r(C-H ₁) ^b	1.092	1.092	1.093	1.095	1.093	1.093	1.093	1.093	1.093
r(C-H ₂)	1.097	1.097	1.097	1.097	1.098	1.099	1.100	1.100	1.099
r(C-H ₃)	1.097	1.097	1.097	1.097	1.098	1.099	1.100	1.100	1.099
r(C-M)	2.169	2.166	2.167	2.333	2.321	2.319	2.441	2.417	2.412
r(M-X)	1.839	2.307	2.471	1.992	2.463	2.623	2.082	2.583	2.753
r(M...H ₁)	2.780	2.789	2.790	2.909	2.951	2.960	3.093	3.064	3.055
∠H ₁ CH ₂	108.0	107.8	107.8	107.2	107.4	107.4	107.5	107.6	107.7
∠H ₂ CH ₃	107.7	107.8	107.8	107.1	107.1	107.0	107.2	107.4	107.6
∠CMX	114.3	120.8	122.3	115.7	115.8	117.4	109.7	110.6	111.2
∠H ₁ CM	112.8	113.6	113.7	110.9	114.8	115.7	116.9	116.4	116.1
∠H ₂ CM	110.1	109.8	109.9	112.1	109.9	109.5	108.6	108.7	108.8
Φ(H ₁ CMH ₃)	120.7	120.8	120.8	119.8	121.2	121.5	121.9	121.7	121.6
Φ(H ₁ CMX)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mol. Sym.	C _s	C _s	C _s	C _s	C _s	C _s	C _s	C _s	C _s
Q(C) ^c	-0.45	-0.44	-0.47	-0.68	-0.67	-0.68	-0.46	-0.45	-0.47
Q(H ₁)	0.00	0.01	0.01	0.00	0.00	-0.02	0.05	0.05	0.05
Q(H ₂)	0.01	0.02	0.01	-0.01	-0.01	0.00	0.01	0.00	0.01
Q(H ₃)	0.01	0.02	0.01	-0.01	-0.01	0.00	0.01	0.00	0.01
Q(X)	-0.51	-0.49	-0.40	-0.54	-0.76	-0.67	-0.65	-0.44	-0.37
Q(M)	0.93	0.89	0.83	1.23	1.44	1.37	1.056	0.84	0.76
S(C) ^d	-0.054	-0.041	-0.026	-0.041	-0.037	-0.023	-0.119	-0.136	-0.110
S(H ₁)	0.018	0.018	0.015	0.030	0.031	0.027	-0.015	-0.009	-0.011
S(H ₂)	0.009	0.006	0.006	0.033	0.038	0.033	0.023	0.024	0.015
S(H ₃)	0.009	0.006	0.006	0.033	0.038	0.033	0.023	0.024	0.015
S(X)	-0.026	0.006	0.045	-0.017	0.024	0.048	0.062	-0.100	-0.097
S(M)	1.044	1.005	0.954	0.961	0.907	0.82	1.026	1.196	1.189

μ^e	2.94	3.64	3.81	2.93	3.45	3.53	3.43	4.29	4.47
State ^f	² A'	² A'	² A'	² A'	² A'	² A'	² A'	² A'	² A'
ΔE^g	94.1	86.1	79.2	99.5	91.7	90.6	110.0	102.3	101.3

^aCalculations are carried out with B3LYP/6-311++G(3df, 3pd), and SDD core potential and basis set are used for Y and La while all electron basis is used for other atoms including Sc. ^bBond lengths and angles are in Å and degrees. ^cMulliken atomic charge. ^dElectron spin density. ^eMolecular dipole moment in D. ^fElectronic state. ^gBinding energies with respect to M + CH₃X in kcal/mol.

Table S4: Geometrical Parameters and Physical Constants Calculated for CH₂-MHX from reactions of Group 3 metals with Methyl Halide^a

Parameters	CH ₂ -ScHF	CH ₂ -ScHCl	CH ₂ -ScHBr	CH ₂ -YHF	CH ₂ -YHCl	CH ₂ -YHBr	CH ₂ -LaHF	CH ₂ -LaHCl	CH ₂ -LaHBr
r(C-H ₁) ^b	1.095	1.094	1.094	1.095	1.095	1.095	1.097	1.097	1.097
r(C-H ₂)	1.092	1.092	1.092	1.093	1.093	1.093	1.095	1.095	1.095
r(C-M)	2.156	2.141	2.138	2.331	2.318	2.316	2.455	2.431	2.428
r(M-H ₃)	1.836	1.820	1.817	2.003	1.989	1.988	2.134	2.111	2.108
r(M-X)	1.846	2.317	2.479	2.011	2.490	2.650	2.105	2.617	2.789
r(M...H ₁)	2.902	2.883	2.879	3.082	3.066	3.059	3.204	3.172	3.171
∠H ₁ CH ₂	108.9	109.3	109.4	108.0	108.2	108.2	107.7	108.1	108.2
∠CMH ₃	118.9	116.1	115.4	115.5	115.0	115.2	110.1	109.8	110.6
∠CMX	120.0	122.4	122.5	116.9	120.6	122.2	111.3	112.7	114.1
∠H ₃ MX	121.0	121.5	122.0	118.4	121.0	122.6	113.3	114.4	114.6
∠H ₁ CM	123.1	122.7	122.6	124.1	123.8	123.5	124.3	123.5	123.7
∠H ₂ CM	128.1	128.1	128.0	127.9	128.0	128.3	127.9	128.3	128.1
Φ(H ₁ CMH ₃)	0.0	0.0	0.0	19.3	9.5	0.0	30.4	23.4	21.7
Φ(H ₁ CMX)	180.0	180.0	180.0	165.7	168.9	180.0	157.0	152.1	152.7
Mol. Sym.	C _s	C _s	C _s	C ₁	C ₁	C _s	C ₁	C ₁	C ₁

Q(C) ^c	-0.53	-0.49	-0.49	-0.75	-0.72	-0.73	-0.63	-0.63	-0.61
Q(H ₁)	0.07	0.06	0.07	0.07	0.06	0.07	0.05	0.05	0.05
Q(H ₂)	0.06	0.08	0.07	0.05	0.06	0.05	0.04	0.05	0.05
Q(H ₃)	-0.36	-0.34	-0.34	-0.45	-0.42	-0.43	-0.48	-0.48	-0.47
Q(X)	-0.54	-0.47	-0.35	-0.57	-0.74	-0.68	-0.63	-0.57	-0.49
Q(M)	1.304	1.15	1.05	1.65	1.76	1.72	1.64	1.58	1.46
S(C) ^d	0.944	0.940	0.936	0.955	0.949	0.946	0.961	0.951	0.948
S(H ₁)	-0.027	-0.030	-0.030	-0.026	-0.026	-0.026	-0.024	-0.024	-0.024
S(H ₂)	-0.026	-0.024	-0.024	-0.023	-0.023	-0.023	-0.022	-0.021	-0.021
S(H ₃)	0.001	0.0007	0.0008	0.001	0.002	0.002	0.006	0.004	0.004
S(X)	-0.0009	0.0005	-0.0013	0.001	0.002	0.001	0.001	0.003	0.004
S(M)	0.109	0.112	0.117	0.092	0.095	0.100	0.077	0.087	0.089
μ ^e	1.47	2.00	2.10	2.92	2.50	2.02	4.51	4.82	4.80
State ^f	² A''	² A''	² A''	² A	² A	² A''	² A	² A	² A
ΔE ^g	70.0	60.9	59.1	73.0	66.3	65.4	82.8	75.9	75.2

^aCalculations are carried out with B3LYP/6-311++G(3df, 3pd), and SDD core potential and basis set are used for Y and La while all electron basis is used for all other atoms including Sc. CH₂-ScHX and CH₂-LaHX have a planar (C_s) and C₁ structure, respectively, at all level of theory used in this study, whereas CH₂-YHX has a C₁ structure with B3LYP and BPW91, but a planar (C_s) structure with MP2 and CCSD. ^bBond lengths and angles are in Å and degrees. ^cMulliken atomic charge. ^dElectron spin density. ^eMolecular dipole moment in D. ^fElectronic state. ^gBinding energies with respect to M + CH₃X in kcal/mol.