Forming Trifluoromethylmetallates: Competition Between Decarboxylation and C-F bond Activation of Group 11 Trifluoroacetate complexes, $[CF_3CO_2ML]^-$

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Supporting Information

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Supporting Information:

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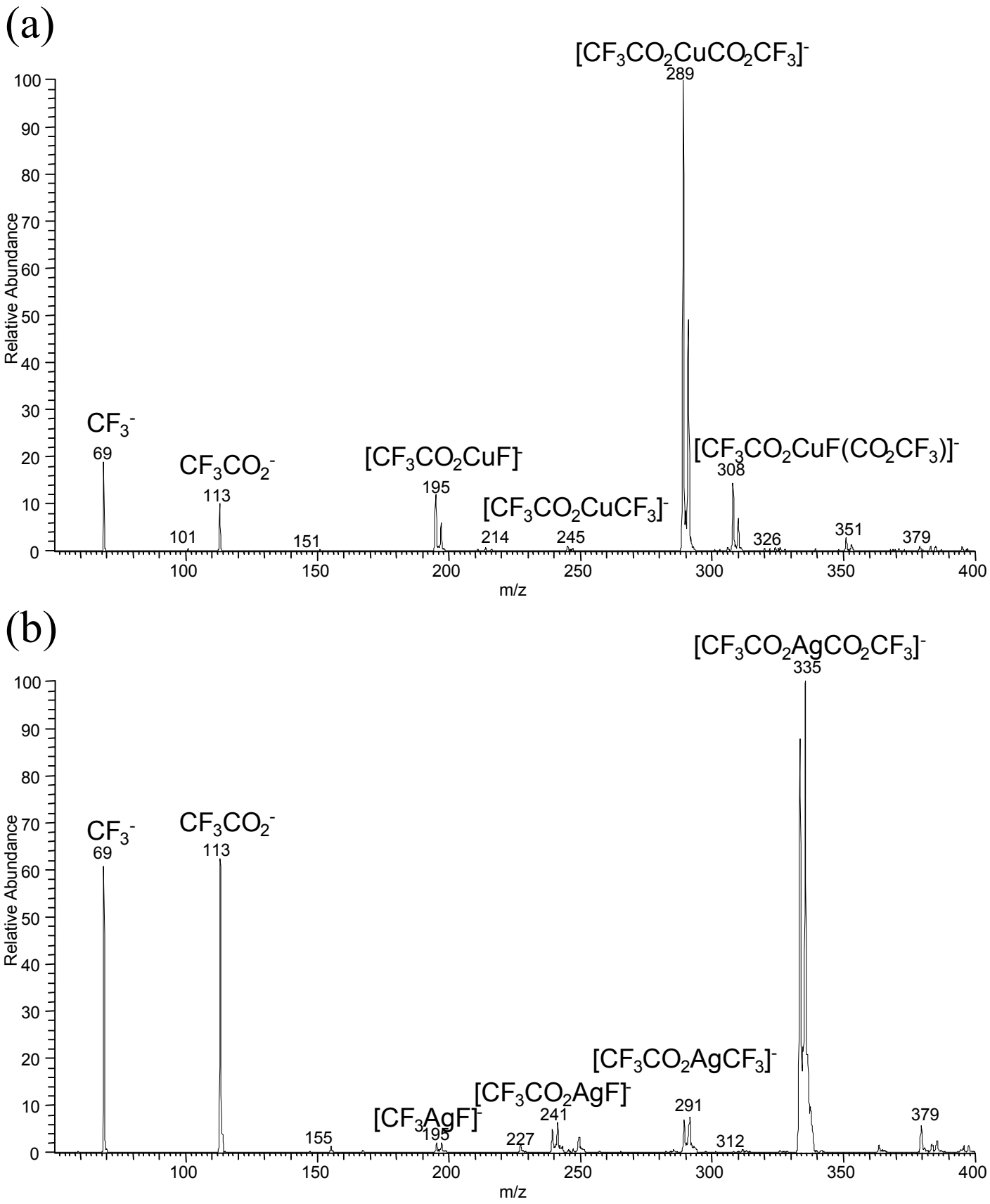


Figure S1. 3D quadrupole ion trap MS^1 mass spectra: electrospray ionization of methanolic (a) copper(II) acetate and trifluroacetic acid; (b) silver(I) acetate and trifluoracetic acid; (c) gold(III) acetate and trifluoracetic acid.

(c)

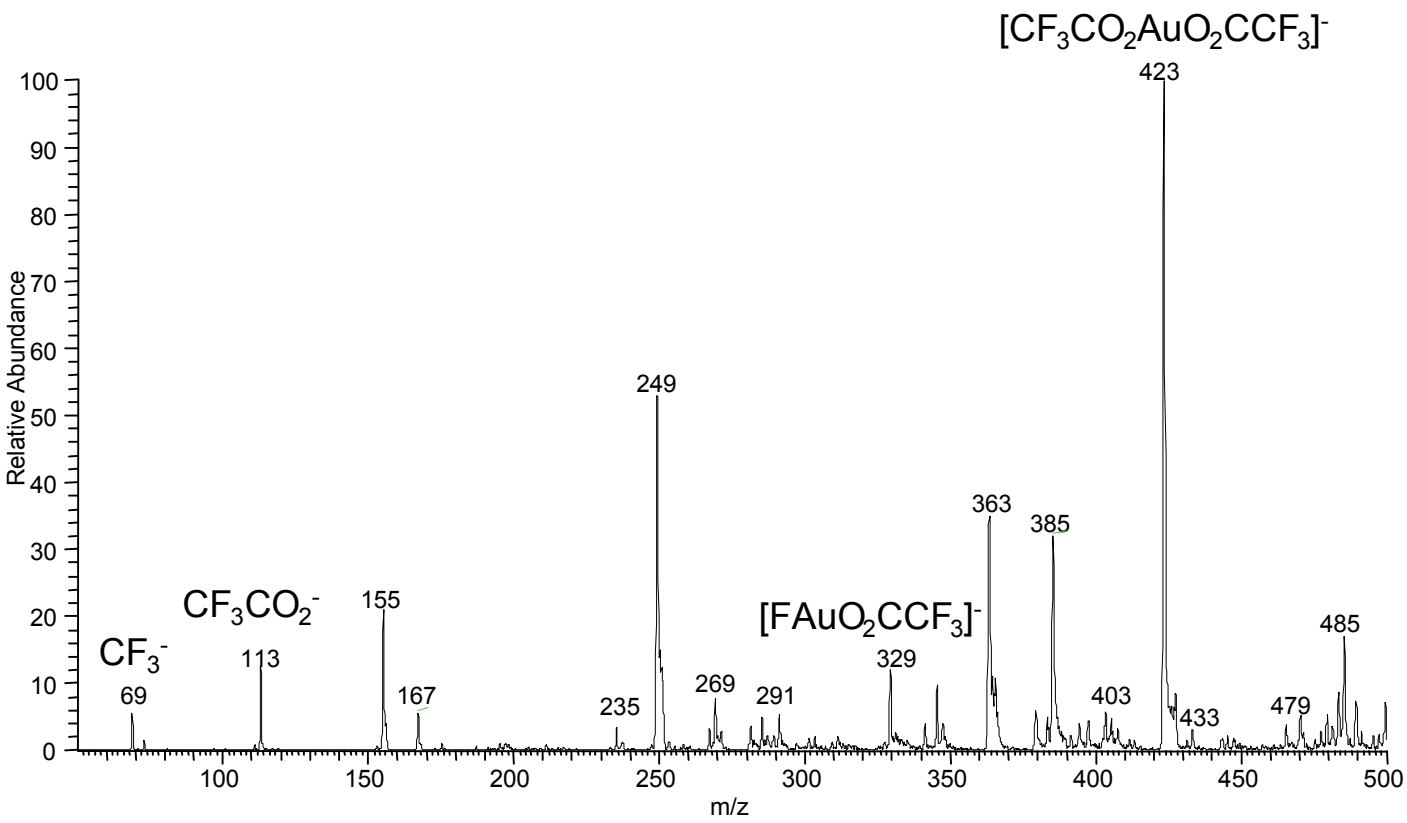


Figure S1. 3D quadrupole ion trap MS^1 mass spectra: electrospray ionization of methanolic (a) copper(II) acetate and trifluroacetic acid; (b) silver(I) acetate and trifluoracetic acid; (c) gold(III) acetate and trifluoracetic acid.

(a)	Bond length/angle	Calc. B3LYP (CF_3CO_2H)	Exp. [1] (CF_3CO_2H)	Calc. MP2 (CF_3CO_2H)	Calc. M06 (CF_3CO_2H)
	C-F	1.34	1.325	1.34	1.32
	C-C	1.55	1.546	1.54	1.54
	C=O	1.20	1.192	1.21	1.20
	C-O	1.34	1.353	1.34	1.33
	C-C=O	123.6	126.8	123.8	123.9
	C-C-O	109.9	111.1	109.3	109.4
	C-C-F	110.4	109.5	110.3	110.6
	F-C-F	108.6	109.4	108.6	108.8

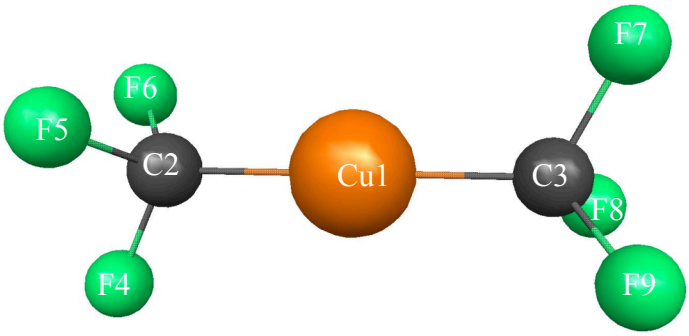
1. Maagdenberg, A. A. J. *Journal of Molecular Structure* 1977, *41*, 61-65.

	Bond length/angle	Calc. B3LYP ($[CF_3CO_2ML]^-$)[1]	Exp.	Calc. MP2 ($[CF_3CO_2ML]^-$)[1]	Calc. M06 ($[CF_3CO_2ML]^-$)[1]
(b)	Cu-O	1.87, 1.90, 1.87	1.842(4)[2]	1.84, 1.85, 1.85	1.86,1.89, 1.86
(c)	Ag-O	2.14, 2.14, 2.13	2.450(4)[3]	2.17, 2.14, 2.16	2.15, 2.15, 2.14
(d)	Au-O	2.06, 2.11, 2.07	2.08(2)[4]	2.05, 2.09, 2.06	2.08, 2.13, 2.08

1. For L = CF_3CO_2, CF_3 and F respectively
2. McReynolds, K. A.; Lewis, R. S.; Ackerman, L. K. G.; Dubinina, G. G.; Brennessel, W. W.; Vicic, D. A. *Journal of Fluorine Chemistry* 2010,*131*, 1108-1112.
3. Effendy; Marchetti, F.; Pettinari, C.; Pettinari, R.; Skelton, B. W.; White, A. H. *Inorganica Chimica Acta* 2007, *360*, 1451-1465. (Average of 8 structures)
4. Preisenberger, M.; Schier, A.; Schmidbaur, H. *Journal of the Chemical Society, Dalton Transactions* 1999, 1645-1650.

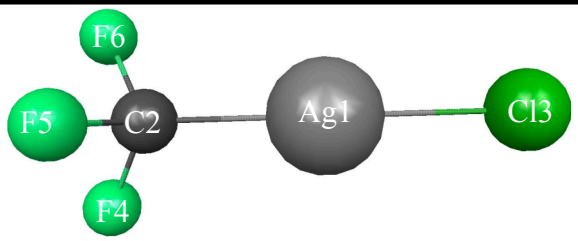
Figure S2. Structural comparison (a) trifluoroacetic acid; monodentate trifluoracetate complexed via oxygen to (b) Cu ; (c) Ag and (d) Au.

(a)



Bond length/angle	Calc. B3LYP	Exp.[1]	Calc. MP2	Calc. M06
C2-Cu1 C3-Cu1	1.95, 1.95	1.970(6), 1.959(5)	1.91	1.94
F-C	1.40	1.437(8), 1.419(7), 1.403(7)	1.40	1.38
C2-Cu1-C3	180	180.0(3)	180	179.9

(b)

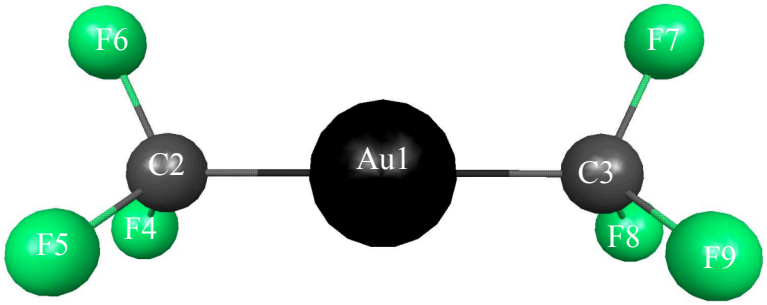


Bond length/angle	Calc. B3LYP	Exp.[2]	Calc. MP2	Calc. M06
C2-Ag1	2.12	2.072	2.12	2.14
Cl3-Ag1	2.38	2.339	2.36	2.37
C2-Ag1-Cl3	180	176.7	180	179.9
F-C2	1.40,1.40,1.40	1.340, 1.375, 1.375	1.40, 1.40, 1.40	1.38

1. Dubinina, G. G.; Ogikubo, J.; Vicic, D. A., *Organometallics* **2008,** 27, (23), 6233-6235.
2. Tyrra, W.; Naumann, D., *Journal of Fluorine Chemistry* **2004,** 125, (6), 823-830.

Figure S3. Crystal structure comparison: (a) $[CF_3CuCF_3]^-$; (b) $[CF_3AgCl]^-$ and (c) $[CF_3AuCF_3]^-$

(c)

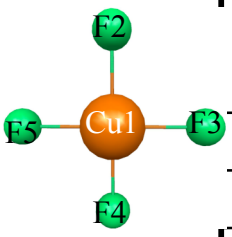


Bond length/angle	Calc. B3LYP	Exp.[3]	Calc. MP2	Calc. M06
C2-Au1 C3-Au1	2.09, 2.09	2.059(6), 2.072(6)	2.07, 2.07	2.10
F-C	1.39		1.40	1.38
C2-Au1-C3	180	178.9(2)°	180	180

3. Zopes, D.; Kremer, S.; Scherer, H.; Belkoura, L.; Pantenburg, I.; Tyrra, W.; Mathur, S. *European Journal of Inorganic Chemistry*, *2011*, 273-280

Figure S3. Crystal structure comparison: (a) $[CF_3CuCF_3]^-$; (b) $[CF_3AgCl]^-$ and (c) $[CF_3AuCF_3]^-$

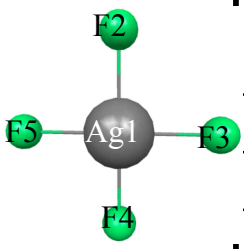
(a)



Bond length(Å)/angle	B3LYP	Exp.[1]	MP2	Calc. M06	Previous theory[2]
Cu1-F	1.77	1.73	1.75	1.76	1.727
F2-Cu-F3	90º		90º	90º	
dihedral	180º		180º	180º	

1. Fleischer, T.; Hoppe, R., *Zeitschrift Fur Anorganische Und Allgemeine Chemie* **1982,** 492, (9), 76-82.
2. Seth, M.; Cooke, F.; Schwerdtfeger, P.; Heully, J.-L.; Pelissier, M., *The Journal of Chemical Physics* **1998,** 109, (10), 3935-3943

(b)



Bond length(Å)/angle	B3LYP	Exp.[1]	MP2	Calc. M06	Previous theory[2]
Ag1-F	1.94	1.889(2)	1.94	1.94	1.898
F2-Ag-F3	90º		90º	90º	
dihedral	180º		180º	180º	

1. Lutar, K.; Milicev, S.; Zemva, B.; Muller, B. G.; Bachmann, B.; Hoppe, R., *European Journal of Solid State and Inorganic Chemistry* **1991,** 28, (6), 1335-1346.
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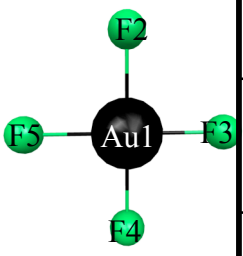
(c)



Bond length(Å)/angle	B3LYP	Exp.[1,2]	MP2	Calc. M06	Previous theory[3]
Au1-F	1.96	1.95(2)[1] , 1.915(3)[2], 1.890(7)[2], 1.946(7)[2], 1.965(6)[2], 1.893(8)[2],	1.95	1.96	1.919
F2-Au-F3	90º	87.1(2)º[1], 92.9(2)º[1]	90º	90º	
dihedral	180º		180º	180º	

1. Edwards, A. J.; Jones, G. R.,.8. *Journal of the Chemical Society a -Inorganic Physical Theoretical* **1969**, (13), 1936
2. Engelmann, U.; Muller, B. G., *Zeitschrift Fur Anorganische Und Allgemeine Chemie* **1991,** 598, (7-8), 103-110.
3. Seth, M.; Cooke, F.; Schwerdtfeger, P.; Heully, J.-L.; Pelissier, M., *The Journal of Chemical Physics* **1998,** 109, (10), 3935-3943

Figure S4. Structure comparison: (a) $[CuF_4]^-$ (b) $[AgF_4]^-$; (c) $[AuF_4]^-$; (d) [CuF] (e) [AgF]; (f) [AuF].

(d)

Bond length(Å)/angle	B3LYP	Exp.[1]	MP2	Calc. M06
Cu1-F	1.77	1.745	1.76	1.75

1. Huber K.P. Herzberg G, Molecular Spectrum and molecular structure constants of diatomic molecules. Van Nostrand New York 1974

(e)

Bond length(Å)/angle	B3LYP	Exp.[2]	MP2	Calc. M06
Ag1-F	2.01	1.983	2.03	2.01

2. Hoeft, J; Lovas, F.J. Tiemann, E Torring T.Z. Naturfosch 1970 25a 35

(f)

Bond length(Å)/angle	B3LYP	Exp.[3,4]	MP2	Calc. M06
Au1-F	1.98	1.918449(5), 1.91844306(12)	1.97	1.99

3. Evans, C. J.; Gerry, M. C. L. *Journal of the American Chemical Society* **2000**, *122*, 1560-1561.
4. Okabayashi, T.; Nakaoka, Y.; Yamazaki, E.; Tanimoto, M. *Chemical Physics Letters* **2002**, *366*, 406-411.

Figure S4. Structure comparison: (a) $[CuF_4]^-$ (b) $[AgF_4]^-$; (c) $[AuF_4]^-$; (d) [CuF] (e) [AgF]; (f) [AuF].

	Cu EA		Ag EA		Au EA	
	Exp	Calc B3LYP	MRCI/SA-CASSCF	Calc B3LYP	Exp	Calc B3LYP
MF_2	-	3.69	2.881[4]	4.68	-	4.92
MCl_2	4.35±0.05[1]	4.28	5.245[4]	4.94	4.60±0.07[3]	4.73
MBr_2	4.35±0.05[1]	4.24	6.349[4]	4.73	4.46±0.07[3]	4.55
MI_2	4.256±0.010[2]	4.20	6.739[4]	4.51	4.226±0.010[2] , 4.18± 0.07[3]	4.42

1. Wang, X. B.; Wang, L. S.; Brown, R.; Schwerdtfeger, P.; Schroder, D.; Schwarz, H. *J. Chem. Phys.* **2001**, *114*, 7388-7395.
2. Wang, Y.-L.; Wang, X.-B.; Xing, X.-P.; Wei, F.; Li, J.; Wang, L.-S. *J. Phys. Chem. A*, *114*, 11244-11251.
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4. No experimental values exist thus far for AgX_2^-, therefore comparison is made with previous calculation: Mishra, S. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3987-3991.

Figure S5. Comparison of experimental and calculated adiabatic electron affinities, Ea, for MX_2 (eV).

	Cu	Ag	Au
$[CF_3CO_2MO_2CCF_3]$	4.24	5.13	5.26
$[CF_3CO_2MCF_3]$	4.42	4.77	5.09
$[CF_3CO_2MF]$	4.07	4.99	5.06
$[CF_3MCF_3]$	4.40	4.79	4.86
$[CF_3MF]$	4.15	4.55	4.98
[FMF]	3.69	4.68	4.92
$[CF_3CO_2M]$	2.02	2.20	3.03
$[CF_3M]$	1.33	1.50	1.68
[FM]	1.51	1.73	2.42

CF_3CO_2	Neutral not stable
CF_3	1.97
F	-3.52

Figure S6. B3LYP predicted adiabatic electron affinities, Ea (eV), relevant to this report.

Summary of B3LYP/SDD6-31+G(d) predicted Gibbs Free energies (in eV) for unimolecular reactions of $[CF_3CO_2ML]^-$. Values in parenthesis are thermicities of separated products.

	Reaction type	M =		
L =		Cu	Ag	Au
CF_3CO_2	Decarboxylation **TS1** (eq 11)	1.99 (-0.20)	1.73 (-0.40)	2.20 (-1.12)
	Secondary α-fluoride **TS2**/Metal(III) Int. /carbene elim. **TS3** (eq 15)	1.14, 0.89, *a*, (0.80)	1.50, *b*, *a*, (0.91)	1.43, 0.88, *a*, (0.84)
	Trifluoroactetate loss[c] (eq 13a)	(2.07)	(1.54)	(2.04)
	Rearrangement **TS4** (eq 16)	1.69 (1.43)	1.39 (1.20)	1.65 (1.59)
	Lactone **TS6** (eq 18)	2.22 (1.73)	2.29 (1.83)	2.26 (1.77)
	Concerted **TS5** (eq 17)	1.81 (0.80)	-	1.91 (0.84)
	Step-wise **TS7** (eq 19)	-	1.73[d], 1.17 (0.91)	-
CF_3	Primary α-fluoride **TS2**/Metal(III) Int. /carbene elim. **TS3** (eq 14)	1.34, 1.09, *a,* (1.01)	1.90, *b, a,* (1.31)	2.55, 2.00, *a,* (1.96)
	Decarboxylation **TS1** (eq 11)	1.83 (-0.31)	1.77 (-0.25)	2.08 (-0.60)
	Secondary α-fluoride **TS2**/Metal(III) Int./carbene elim. **TS3** (eq 15)	1.21, 0.95, 1.25, (0.69)	1.83, 1.64, *a*, (0.95)	1.90, 1.57, 1.80, (0.87)
	Trifluoroactetate loss[c] (eq 13a)	(1.53)	(1.32)	(1.45)
	Rearrangement **TS4** (eq 16)	1.22 (1.19)	*e*, (1.08)	1.41 (1.33)
	Lactone **TS6** (eq 18)	2.03 (1.62)	2.24 (1.88)	2.24 (1.80)
	Concerted **TS5** (eq 17)	1.53 (0.69)	-	1.76 (0.87)
	Step-wise **TS7** (eq 19)	-	1.71[d], 1.23 (0.95)	-
F	Decarboxylation **TS1** (eq 11)	1.97 (-0.31)	1.72 (-0.36)	2.08 (-1.09)
	Secondary α-fluoride **TS2**/ Metal(III) int. /carbene elim. **TS3** (eq 15)	1.26, 1.09, 1.28, (0.97)	1.67, 1.65, *a*, (1.09)	1.42, 1.07, 1.66, (0.91)
	Trifluoroactetate loss[c] (eq 13a)	(1.80)	(1.40)	(1.79)
	Rearrangement **TS4** (eq 16)	1.35 (1.27)	1.29 (1.11)	1.48 (1.40)
	Lactone **TS6** (eq 18)	2.21 (1.89)	2.35 (2.02)	2.27 (1.84)
	Concerted **TS5** (eq 17)	1.75 (0.97)	-	1.81 (0.91)
	Step-wise **TS7** (eq 19)	-	1.68[d], 1.18 (1.09)	-

[a] Attempts to optimize the carbene elimination transition state (**TS3**) resulted in a carbene-insertion product.
[b] Attempts to optimize the Metal(III) intermediate resulted in a carbene-insertion product.
[c] Presumed to be barrierless.
[d] Estimate based on non-converged SCF wavefunction.
[e] No TS to isomerization found.

Figure S7. B3LYP basis set energetics for comparison.; SDD6-31+G(d)

Table A. Summary of M06/SDD6-31+G(d) predicted Gibbs Free energies (in eV) for unimolecular reactions of $[CF_3CO_2ML]^-$. Values in parenthesis are thermicities of separated products.

	Reaction type	M =		
L =		Cu	Ag	Au
F	Decarboxylation **TS1** (eq 11)	1.86 (-0.30)	1.63 (-0.28)	1.95 (-0.92)
	Secondary α-fluoride **TS2**/ Metal(III) int. /carbene elim. **TS3** (eq 15)	1.41, 1.48, 1.41, (1.18)	1.95, *a*, *a*, (1.41)	1.68, 1.40, 1.64, (1.18)
	Trifluoroactetate loss[b] (eq 13a)	(1.88)	(1.45)	(1.89)
	Rearrangement **TS4** (eq 16)	1.42 (1.35)	1.20 (1.14)	1.56 (1.47)
	Lactone **TS6** (eq 18)	2.36 (1.99)	2.44 (2.22)	2.41 (1.99)
	Concerted **TS5** (eq 17)	1.88 (1.18)	-	1.93 (1.18)
	Step-wise **TS7** (eq 19)	-	1.61, 1.34 (1.41)	-

[a] Ag(III) complex optimizes to a carbene-insertion product. Thus no elimination TS is found either.
[b] Pressumed to be barrierless

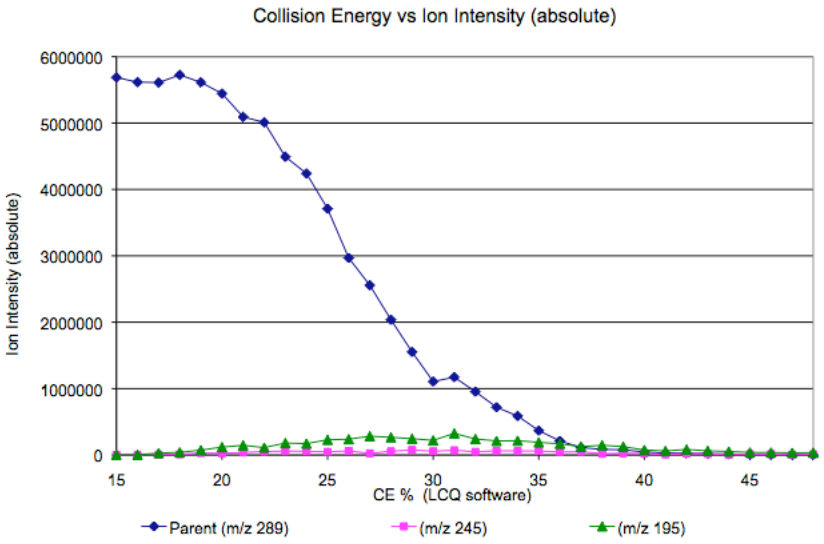
Table B. Summary of MP2/SDD6-31+G(d) predicted Gibbs Free energies (in eV) for unimolecular reactions of $[CF_3CO_2ML]^-$. Values in parenthesis are thermicities of separated products.

	Reaction type	M =		
L =		Cu	Ag	Au
F	Decarboxylation **TS1** (eq 11)	2.66 (0.13)	2.24 (0.13)	2.79 (-0.69)
	Secondary α-fluoride **TS2**/ Metal(III) int. /carbene elim. **TS3** (eq 15)	2.29, 1.76, 2.29, (0.91)	2.75, 3.05, *a*, (1.07)	2.41, 2.50, 2.99, (0.87)
	Trifluoroactetate loss[b] (eq 13a)	(1.38)	(1.11)	(1.54)
	Rearrangement **TS4** (eq 16)	1.27 (1.22)	1.06 (*a*)	1.48 (1.42)
	Lactone **TS6** (eq 18)	2.94 (2.47)	3.04 (2.63)	3.01 (2.44)
	Concerted **TS5** (eq 17)	n/a (0.91)	-	n/a (0.87)
	Step-wise **TS7** (eq 19)	-	n/a, 1.21 (1.07)	-

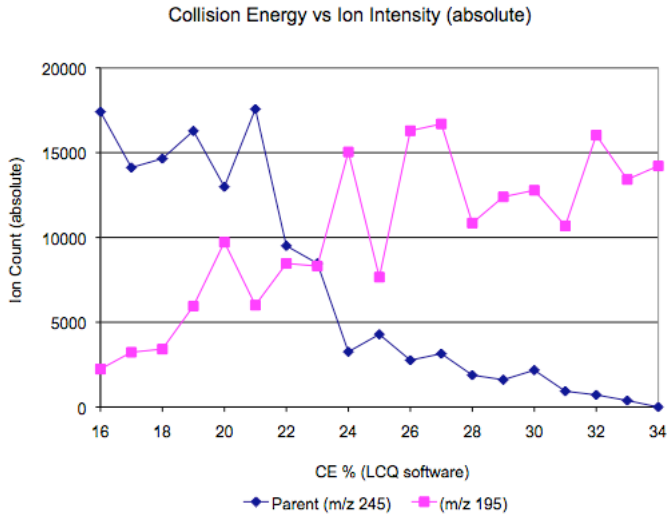
[a] No stable F-bound linkage isomer located.
[b] Pressumed to be barrierless.

Figure S8. Energies for decomposition of [CF3CO2MF]- calculated with (a) M06/SDD6-31+G(D) and (b) MP2/SDD6-31+G(d).

(a)



(b)



(c)

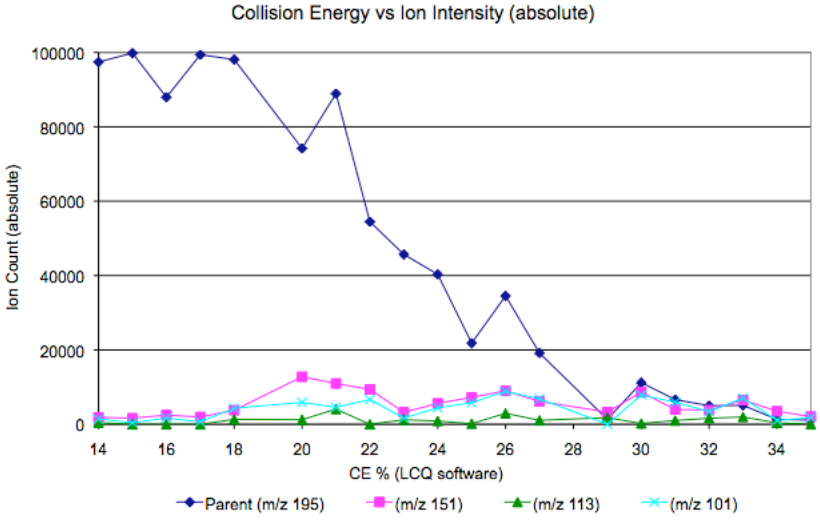
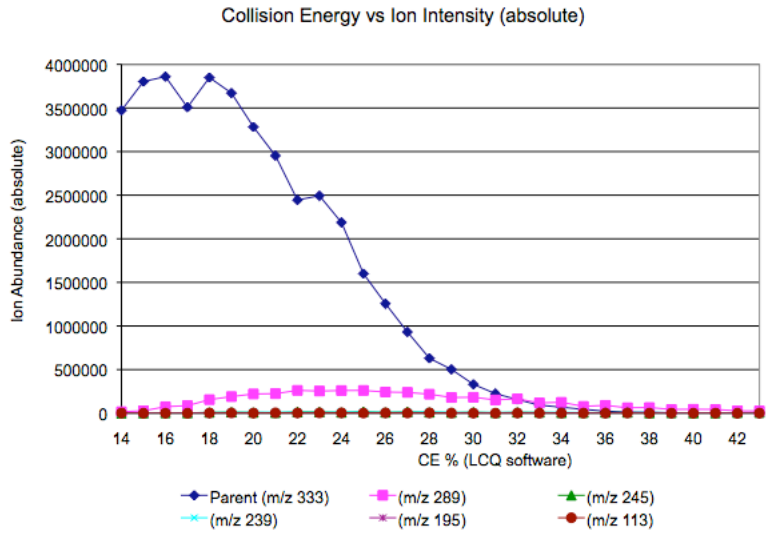
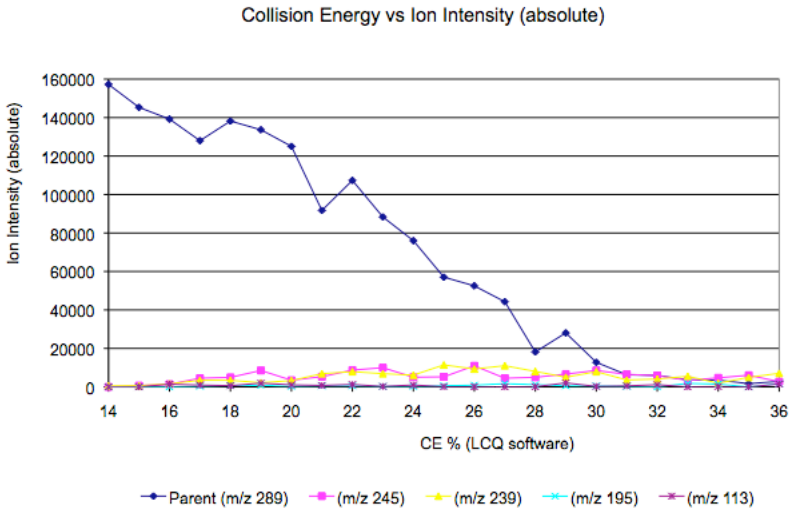


Figure S9. Energy resolved 3D quadrupole ion trap CID experiments on the precursor ions; (a) $[(CF_3CO_2)_2Cu]^-$, *m/z* 289; (b) $[CF_3CO_2CuCF_3]^-$, *m/z* 245; and (c) $[CF_3CO_2CuF]^-$, *m/z* 195.

(a)



(b)



(c)

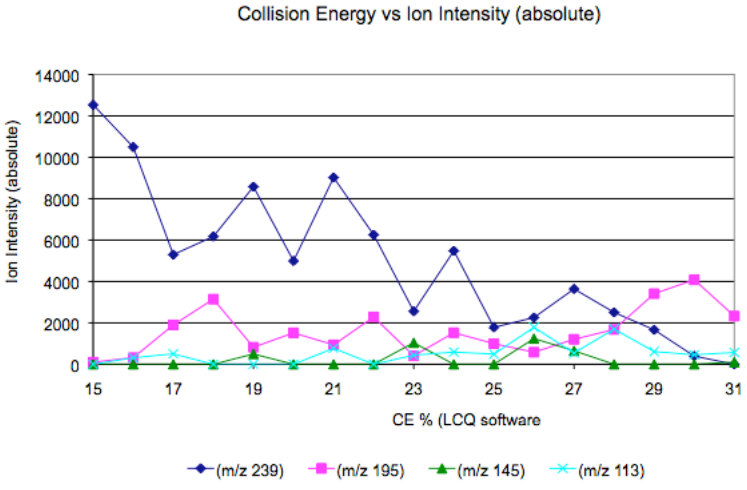
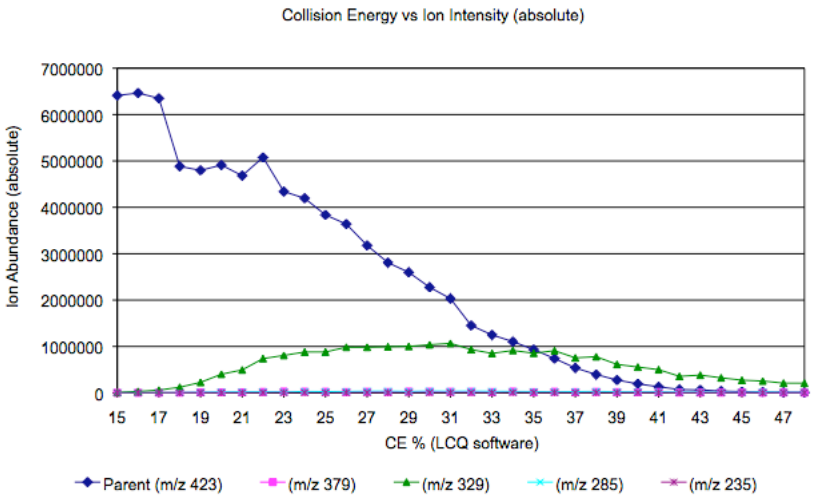
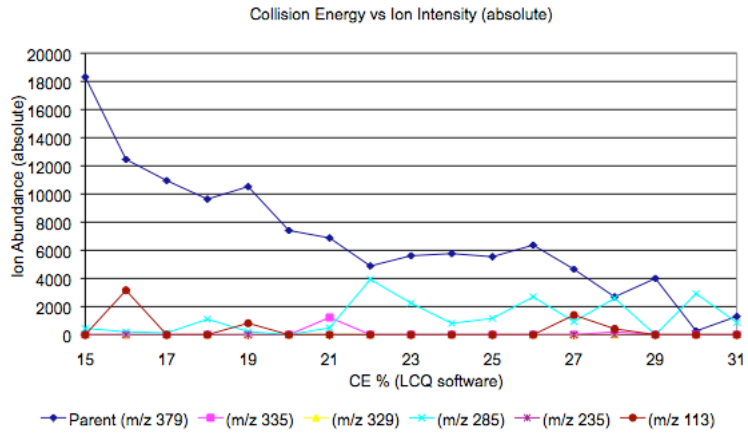


Figure S10. Energy resolved 3D quadrupole ion trap CID experiments on the precursor ions; (a) $[(CF_3CO_2)_2Ag]^-$, *m/z* 333; (b) $[CF_3CO_2AgCF_3]^-$, *m/z* 289; and (c) $[CF_3CO_2AgF]^-$, *m/z* 239.

(a)



(b)



(c)

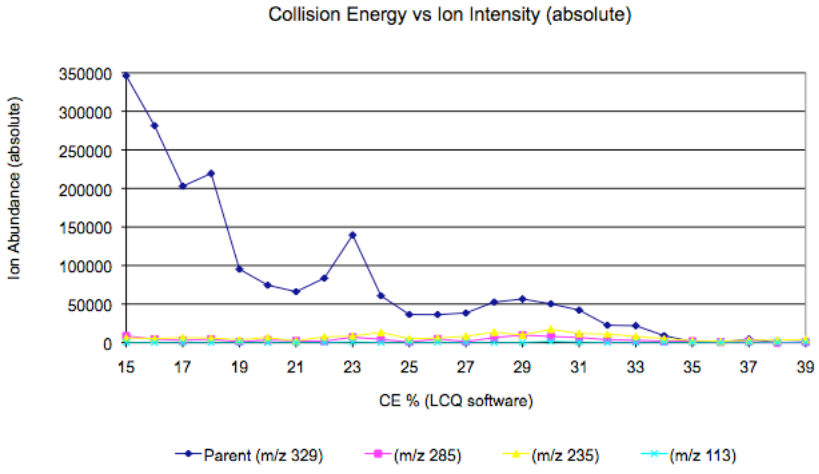


Figure S11. Energy resolved 3D quadrupole ion trap CID experiments on the precursor ions; (a) $[(CF_3CO_2)_2Au]^-$, *m/z* 423; (b) $[CF_3CO_2AuCF_3]^-$, *m/z* 379; and (c) $[CF_3CO_2AuF]^-$, *m/z* 329.

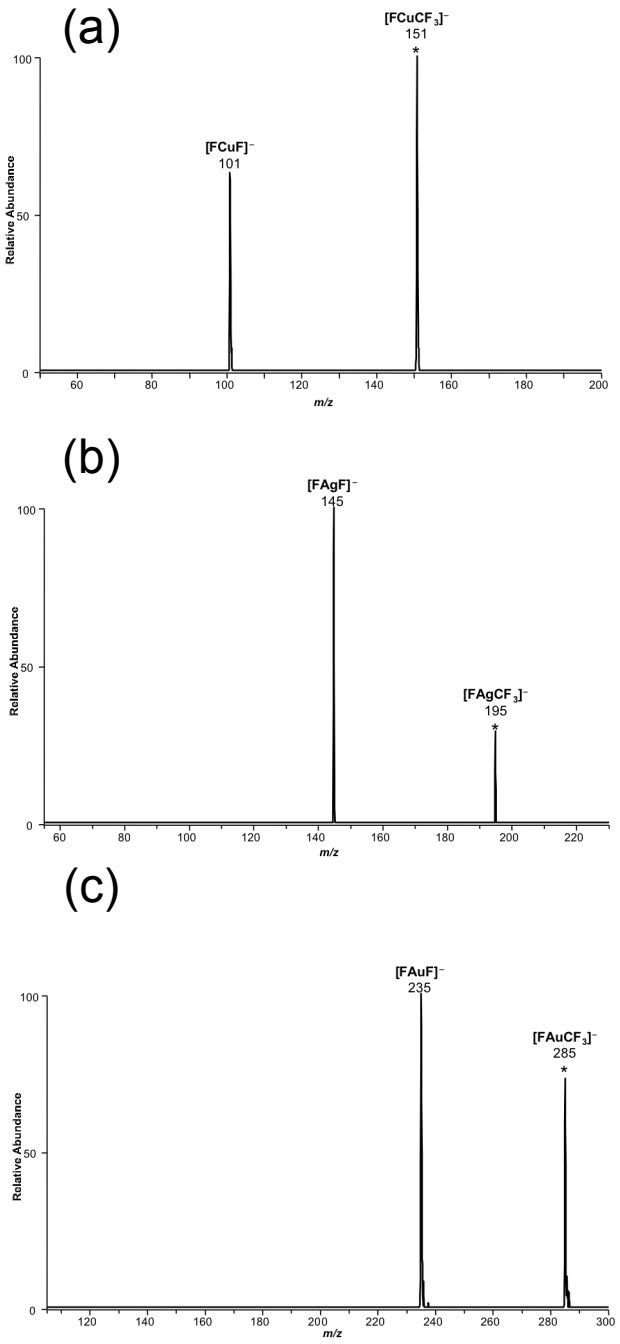


Figure S12. 3D quadrupole ion trap MS^3 spectra: CID of $[FMCF_3]^-$; (a) M = ^{63}Cu, *m/z* 151 ; (b) M = ^{107}Ag, *m/z* 195 ; and (c) M = ^{197}Au, *m/z* 285. The mass selected ion is marked with an * in each.

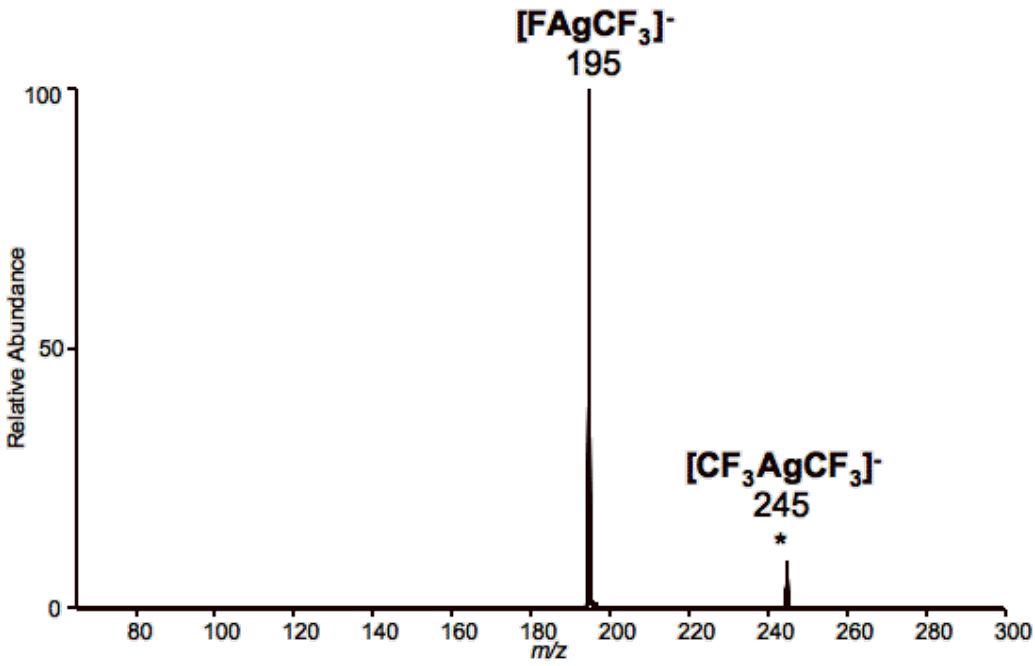
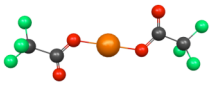


Figure S13. 3D quadrupole ion trap MS^3 spectra: Collision Induced dissociation of $[CF_3AgCF_3]^-$ (*m/z* 245);The mass selected ion is marked with an * .

	M	Linkage Isomer	Complex	Solvent	E+ZPVE (a.u)	Rel. Energy (E_0, eV)
(a)	Cu	O-bound	$[CF_3CO_2CuO_2CCF_3]^-$	Methanol	-1249.993183	0.0
(b)	Cu	F-bound	$[CO_2CF_3CuO_2CCF_3]^-$	Methanol	-1249.951828	+1.13
(c)	Cu	O-bound	$[CF_3CO_2CuO_2CCF_3]^-$	Gas-phase	-1249.923284	0.0
(d)	Cu	F-bound	$[CO_2CF_3CuO_2CCF_3]$-	Gas-phase	-1249.868823	+1.48
(e)	Ag	O-bound	$[CF_3CO_2AgO_2CCF_3]^-$	Methanol	-1199.629775	0.0
(f)	Ag	F-bound	$[CO_2CF_3AgO_2CCF_3]^-$	Methanol	-1199.602228	+0.75
(g)	Ag	O-bound	$[CF_3CO_2AgO_2CCF_3]^-$	Gas-phase	-1199.560121	0.0
(h)	Ag	F-bound	$[CO_2CF_3AgO_2CCF_3]^-$	Gas-phase	-1199.512526	+1.30
(i)	Au	O-bound	$[CF_3CO_2AuO_2CCF_3]^-$	Methanol	-1188.385457	0.0
(j)	Au	F-bound	$[CO_2CF_3AuO_2CCF_3]^-$	Methanol	-1188.340027	+1.24
(k)	Au	O-bound	$[CF_3CO_2AuO_2CCF_3]^-$	Gas-phase	-1188.315829	0.0
(l)	Au	F-bound	$[CO_2CF_3AuO_2CCF_3]^-$	Gas-phase	-1188.255897	+1.63

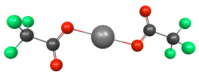
Figure S14. Linkage isomers calculated with and without solvent (implicit method). Energies are relative to O-bound isomer. Energies and vibrational frequencies are calculated at the optimization level (B3LYP/SDD6-31+G(d)).



$[CF_3CO_2CuO_2CCF_3]^-$

Cu	29.0	0.00000900	-0.00003500	0.03710300
O	8.0	-1.82735705	0.38996601	0.04778900
O	8.0	-2.65326595	-1.72761297	-0.14772899
C	6.0	-2.73673201	-0.50856799	-0.04320100
C	6.0	-4.16100693	0.13610300	0.00082400
F	9.0	-5.14989901	-0.77056003	-0.15951000
F	9.0	-4.39003420	0.75835103	1.18929398
F	9.0	-4.32571077	1.07054198	-0.97242600
O	8.0	1.82740104	-0.39006501	0.04764400
O	8.0	2.65319896	1.72757602	-0.14773400
C	6.0	2.73670602	0.50853300	-0.04322900
C	6.0	4.16100502	-0.13606399	0.00085100
F	9.0	4.38972378	-0.75908500	1.18894804
F	9.0	4.32605982	-1.06982505	-0.97298199
F	9.0	5.14986897	0.77080899	-0.15857100

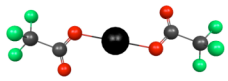
Sum of electronic and zero-point Energies= -1249.923284



$[CF_3CO_2AgO_2CCF_3]^-$

Ag	47.0	0.00000900	-0.00012200	0.07707300
C	6.0	2.90829301	0.41974199	-0.06357900
C	6.0	4.38001394	-0.10944900	-0.02217900
O	8.0	2.06874990	-0.52809399	0.10510000
O	8.0	2.72960997	1.62256896	-0.24367200
F	9.0	4.66729498	-0.70077300	1.16889405
F	9.0	5.29624796	0.86785698	-0.20051900
F	9.0	4.60688686	-1.03850901	-0.98925000
C	6.0	-2.90833807	-0.41973099	-0.06366100
C	6.0	-4.38000298	0.10961000	-0.02218700
O	8.0	-2.72979498	-1.62258196	-0.24374400
O	8.0	-2.06868505	0.52800798	0.10501000
F	9.0	-5.29633379	-0.86755502	-0.20081399
F	9.0	-4.60676718	1.03896701	-0.98897302
F	9.0	-4.66724396	0.70062000	1.16907001

Sum of electronic and zero-point Energies= -1199.560121



$[CF_3CO_2AuO_2CCF_3]^-$

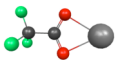
Au	79.0	-0.00000400	0.00017800	0.13588400
C	6.0	2.89178300	0.44719601	-0.24529999
C	6.0	4.33522320	-0.11736200	-0.03783100
O	8.0	2.02583003	-0.38616100	0.21501000
O	8.0	2.75618601	1.53700805	-0.78207302
F	9.0	4.60378218	-0.34091300	1.27561295
F	9.0	5.28787518	0.72432202	-0.49297100
F	9.0	4.51101923	-1.29843998	-0.68607098
C	6.0	-2.89169693	-0.44717500	-0.24558800
C	6.0	-4.33524704	0.11701100	-0.03786300
O	8.0	-2.75593400	-1.53716099	-0.78195900
O	8.0	-2.02587295	0.38655701	0.21429200
F	9.0	-5.28767776	-0.72401702	-0.49466899
F	9.0	-4.51099300	1.29911900	-0.68418503
F	9.0	-4.60419703	0.33837399	1.27589297

Sum of electronic and zero-point Energies= -1188.315829

$[CF_3CO_2Cu]$

Cu	29.0	2.20085001	-0.00327500	-0.00001600
O	8.0	0.41562700	-1.09824896	-0.00012300
O	8.0	0.42971501	1.13305497	-0.00001200
C	6.0	-0.16550000	0.02222900	0.00018000
C	6.0	-1.71593595	0.00630100	-0.00005600
F	9.0	-2.23912501	1.24172103	-0.00490600
F	9.0	-2.17481089	-0.64476299	-1.09023499
F	9.0	-2.17481589	-0.63636202	1.09522998

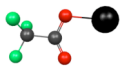
Sum of electronic and zero-point Energies= -723.547378



$[CF_3CO_2Ag]$

C	6.0	-0.66885799	0.03283000	-0.00031500
C	6.0	-2.22241902	0.00413400	-0.00028000
O	8.0	-0.09746000	1.15195298	-0.00007800
O	8.0	-0.10197400	-1.09263396	-0.00024200
F	9.0	-2.76195693	1.23403299	-0.00363400
F	9.0	-2.67814302	-0.64343703	1.09499896
F	9.0	-2.67951298	-0.65003002	-1.09056306
Ag	47.0	1.95786500	-0.00343500	-0.00002300

Sum of electronic and zero-point Energies= -673.203938



$[CF_3CO_2Au]$

Au	79.0	-1.53599799	-0.03875900	-0.00029400
O	8.0	0.96158701	1.53290403	-0.25225699
C	6.0	1.24742198	0.37146899	-0.02634300
O	8.0	0.45408699	-0.63942897	0.17761999
C	6.0	2.73990297	-0.08845000	0.01387300
F	9.0	3.57058311	0.96220303	0.00837000
F	9.0	3.01295805	-0.84478301	-1.07307398
F	9.0	3.00323606	-0.82374501	1.11254799

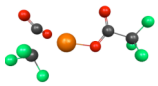
Sum of electronic and zero-point Energies= -661.938041

$CF_3CO_2^-$

O	8.0	-1.54571700	-1.14396095	-0.00149500
O	8.0	-1.59529901	1.14322197	-0.00171600
C	6.0	-1.07194901	0.01113400	-0.00305800
C	6.0	0.51640499	0.01215900	-0.00122200
F	9.0	1.09096706	1.24702096	-0.04673000
F	9.0	1.03131902	-0.58899599	1.11817300
F	9.0	1.04009199	-0.67289603	-1.06573498

Sum of electronic and zero-point Energies= -526.270494

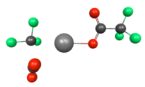
Figure S15. DFT calculated Calculated Cartesian coordinates and energies (Hartrees) for $[CF_3CO_2MO_2CCF_3]^-$ M = Cu, Ag and Au.



TS $[CF_3CO_2CuO_2CCF_3]^-$ → CO_2 + $[CF_3CuO_2CCF_3]^-$ (306 cm^{-1})

Cu	29.0	0.59545302	-0.16266701	-0.34336901
O	8.0	-1.24879801	0.29496101	-0.38957900
C	6.0	-2.11290598	-0.37980199	0.27220401
O	8.0	-1.97254705	-1.34751105	1.01317000
C	6.0	-3.55652308	0.17321000	0.03783600
F	9.0	-3.93931603	0.02258500	-1.26011801
F	9.0	-4.48563004	-0.45349699	0.79198402
F	9.0	-3.64811110	1.49811900	0.32469401
O	8.0	2.08503699	-1.55446005	-1.22134602
C	6.0	2.54478598	-1.31668699	-0.11355800
O	8.0	3.09406209	-1.74544203	0.85676003
C	6.0	2.65727210	0.77509397	0.16571800
F	9.0	2.59729910	1.14749002	1.47951400
F	9.0	3.99773407	0.81962597	-0.15692100
F	9.0	2.13069701	1.85746205	-0.54443502

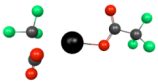
Sum of electronic and zero-point Energies= -1249.850355



TS $[CF_3CO_2AgO_2CCF_3]^-$ → CO_2 + $[CF_3AgO_2CCF_3]^-$ (289cm^{-1})

Ag	47.0	-0.47446099	0.13700400	-0.04016800
O	8.0	1.60859799	0.53687400	0.47020200
C	6.0	2.37107611	-0.24677500	-0.18606301
O	8.0	2.08113599	-1.12191105	-1.00335205
C	6.0	3.88302493	0.00713800	0.11378900
F	9.0	4.14004612	0.08600500	1.44408798
F	9.0	4.68582201	-0.96034801	-0.38102600
F	9.0	4.29517221	1.18107903	-0.43979600
O	8.0	-2.35886097	1.56114495	-1.31077194
C	6.0	-2.79036403	1.37620497	-0.19646800
O	8.0	-3.29166007	1.81346703	0.79741400
C	6.0	-2.86905098	-0.73636103	0.12756900
F	9.0	-2.77304506	-1.19135702	1.42510200
F	9.0	-4.21283484	-0.82090098	-0.16462700
F	9.0	-2.31095409	-1.75636899	-0.64962798

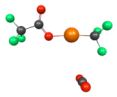
Sum of electronic and zero-point Energies= -1199.495006



TS $[CF_3CO_2AuO_2CCF_3]^-$ → CO_2 + $[CF_3AuO_2CCF_3]^-$ (342 cm^{-1})

Au	79.0	0.38633099	-0.21586099	-0.02529700
O	8.0	-1.67193699	-0.47828400	0.26737800
C	6.0	-2.46854496	0.41913000	-0.20282701
O	8.0	-2.23640609	1.45057499	-0.81453699
C	6.0	-3.95254111	0.03523500	0.10269600
F	9.0	-4.16616011	-0.13345000	1.43217802
F	9.0	-4.82068491	0.97757399	-0.31888801
F	9.0	-4.30007315	-1.12635398	-0.50945002
O	8.0	2.50256395	-1.31977606	-1.38073504
C	6.0	2.69766593	-1.14155197	-0.18772000
O	8.0	3.02360106	-1.68275595	0.84356999
C	6.0	2.80600691	0.80583203	0.14468400
F	9.0	2.54240704	1.29034197	1.39602304
F	9.0	4.17258978	0.86568898	0.02917200
F	9.0	2.35433888	1.74653995	-0.74769199

Sum of electronic and zero-point Energies= -1188.234929



$[CF_3CO_2CuCF_3]$-(CO_2)

Cu	29.0	0.57227600	-0.64407599	0.02304300
O	8.0	-1.17795897	0.07577600	0.05528900
C	6.0	-2.26343298	-0.59011799	-0.06774200
O	8.0	-2.45899010	-1.78983998	-0.23392400
C	6.0	-3.50925994	0.35427001	0.02100300
F	9.0	-3.48813009	1.31066203	-0.94683498
F	9.0	-4.68106699	-0.30595800	-0.11286000
F	9.0	-3.56300902	1.00494003	1.21517098
C	6.0	2.40246105	-1.20502102	0.01759600
F	9.0	2.77439189	-2.04633904	-1.02602899
F	9.0	3.34002995	-0.16222399	-0.07326200
F	9.0	2.82085109	-1.89785194	1.15028298
C	6.0	2.62984991	2.70413995	-0.04195500
O	8.0	2.65030694	2.72552109	1.12751603
O	8.0	2.61397791	2.73473406	-1.21136296

Sum of electronic and zero-point Energies= -1249.911310

$[CF_3CO_2AgCF_3]$-(CO_2)

Ag	47.0	0.49694899	-0.54570800	0.01303900
O	8.0	-1.47083104	0.28283799	0.03311700
C	6.0	-2.51131201	-0.45131099	-0.04807300
O	8.0	-2.63190198	-1.66987097	-0.15272100
C	6.0	-3.81698489	0.41278601	0.00996900
F	9.0	-3.84303093	1.36265504	-0.96383202
F	9.0	-4.94403315	-0.31985599	-0.13569400
F	9.0	-3.92973590	1.06693101	1.19913995
C	6.0	2.50992703	-1.17769206	0.00672800
F	9.0	2.86510491	-2.02770305	-1.03169799
F	9.0	3.45289207	-0.14592101	-0.09327500
F	9.0	2.91927910	-1.86623597	1.14122200
C	6.0	2.89294910	2.77369809	-0.02340400
O	8.0	2.91212797	2.78053689	1.14618194
O	8.0	2.87955594	2.81581807	-1.19244397

Sum of electronic and zero-point Energies= -1199.550024

$[CF_3CO_2AuCF_3]$-(CO_2)

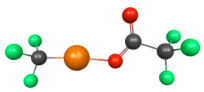
Au	79.0	0.46610200	-0.43601701	0.01225200
O	8.0	-1.51210499	0.31233999	0.04203800
C	6.0	-2.54662991	-0.43847701	-0.05383800
O	8.0	-2.65678596	-1.65235698	-0.17709500
C	6.0	-3.85287309	0.42258200	0.01150100
F	9.0	-3.88994789	1.36505306	-0.96827102
F	9.0	-4.97448111	-0.31943601	-0.12201400
F	9.0	-3.96020889	1.08208704	1.19687104
C	6.0	2.40301704	-1.02834702	0.00353700
F	9.0	2.75189590	-1.87079895	-1.03454697
F	9.0	3.32524800	0.01110500	-0.09588500
F	9.0	2.80684710	-1.71122503	1.13554502
C	6.0	2.54047704	2.90976810	-0.03012400
O	8.0	2.57073689	2.92051792	1.13925803
O	8.0	2.52063298	2.94964504	-1.19915903

Sum of electronic and zero-point Energies= -1188.330940

CO_2

C	6.0	0.00000000	0.00000000	0.00000000
O	8.0	0.00000000	0.00000000	1.16979396
O	8.0	0.00000000	0.00000000	-1.16979396

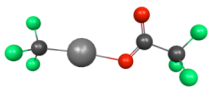
Sum of electronic and zero-point Energies= -188.575853



$[CF_3CuO_2CCF_3]^-$

Cu	29.0	-0.20335500	-1.07428098	0.00000000
O	8.0	1.75597799	1.52613902	0.00000000
O	8.0	-0.41026199	0.80959100	0.00000000
C	6.0	0.53586900	1.66773903	0.00000000
C	6.0	0.02459800	3.14833403	0.00000000
F	9.0	-1.32195997	3.28158593	0.00000000
F	9.0	0.48101300	3.82069206	1.09164405
F	9.0	0.48101300	3.82069206	-1.09164405
C	6.0	-0.15838300	-2.98785400	0.00000000
F	9.0	-1.41108596	-3.60815191	0.00000000
F	9.0	0.48101300	-3.57413101	-1.09222698
F	9.0	0.48101300	-3.57413101	1.09222698

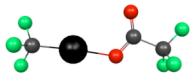
Sum of electronic and zero-point Energies= -1061.332287



$[CF_3AgO_2CCF_3]$

Ag	47.0	-0.96497399	-0.14191400	-0.00884000
O	8.0	1.14289999	-0.51384002	-0.01444800
C	6.0	1.98227799	0.44666100	-0.01328100
O	8.0	1.81472397	1.66453099	-0.01150400
C	6.0	3.45532393	-0.08738700	0.00220400
F	9.0	3.69429898	-0.96539199	-1.00892901
F	9.0	4.37670708	0.89567399	-0.11580000
F	9.0	3.73353410	-0.74239302	1.16435301
C	6.0	-3.06740999	0.04018200	0.00552800
F	9.0	-3.57449293	1.15204406	-0.65810698
F	9.0	-3.75683594	-1.02103603	-0.57887602
F	9.0	-3.64302897	0.13306800	1.27029300

Sum of electronic and zero-point Energies= -1010.971565



$[CF_3AuO_2CCF_3]^-$

Au	79.0	-0.79657102	-0.11456300	-0.00589000
O	8.0	1.29298699	-0.44531399	-0.01402200
C	6.0	2.15723491	0.50053900	-0.01298600
O	8.0	2.02630210	1.71890795	-0.01159700
C	6.0	3.60953593	-0.08585800	0.00258900
F	9.0	3.81918192	-0.96946800	-1.00899100
F	9.0	4.55967808	0.86874098	-0.11461700
F	9.0	3.86518192	-0.74915397	1.16427004
C	6.0	-2.81237102	0.07828900	0.00708900
F	9.0	-3.29238296	1.21774399	-0.61443001
F	9.0	-3.49880791	-0.95096397	-0.61958098
F	9.0	-3.38080907	0.12797700	1.27002597

Sum of electronic and zero-point Energies= -999.752370

Figure S16: Calculated Cartesian coordinates and energies (Hartrees) for species relevant to the fragmentation of $[CF_3CO_2MO_2CCF_3]^-$ M = Cu, Ag and Au.

[CF_3Cu]

Cu	29.0	1.24927902	-0.00001800	0.00042700
C	6.0	-0.66461301	-0.00001300	0.00015400
F	9.0	-1.19593704	-0.02939800	1.25892401
F	9.0	-1.19319105	1.10555899	-0.60472602
F	9.0	-1.19325304	-1.07609403	-0.65567702

Sum of electronic and zero-point Energies= -534.970957

[CF_3Ag]

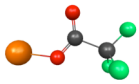
Ag	47.0	1.05947006	-0.00006100	0.00003500
C	6.0	-1.07610595	-0.00006500	0.00000600
F	9.0	-1.60514903	-0.65471798	-1.07495904
F	9.0	-1.60557401	-0.60352498	1.10438597
F	9.0	-1.60466003	1.25860405	-0.02961200

Sum of electronic and zero-point Energies= -484.623448

[CF_3Au]

Au	79.0	0.72031897	0.00001700	0.00007200
C	6.0	-1.31546497	0.00000200	-0.00001500
F	9.0	-1.81465900	-1.06835794	-0.66149801
F	9.0	-1.81611502	-0.03874900	1.25536501
F	9.0	-1.81505203	1.10695696	-0.59448802

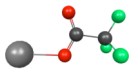
Sum of electronic and zero-point Energies= -473.399612



[CF_3CO_2Cu].-

C	6.0	0.36572000	0.49641401	-0.01064300
C	6.0	1.80597496	-0.13406600	-0.00251400
O	8.0	-0.52856398	-0.40773001	-0.00992700
O	8.0	0.29308599	1.72580397	-0.00548800
F	9.0	2.05317593	-0.80488998	1.15987206
F	9.0	2.79562902	0.78372699	-0.12850200
F	9.0	1.98651600	-1.03004801	-1.01236904
Cu	29.0	-2.50566292	-0.11233700	0.00107800

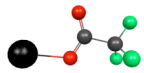
Sum of electronic and zero-point Energies= -723.621611



[CF_3CO_2Ag].-

C	6.0	-0.89933401	0.38964900	-0.01014100
C	6.0	-2.39478707	-0.10408000	-0.00319800
O	8.0	-0.72307599	1.61349297	-0.00580300
O	8.0	-0.08502800	-0.57791799	-0.00620500
F	9.0	-3.30057192	0.89557701	-0.14787400
F	9.0	-2.70892501	-0.73390597	1.16747904
F	9.0	-2.65371704	-0.99572802	-1.00113499
Ag	47.0	2.21698904	-0.05301100	0.00021000

Sum of electronic and zero-point Energies= -673.284719



[CF_3CO_2Au].-

C	6.0	1.43114495	0.42818999	-0.01054600
C	6.0	2.90880394	-0.11614800	-0.00322700
O	8.0	0.59545898	-0.52848297	-0.00653200
O	8.0	1.29068005	1.65181899	-0.00601700
F	9.0	3.20481205	-0.74610198	1.17082000
F	9.0	3.84016800	0.85732901	-0.15581600
F	9.0	3.13805199	-1.01989496	-0.99589199
Au	79.0	-1.68070996	-0.03393600	0.00014000

Sum of electronic and zero-point Energies= -662.049271

CF_3^-

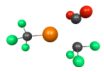
C	6.0	0.00146300	-0.00000500	0.55599600
F	9.0	-1.27552998	-0.00111600	-0.12320800
F	9.0	0.63630998	1.10431004	-0.12372700
F	9.0	0.63824499	-1.10319102	-0.12372900

Sum of electronic and zero-point Energies= -337.636109

CF_3^-

C	6.0	0.00000000	0.00007600	0.33049199
F	9.0	-0.00074100	1.26632202	-0.07345300
F	9.0	1.09713995	-0.63254499	-0.07343700
F	9.0	-1.09639800	-0.63382798	-0.07343700

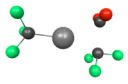
Sum of electronic and zero-point Energies= -337.563830



TS [$CF_3CuO_2CCF_3$]$^-$ → CO_2 + [CF_3CuCF_3]$^-$ (-288 cm^{-1})

Cu	29.0	-0.37892300	0.14903800	-0.15562600
O	8.0	2.09678292	1.71091795	1.06302202
C	6.0	1.58504903	1.39031398	0.02810300
O	8.0	1.12968600	1.74735105	-1.04250503
C	6.0	1.80087805	-0.69183302	0.00013600
F	9.0	1.28455496	-1.65193498	-0.87216502
F	9.0	3.12707901	-0.61515802	-0.37720299
F	9.0	1.82321703	-1.29712903	1.22742200
C	6.0	-2.28659511	-0.06894900	0.07700200
F	9.0	-2.82670403	-1.20168102	-0.52866501
F	9.0	-2.71921301	-0.17426699	1.39609504
F	9.0	-3.06882095	0.96623200	-0.43241999

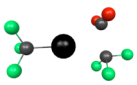
Sum of electronic and zero-point Energies= -1061.260345



TS [$CF_3AgO_2CCF_3$]$^-$ → CO_2 + [CF_3AgCF_3]$^-$ (-270 cm^{-1})

Ag	47.0	0.38692501	0.00612000	-0.05508200
C	6.0	2.52184796	-0.04699700	0.04413500
O	8.0	-1.64102304	1.75757205	-1.13999295
C	6.0	-1.82856095	1.43083894	0.00687200
O	8.0	-2.04846811	1.75928605	1.14154398
C	6.0	-2.09708095	-0.64923102	0.01075700
F	9.0	-1.95255899	-1.35311997	1.18803298
F	9.0	-3.46216202	-0.56086498	-0.16225500
F	9.0	-1.70626903	-1.53808904	-0.99022800
F	9.0	3.16491008	1.03655398	-0.53722799
F	9.0	3.04830098	-0.08835100	1.32789302
F	9.0	3.10258007	-1.14392805	-0.58111900

Sum of electronic and zero-point Energies= -1010.905912



TS [$CF_3AuO_2CCF_3$]$^-$ → CO_2 + [CF_3AuCF_3]$^-$ (-289 cm^{-1})

Au	79.0	0.37014699	0.02301200	-0.01959100
C	6.0	2.40659189	-0.06721300	0.02454200
O	8.0	-1.88301599	1.69876206	-1.14868903
C	6.0	-1.93033004	1.33826494	0.00812600
O	8.0	-2.02656889	1.69740403	1.15973604
C	6.0	-2.22656488	-0.63481301	0.00790900
F	9.0	-1.99882901	-1.37809205	1.14035797
F	9.0	-3.59841704	-0.53206497	-0.05705200
F	9.0	-1.90892196	-1.45250702	-1.05615902
F	9.0	3.02995610	0.99918801	-0.58019602
F	9.0	2.93958092	-0.10628900	1.29233003
F	9.0	2.92962003	-1.17520702	-0.60418499

Sum of electronic and zero-point Energies= -999.676195

[CF_3CuCF_3]-(CO_2)

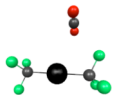
C	6.0	1.26487398	2.71708894	-0.00188100
O	8.0	1.31592202	2.72050405	-1.17062104
O	8.0	1.22169495	2.76633191	1.16621101
Cu	29.0	-0.30136901	-0.65869200	0.00155100
C	6.0	-2.16789603	-0.09689000	-0.00469200
F	9.0	-2.97389102	-0.66733098	-0.99482900
F	9.0	-2.88591003	-0.35699499	1.16660500
F	9.0	-2.37243700	1.27671802	-0.19348000
C	6.0	1.57903194	-1.17401898	0.00556500
F	9.0	2.48812795	-0.10662900	0.11348500
F	9.0	1.97910202	-2.02078390	1.04187500
F	9.0	2.02975202	-1.84383404	-1.13406301

Sum of electronic and zero-point Energies= -1061.314016

[CF_3AgCF_3]-(CO_2)

C	6.0	1.93284404	2.62395597	-0.00264700
O	8.0	1.97328901	2.62368202	-1.17179799
O	8.0	1.90190196	2.67795491	1.16563904
Ag	47.0	-0.38259301	-0.52675700	0.00237100
C	6.0	-2.38667011	0.22252800	-0.00422000
F	9.0	-2.79439712	0.85715199	1.17107797
F	9.0	-2.66410494	1.17747498	-0.98539102
F	9.0	-3.38718390	-0.73090798	-0.20576800
C	6.0	1.63381302	-1.24837303	0.00404200
F	9.0	2.02183008	-1.95980096	-1.13008595
F	9.0	2.62478495	-0.25696099	0.09990800
F	9.0	1.96578395	-2.11408496	1.04523396

Sum of electronic and zero-point Energies= -1010.955421

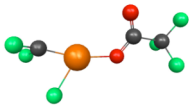


[CF_3AuCF_3]-(CO_2)

Au	79.0	-0.31033501	-0.41285700	0.00162400
C	6.0	1.62622201	-1.19655204	0.00686200
F	9.0	1.99540496	-1.87760103	-1.14602900
F	9.0	2.64624190	-0.25031000	0.15470999
F	9.0	1.89616597	-2.10940099	1.01866901
C	6.0	-2.24182200	0.37970400	-0.00639600
F	9.0	-2.65257192	0.95245802	1.19300902
F	9.0	-2.45792508	1.39450300	-0.93399000
F	9.0	-3.25531602	-0.53108901	-0.28830299
C	6.0	2.02391195	2.67589688	-0.00469200
O	8.0	1.97904599	2.74955893	1.16206801
O	8.0	2.08577895	2.65723491	-1.17275906

Sum of electronic and zero-point Energies= -999.750900

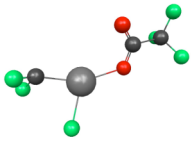
Figure S17: Calculated Cartesian coordinates and energies (Hartrees) of $[CF_3CO_2MF]^-$ and $[CF_3CO_2MCF_3]^-$, M = Cu, Ag and Au.



TS $[CF_3CuO_2CCF_3]^-$ → $[CF_2(F)CuO_2CCF_3]^-$ (161 cm^{-1})

Cu	29.0	1.18186998	-0.15662301	0.00667000
O	8.0	-1.43538105	1.66491997	-0.38579401
O	8.0	-0.72562099	-0.45292601	0.07112400
C	6.0	-1.58134103	0.47675100	-0.10554800
C	6.0	-3.04244804	-0.05877400	0.06988800
F	9.0	-3.34973598	-0.99689001	-0.86705899
F	9.0	-3.22881889	-0.64245200	1.28547502
F	9.0	-3.97773099	0.91329801	-0.03637800
C	6.0	2.88905191	0.47726199	0.31748199
F	9.0	2.43443608	-1.43460405	-0.88008898
F	9.0	3.74671412	-0.07522600	1.17006004
F	9.0	3.64426804	1.06639504	-0.60167700

Sum of electronic and zero-point Energies= -1061.278174



TS $[CF_3AgO_2CCF_3]^-$ → $[CF_2(F)AgO_2CCF_3]^-$ (55 cm^{-1})

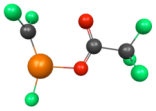
Ag	47.0	-1.09070694	0.24228001	0.02519100
O	8.0	1.53237402	-1.44827497	-0.68211901
O	8.0	1.07533097	0.57900202	0.24377000
C	6.0	1.82055902	-0.36739501	-0.16256000
C	6.0	3.33717203	-0.05336300	0.06915900
F	9.0	3.71771908	1.10332203	-0.53601402
F	9.0	3.62034702	0.08626300	1.39521003
F	9.0	4.16012383	-1.02097797	-0.39820099
C	6.0	-2.85189700	-0.81351799	0.29775500
F	9.0	-2.34723496	1.78870296	-0.74271101
F	9.0	-3.77069211	-0.38972399	1.15740705
F	9.0	-3.53953409	-1.23728800	-0.75383598

Sum of electronic and zero-point Energies= -1010.900792

TS $[CF_3AuO_2CCF_3]^-$ → $[CF_2(F)AuO_2CCF_3]^-$ (151 cm^{-1})

Au	79.0	-0.87871897	0.01490000	0.09678300
O	8.0	1.91852903	-1.57338703	-0.70101202
O	8.0	1.20126498	0.39196399	0.21110401
C	6.0	2.06190109	-0.46720999	-0.19284301
C	6.0	3.51587701	0.05794100	0.04651900
F	9.0	3.74050403	1.24228704	-0.57743597
F	9.0	3.76274395	0.25459599	1.37109995
F	9.0	4.45994520	-0.80207300	-0.39815101
C	6.0	-2.74073601	-0.47463599	0.19599000
F	9.0	-1.85400605	1.77380002	-1.06896901
F	9.0	-3.62880206	0.07350400	1.00493705
F	9.0	-3.43169308	-1.03347600	-0.77865303

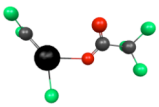
Sum of electronic and zero-point Energies= -999.659663



$[CF_2(F)CuO_2CCF_3]^-$

Cu	29.0	-1.56585598	0.72650898	-0.00041200
O	8.0	0.74596697	-1.44564402	-0.02768500
O	8.0	0.49192300	0.82076299	-0.01012000
C	6.0	1.13566196	-0.27251500	-0.01948600
C	6.0	2.68563795	-0.03575000	-0.00153800
F	9.0	3.08860493	0.79808903	-0.99625701
F	9.0	3.08516908	0.52881598	1.17212796
F	9.0	3.40354300	-1.17579305	-0.14265600
C	6.0	-2.13404894	-0.99262899	0.00435800
F	9.0	-2.10694909	2.48801708	0.00060300
F	9.0	-2.31530809	-1.77876604	1.06138301
F	9.0	-2.33470511	-1.77862501	-1.04915798

Sum of electronic and zero-point Energies= -1061.286757



$[CF_2(F)AuO_2CCF_3]^-$

Au	79.0	-1.07735503	0.37688401	-0.00571000
O	8.0	1.60404003	-1.11600995	-1.24472201
O	8.0	1.15322900	0.36136800	0.43452901
C	6.0	1.88290799	-0.37926099	-0.29712701
C	6.0	3.39024806	-0.28801900	0.13161600
F	9.0	3.90289903	0.95103502	-0.09443000
F	9.0	3.56253600	-0.54844201	1.45754302
F	9.0	4.18521404	-1.16064799	-0.53339899
C	6.0	-2.36946988	-0.98396897	0.12524700
F	9.0	-0.70945102	2.34751391	-0.39627099
F	9.0	-3.06017995	-1.34645104	1.21071994
F	9.0	-2.81092811	-1.77959001	-0.84702897

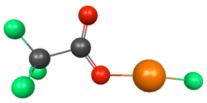
Sum of electronic and zero-point Energies= -999.678188'

CF_2

C	6.0	0.00000000	0.60527700	0.00000000
F	9.0	1.03800201	-0.20179801	0.00000000
F	9.0	-1.03800201	-0.20172000	0.00000000

Sum of electronic and zero-point Energies= -237.701748

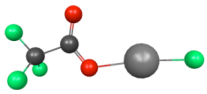
Figure S18: Calculated Cartesian coordinates and energies (Hartrees) relevant to fragmentation of $[CF_3CO_2MF]^-$ and $[CF_3CO_2MCF_3]^-$, M = Cu, Ag and Au.



$[CF_3CO_2CuF]^-$

Cu	29.0	-2.01542401	-0.10819000	-0.00051300
O	8.0	-0.16210400	-0.38041401	-0.00782700
O	8.0	0.68285900	1.74298894	-0.00568200
C	6.0	0.74707001	0.51695901	-0.01079600
C	6.0	2.16918898	-0.14082000	-0.00295800
F	9.0	3.16774392	0.75935501	-0.15541300
F	9.0	2.41016698	-0.79088598	1.17098403
F	9.0	2.32173109	-1.05845797	-0.99541998
F	9.0	-3.81256604	-0.02333600	0.00268100

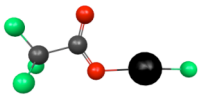
Sum of electronic and zero-point Energies= -823.558855



$[CF_3CO_2AgF]^-$

Ag	47.0	-1.77701104	-0.08207500	-0.00497700
F	9.0	-3.80257201	0.06795600	0.01890500
C	6.0	1.17774606	0.45997500	-0.00245800
C	6.0	2.63548398	-0.11486700	0.00153600
O	8.0	1.04267299	1.68193603	-0.00296200
O	8.0	0.31769300	-0.48143801	-0.00219300
F	9.0	3.58586693	0.84748101	-0.02964700
F	9.0	2.86616611	-0.92106098	-1.07117701
F	9.0	2.87912107	-0.86294401	1.11310899

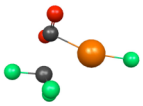
Sum of electronic and zero-point Energies= -773.191323



$[CF_3CO_2AuF]^-$

Au	79.0	-1.36149096	-0.06777700	-0.00459100
F	9.0	-3.34528804	0.16539800	0.04585000
C	6.0	1.55396295	0.50114298	-0.03096300
C	6.0	2.99162698	-0.11745900	0.00444000
O	8.0	1.44716895	1.72051501	-0.01962100
O	8.0	0.67540002	-0.43405300	-0.05009800
F	9.0	3.96051097	0.81347001	-0.14657000
F	9.0	3.18644595	-1.04282403	-0.97113800
F	9.0	3.23207498	-0.74041998	1.19181204

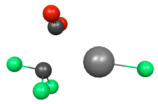
Sum of electronic and zero-point Energies= -761.951124



TS $[FCuO_2CCF_3]^- \rightarrow CO_2 + [FCuCF_3]^-$ (-307 cm^{-1})

Cu	29.0	-1.12474203	-0.00303200	-0.03165200
O	8.0	0.98594898	1.80927002	1.03831196
C	6.0	0.57277399	1.36296296	-0.00547400
O	8.0	0.14307600	1.67132294	-1.11222005
C	6.0	1.10949194	-0.58247000	-0.01743500
F	9.0	0.75721103	-1.55342805	-0.94359601
F	9.0	2.42637205	-0.31657699	-0.32620201
F	9.0	1.15900099	-1.22078800	1.19141901
F	9.0	-2.84350491	-0.51362598	0.26133800

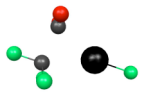
Sum of electronic and zero-point Energies= -823.486380



TS $[FAgO_2CCF_3]^- \rightarrow CO_2 + [FAgCF_3]^-$ (-277cm^{-1})

Ag	47.0	-1.06053102	-0.04967800	-0.00000400
O	8.0	1.03364503	1.77033305	1.15363204
C	6.0	1.00841403	1.42431700	-0.00336100
O	8.0	0.98627299	1.76829195	-1.16159904
C	6.0	1.42996395	-0.59478003	-0.00133100
F	9.0	1.17665100	-1.43456602	-1.07342505
F	9.0	2.79448891	-0.40711501	-0.05169200
F	9.0	1.24501503	-1.37361300	1.12519300
F	9.0	-3.09889293	-0.22374400	0.01015600

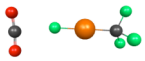
Sum of electronic and zero-point Energies= -773.127222



TS $[FAuO_2CCF_3]^- \rightarrow CO_2 + [FAuCF_3]^-$ (-322 cm^{-1})

Au	79.0	0.85253298	-0.01007300	-0.00716800
F	9.0	2.84175110	-0.33043000	0.06870500
O	8.0	-1.18113601	1.68506002	-1.15690196
C	6.0	-1.24630702	1.30844104	0.00253000
O	8.0	-1.33161902	1.70554602	1.14963198
C	6.0	-1.72613502	-0.57514000	0.00032800
F	9.0	-1.53722894	-1.34218299	1.11734700
F	9.0	-3.08376098	-0.35809100	-0.03710500
F	9.0	-1.48892105	-1.38361895	-1.08146703

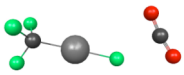
Sum of electronic and zero-point Energies= -761.871875



$[CF_3CuF]$-(CO_2)

C	6.0	-3.91547394	-0.07468400	-0.00857300
O	8.0	-3.90020394	-1.24669802	-0.00530800
O	8.0	-4.10760498	1.08161199	-0.01367300
Cu	29.0	0.34924400	0.07420200	0.01100600
C	6.0	2.25267005	-0.02599100	-0.00445500
F	9.0	2.92666793	1.18101501	-0.22542500
F	9.0	2.84537506	-0.49546599	1.17405295
F	9.0	2.80363989	-0.86651200	-0.97954798
F	9.0	-1.47443497	0.15572800	0.02101200

Sum of electronic and zero-point Energies= -823.552450



$[CF_3AgF]$-(CO_2)

C	6.0	3.86938596	0.40263700	-0.00220600
O	8.0	3.43277311	1.49190700	0.00326200
O	8.0	4.49955511	-0.58736497	-0.00828900
Ag	47.0	-0.23619901	-0.25791201	0.00197700
C	6.0	-2.29084802	0.17049800	-0.00166200
F	9.0	-2.71997404	1.05421102	-0.99278098
F	9.0	-3.12991095	-0.93076003	-0.18311501
F	9.0	-2.78682709	0.74909198	1.16752398
F	9.0	1.76687896	-0.71179801	0.00509700

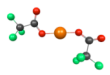
Sum of electronic and zero-point Energies= -773.187983

$[CF_3AuF]$-(CO_2)

C	6.0	3.99966192	0.42182499	-0.00385600
O	8.0	3.60347009	1.52470303	0.00501100
O	8.0	4.55555820	-0.61030799	-0.01346500
Au	79.0	-0.22001401	-0.19088300	0.00215500
C	6.0	-2.18946290	0.23023000	-0.00327100
F	9.0	-2.60289192	1.11298394	-0.99427402
F	9.0	-3.02719307	-0.86487103	-0.18343399
F	9.0	-2.67304611	0.81163502	1.16315305
F	9.0	1.77509701	-0.63171601	0.00790300

Sum of electronic and zero-point Energies= -761.971125

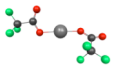
Figure S18: Calculated Cartesian coordinates and energies (Hartrees) relevant to fragmentation of $[CF_3CO_2MF]^-$ and $[CF_3CO_2MCF_3]^-$, M = Cu, Ag and Au.



Conformer #2 $[CF_3CO_2CuO_2CCF_3]^-$

Cu	29.0	0.24746600	-0.56048799	0.15854999
C	6.0	-2.51085711	-0.47836000	-0.20602100
C	6.0	-3.80587506	0.36856800	0.02057600
O	8.0	-1.47906494	0.14318199	0.23339400
O	8.0	-2.61838007	-1.57629597	-0.74060798
F	9.0	-4.02944422	0.59387600	1.34368503
F	9.0	-4.91393089	-0.23286000	-0.46407899
F	9.0	-3.72663403	1.58587205	-0.57925099
C	6.0	3.16493392	-0.82460499	0.09273000
C	6.0	3.28432608	0.72672498	-0.10872000
O	8.0	4.21100998	-1.46124995	0.15191500
O	8.0	1.96697402	-1.26743197	0.17640699
F	9.0	4.56184578	1.14596903	-0.21702100
F	9.0	2.63900495	1.14030600	-1.23405004
F	9.0	2.73404694	1.41067505	0.93313801

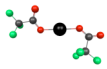
Sum of electronic and zero-point Energies= -1249.918158



Conformer #2 $[CF_3CO_2AgO_2CCF_3]^-$

Ag	47.0	-0.23174900	-0.49470699	-0.19241700
C	6.0	2.66387296	-0.28422001	0.29404899
C	6.0	4.05798388	0.36224401	0.00174100
O	8.0	1.74903798	0.24349600	-0.42599601
O	8.0	2.60205293	-1.17967403	1.13287199
F	9.0	4.43113089	0.17828500	-1.29385400
F	9.0	5.04578114	-0.15071900	0.76721001
F	9.0	4.04798603	1.70361197	0.22284400
C	6.0	-3.37664795	-0.76274902	-0.03098400
C	6.0	-3.40924311	0.79802102	0.13914301
O	8.0	-4.45958614	-1.34095800	-0.04120700
O	8.0	-2.20735788	-1.26376903	-0.14432199
F	9.0	-4.65518999	1.29181504	0.28582901
F	9.0	-2.69652510	1.20221198	1.22886395
F	9.0	-2.86170912	1.43020403	-0.93876499

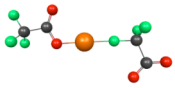
Sum of electronic and zero-point Energies= -1199.553750



Conformer #2 $[CF_3CO_2AuO_2CCF_3]^-$

Au	79.0	-0.20047501	-0.43367800	-0.14594500
C	6.0	2.68386698	-0.24240500	0.34430099
C	6.0	4.03329420	0.46991900	0.00632800
O	8.0	1.72653198	0.27449399	-0.34559301
O	8.0	2.68430901	-1.14654195	1.16657603
F	9.0	4.34346485	0.35888201	-1.31212795
F	9.0	5.07197523	-0.04556900	0.69719201
F	9.0	3.98797989	1.79683602	0.29417101
C	6.0	-3.27240205	-0.64256603	0.02217300
C	6.0	-3.29749298	0.92065603	0.14875400
O	8.0	-4.35497093	-1.21421397	0.00183500
O	8.0	-2.11382294	-1.19844306	-0.04615400
F	9.0	-4.55251789	1.39919496	0.27777299
F	9.0	-2.60019898	1.35542202	1.23083699
F	9.0	-2.75986505	1.52463496	-0.94484198

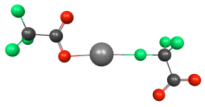
Sum of electronic and zero-point Energies= -1188.308464



TS $[CF_3CO_2CuO_2CCF_3]^- \rightarrow [CF_3CO_2CuF_3CCO_2]^-$
(- 69 cm^{-1},)

Cu	29.0	0.00026700	0.18046699	-0.00074700
O	8.0	-1.82273996	0.54920101	-0.03435100
C	6.0	-2.64416695	-0.44049001	0.02390800
O	8.0	-2.42280793	-1.64220798	0.10183600
C	6.0	-4.12314415	0.05606800	-0.02158700
F	9.0	-4.38849688	0.71036500	-1.18168998
F	9.0	-4.39244890	0.91546202	0.99399000
F	9.0	-5.00825596	-0.95653999	0.07229900
C	6.0	4.17980909	0.97406602	-0.01756700
C	6.0	3.35410810	-0.38689801	0.05175100
O	8.0	5.40013695	0.73735100	-0.00712600
O	8.0	3.48569703	2.00181603	-0.06682100
F	9.0	3.54230690	-1.21834004	-0.98592198
F	9.0	3.52939010	-1.09694195	1.17826295
F	9.0	1.92096603	-0.14445600	0.02977600

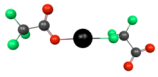
Sum of electronic and zero-point Energies=-1249.865706



TS $[CF_3CO_2AgO_2CCF_3]^- \rightarrow + [CF_3CO_2AgF_3CCO_2]^-$
(- 57 cm^{-11})

Ag	47.0	-0.09389500	0.29240999	0.04585800
O	8.0	-2.18916702	0.85828000	0.04254200
C	6.0	-2.83687806	-0.24164499	-0.00564800
O	8.0	-2.39653611	-1.39275301	-0.04279400
C	6.0	-4.38080215	-0.02873100	-0.00665600
F	9.0	-4.77130795	0.77060801	-1.03083897
F	9.0	-4.79163408	0.56311899	1.14458704
F	9.0	-5.06577206	-1.18420398	-0.12349800
C	6.0	4.39359093	0.89536399	-0.09268400
C	6.0	3.52629495	-0.41975400	0.13355900
O	8.0	5.61059284	0.64319903	-0.05597700
O	8.0	3.72358489	1.92957497	-0.26419500
F	9.0	3.69732404	-1.36942601	-0.81048101
F	9.0	3.71481395	-1.01197195	1.33241999
F	9.0	2.13041091	-0.14514901	0.09981800

Sum of electronic and zero-point Energies= -1199.510570

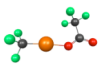


TS $[CF_3CO_2AgO_2CCF_3]^- \rightarrow + [CF_3CO_2AgF_3CCO_2]^-$
(- 19 cm^{-1})

Au	79.0	0.07226100	0.13998900	-0.30770400
O	8.0	-1.91663694	0.49446899	0.04341600
C	6.0	-2.74624491	-0.48728499	-0.11265500
O	8.0	-2.55050492	-1.64332402	-0.44604599
C	6.0	-4.20143080	-0.00600600	0.18480600
F	9.0	-4.60463190	0.91762000	-0.72426099
F	9.0	-4.30490923	0.56162298	1.41050506
F	9.0	-5.08546877	-1.02129400	0.13977800
C	6.0	4.36517191	0.88841498	-0.12157700
C	6.0	3.29469895	-0.27099001	0.13888600
O	8.0	5.53383303	0.49028701	0.00400100
O	8.0	3.82738900	1.98113501	-0.36314800
F	9.0	3.70337510	-1.53344405	-0.02647800
F	9.0	2.69950509	-0.19426300	1.34774303
F	9.0	2.18421793	-0.15801200	-0.80125397

Sum of electronic and zero-point Energies= -1188.255522

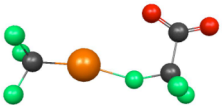
Figure S19. DFT calculated Calculated Cartesian coordinates and energies (Hartrees) for species related to the isomerization of $[CF_3CO_2MO_2CCF_3]^-$ M = Cu, Ag and Au.



Conformer #2 $[CF_3CuO_2CCF_3]^-$

Cu	29.0	0.82523799	0.49817801	0.00313900
C	6.0	2.61929488	-0.16113800	-0.00113500
F	9.0	3.20757103	-0.30145299	1.25681496
F	9.0	3.53985000	0.63052702	-0.69158298
F	9.0	2.79494691	-1.41962194	-0.57353503
C	6.0	-2.12219191	0.95551503	-0.00133600
C	6.0	-2.38741302	-0.59148300	-0.00021400
O	8.0	-3.10686207	1.68877101	-0.00686900
O	8.0	-0.88837200	1.28312695	0.00485400
F	9.0	-3.70209789	-0.90272200	-0.01135400
F	9.0	-1.83395100	-1.19745100	-1.08647501
F	9.0	-1.85389495	-1.19147098	1.09959805

Sum of electronic and zero-point Energies= -1061.328430



TS $[CF_3CuO_2CCF_3]^-$ → $[CF_3CuF_3CCO_2]^-$
(- 66 cm^{-1}, -30cm^{-1})

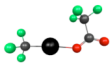
Cu	29.0	0.22987001	0.25966799	-0.07013200
C	6.0	-1.63326097	0.63606602	0.10412900
F	9.0	-2.21823907	1.19689095	-1.02271402
F	9.0	-1.96460199	1.51445997	1.12181699
F	9.0	-2.42351389	-0.47958899	0.36172700
C	6.0	3.94822788	0.96971399	-0.00075500
C	6.0	3.40038800	-0.51748800	0.01705400
O	8.0	5.18358517	1.03791702	-0.09914000
O	8.0	3.03361511	1.81008506	0.12356900
F	9.0	3.99637604	-1.41395295	-0.79334599
F	9.0	3.37251806	-1.06031406	1.25549698
F	9.0	2.04646611	-0.54753298	-0.41891801

Sum of electronic and zero-point Energies= -1061.286184

Conformer #2 $[CF_3AgO_2CCF_3]^-$

Ag	47.0	-0.73924899	-0.43714499	0.00238500
C	6.0	-2.72770500	0.25740501	-0.00164800
F	9.0	-3.31059408	0.39125901	1.25517297
F	9.0	-3.63185501	-0.54921103	-0.68806100
F	9.0	-2.91595697	1.50911498	-0.57647800
C	6.0	2.42900705	-0.90701401	-0.00181900
C	6.0	2.62408590	0.65171099	-0.00004600
O	8.0	3.45039797	-1.59117496	-0.00887500
O	8.0	1.21300697	-1.28721905	0.00537100
F	9.0	3.92129803	1.02795601	-0.00973300
F	9.0	2.04216194	1.23304999	-1.08687305
F	9.0	2.05996394	1.22786999	1.09897399

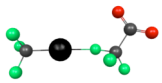
Sum of electronic and zero-point Energies= -1010.966423



Conformer #2 $[CF_3AuO_2CCF_3]^-$

Au	79.0	-0.61187702	-0.35188001	0.00078900
C	6.0	-2.49357891	0.38622099	-0.00107700
F	9.0	-3.06683397	0.51595998	1.25313902
F	9.0	-3.41227603	-0.37632701	-0.70458800
F	9.0	-2.62102795	1.64781797	-0.55381799
C	6.0	2.51433706	-0.85269898	-0.00139800
C	6.0	2.72149491	0.70308298	-0.00015200
O	8.0	3.52858400	-1.54401696	-0.00528200
O	8.0	1.29832399	-1.25163805	0.00303300
F	9.0	4.02685881	1.05293596	-0.01126900
F	9.0	2.15268207	1.29071903	-1.08690798
F	9.0	2.17276907	1.28490806	1.10026705

Sum of electronic and zero-point Energies= -999.746532



TS $[CF_3AuO_2CCF_3]^-$ → $[CF_3AuF_3CCO_2]^-$ (- 23cm^{-1})

Au	79.0	-0.70596302	-0.03851300	-0.17292599
C	6.0	-2.68229198	0.11828800	0.19665700
C	6.0	3.57432508	0.81154197	0.06645600
C	6.0	2.60803008	-0.45660600	0.10275600
O	8.0	4.76889896	0.50098801	0.21235301
O	8.0	2.95929408	1.88391995	-0.06122800
F	9.0	3.13018489	-1.61949503	-0.31977400
F	9.0	2.07254601	-0.68104500	1.32601798
F	9.0	1.46649897	-0.27470401	-0.75299299
F	9.0	-3.00868511	1.13795495	1.05322599
F	9.0	-3.23063993	-1.00744796	0.76236802
F	9.0	-3.43600011	0.34739700	-0.92918903

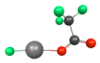
Sum of electronic and zero-point Energies= -999.702643

Figure S20. DFT calculated Calculated Cartesian coordinates and energies (Hartrees) for species related to the isomerization of $[CF_3MO_2CCF_3]^-$ M = Cu, Ag and Au.

Conformer #2 $[FCuO_2CCF_3]^-$

Cu	29.0	-1.69082499	0.19305401	0.00017100
O	8.0	-0.11503300	1.19440496	0.00138100
C	6.0	1.58980095	-0.50439501	-0.00002200
C	6.0	1.14576101	1.00169396	-0.00028700
O	8.0	2.04300690	1.84201705	-0.00144300
F	9.0	-3.27483201	-0.65814900	-0.00091200
F	9.0	2.93402100	-0.65584600	-0.00348500
F	9.0	1.12278700	-1.17064297	-1.09128296
F	9.0	1.12877595	-1.16799903	1.09538996

Sum of electronic and zero-point Energies= -823.554302



Conformer #2 $[FAgO_2CCF_3]^-$

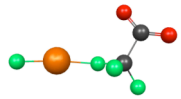
Ag	47.0	1.48566997	0.15424500	-0.00241900
O	8.0	-0.33604300	1.24792898	-0.00312900
C	6.0	-1.95068097	-0.53234798	-0.00011600
C	6.0	-1.58452201	0.99601102	0.00142700
O	8.0	-2.52742100	1.78615201	0.00710700
F	9.0	3.32310390	-0.70562202	0.00974200
F	9.0	-1.44458103	-1.17281604	-1.09157395
F	9.0	-3.28295708	-0.76048797	-0.00471800
F	9.0	-1.45196199	-1.17264295	1.09477603

Sum of electronic and zero-point Energies= -773.185852

Conformer #2 $[FAuO_2CCF_3]^-$

Au	79.0	-1.13483703	0.11185800	-0.00002200
F	9.0	-2.87782693	-0.85709101	0.00020300
C	6.0	1.84844899	0.97617197	-0.00000400
C	6.0	2.24237490	-0.54297000	0.00000000
O	8.0	2.77327800	1.78330100	0.00020900
O	8.0	0.59558398	1.24776995	-0.00020700
F	9.0	3.58335710	-0.72042501	-0.00015800
F	9.0	1.76714897	-1.19364202	1.09424698
F	9.0	1.76691103	-1.19379103	-1.09409595

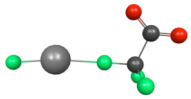
Sum of electronic and zero-point Energies= -761.944458



TS $[FCuO_2CCF_3]^- \rightarrow [FCuF_3CCO_2]^-$ (- 33 cm^{-1})

Cu	29.0	-1.78928196	0.07669000	-0.13011999
F	9.0	-3.50553012	0.22846700	0.33494601
C	6.0	2.20975304	0.76382202	0.01762900
C	6.0	1.23523903	-0.49676299	0.02565000
O	8.0	3.40209603	0.43475801	0.13893500
O	8.0	1.60455894	1.84571505	-0.06786800
F	9.0	1.72163200	-1.63285506	-0.49596101
F	9.0	0.75345403	-0.79189599	1.25397301
F	9.0	0.04888800	-0.25595501	-0.76570600

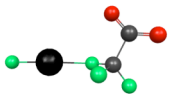
Sum of electronic and zero-point Energies= -823.510043



TS $[FAgO_2CCF_3]^- \rightarrow [FAgF_3CCO_2]^-$ (- 58 cm^{-1}, $^{-1}$)

Ag	47.0	1.76829600	0.05517100	-0.00008400
O	8.0	-3.93531489	0.63157201	-0.00119000
O	8.0	-2.01174212	1.87946904	0.00069500
C	6.0	-2.71047091	0.85051298	-0.00020300
C	6.0	-1.88388801	-0.50876600	0.00015300
F	9.0	-0.48347399	-0.29252601	-0.00013800
F	9.0	-2.09719706	-1.28384900	1.08757997
F	9.0	-2.09748793	-1.28488398	-1.08644497
F	9.0	3.79290199	0.11327600	-0.00008500

Sum of electronic and zero-point Energies= -773.146196

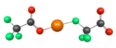


TS $[FAuO_2CCF_3]^- \rightarrow [FAuF_3CCO_2]^-$ (- 28 cm^{-1})

Au	79.0	-1.23664999	0.01345300	-0.06333000
F	9.0	-3.14739203	0.27541700	0.38188100
C	6.0	2.93840098	0.81392199	0.00502100
C	6.0	2.03366494	-0.49887100	0.05644300
O	8.0	4.15190792	0.55148101	0.05622500
O	8.0	2.26940489	1.85976100	-0.03545800
F	9.0	2.56978703	-1.61970699	-0.44846699
F	9.0	1.58307695	-0.79039299	1.29481399
F	9.0	0.82701898	-0.33676401	-0.73176497

Sum of electronic and zero-point Energies= -761.895577

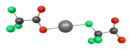
Figure S21. DFT calculated Calculated Cartesian coordinates and energies (Hartrees) for species related to the isomerization of $[FMO_2CCF_3]^-$ M = Cu, Ag and Au.



$[CF_3CO_2CuF_3C\ CO_2]^-$

Cu	29.0	0.08160500	0.12763999	-0.03485200
O	8.0	5.38875389	-0.50366199	-0.09179700
O	8.0	4.46767378	1.59617805	0.01876900
C	6.0	4.49586821	0.35866401	-0.02644800
C	6.0	3.06478000	-0.34929901	0.03296100
F	9.0	1.96974003	0.60796499	-0.06524600
F	9.0	2.80760908	-1.21221197	-0.96664202
F	9.0	2.80988312	-0.99099702	1.19010997
O	8.0	-1.69533396	-0.41148701	-0.03121800
C	6.0	-2.61858201	0.48662999	-0.01416400
O	8.0	-2.52757001	1.70683503	-0.00070600
C	6.0	-4.03515577	-0.16814899	0.00472300
F	9.0	-4.24115896	-0.85040700	1.16184199
F	9.0	-4.19777679	-1.04942596	-1.01386595
F	9.0	-5.02342796	0.74268103	-0.09865300

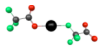
Sum of electronic and zero-point Energies= -1249.868823



$[CF_3CO_2AgF_3C\ CO_2]^-$

Ag	47.0	0.04411100	0.05135100	-0.08413500
O	8.0	5.56626987	-0.56666100	0.14149500
O	8.0	4.76510477	1.55153096	-0.22773799
C	6.0	4.72028399	0.33013701	-0.01755700
C	6.0	3.24421692	-0.27660200	0.07179600
F	9.0	2.22036505	0.70156503	-0.06486000
F	9.0	2.95635390	-1.17615700	-0.90119201
F	9.0	2.95606899	-0.87716699	1.25053406
O	8.0	-1.98272097	-0.67742598	-0.18177500
C	6.0	-2.75563192	0.31186599	0.06233100
O	8.0	-2.45859098	1.47982395	0.31503201
C	6.0	-4.26154518	-0.09004000	0.02115900
F	9.0	-4.54585218	-1.02405798	0.96484703
F	9.0	-4.59956503	-0.61953598	-1.18202996
F	9.0	-5.08489084	0.95492899	0.23846400

Sum of electronic and zero-point Energies= -1199.512526



$[CF_3CO_2AuF_3C\ CO_2]^-$

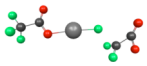
Au	79.0	-0.04616500	-0.08905800	-0.09477100
O	8.0	-5.57713413	0.39728600	0.40344301
O	8.0	-4.63698483	-1.41235495	-0.64939803
C	6.0	-4.67776680	-0.32590401	-0.05588800
C	6.0	-3.24802303	0.37109700	0.14231300
F	9.0	-2.16280198	-0.59415102	0.03691300
F	9.0	-2.95507312	1.28130996	-0.80816197
F	9.0	-3.03112888	0.95242500	1.33165395
O	8.0	1.93693697	0.36853099	-0.33236000
C	6.0	2.81281090	-0.37934700	0.26078999
O	8.0	2.66591001	-1.36592901	0.96064597
C	6.0	4.24970818	0.16618700	-0.01325300
F	9.0	4.43011808	1.37194097	0.58362401
F	9.0	4.48666716	0.33140299	-1.33665502
F	9.0	5.20075893	-0.66035998	0.46201399

Sum of electronic and zero-point Energies= -1188.255897

TS $[CF_3CO_2CuF_3CCO_2]^- \rightarrow [CF_3CO_2CuF]^- + CF_2CO_2$ (- 374 cm^{-1})

Cu	29.0	-0.01705700	0.28718299	0.04920100
O	8.0	5.29749107	-0.67837203	-0.04841400
O	8.0	4.88347721	1.61171901	0.20760000
C	6.0	4.63856983	0.44477800	0.06893800
C	6.0	3.56294298	-0.55210501	-0.06487000
F	9.0	1.75621700	0.70707601	0.04528300
F	9.0	3.15633106	-1.01431298	-1.21873295
F	9.0	3.11768794	-1.26244199	0.93917203
O	8.0	-1.79913104	-0.26563501	0.08309200
C	6.0	-2.79597807	0.52268499	-0.08068700
O	8.0	-2.84282088	1.72966099	-0.29122600
C	6.0	-4.14424419	-0.26483199	0.01887600
F	9.0	-4.28468895	-0.87365103	1.22756004
F	9.0	-4.22883797	-1.24084103	-0.92549998
F	9.0	-5.22617579	0.52745497	-0.14431401

Sum of electronic and zero-point Energies= -1249.840990



TS $[CF_3CO_2AgF_3CCO_2]^- \rightarrow [CF_3CO_2AgF]^- + CF_2CO_2$ (- 382 cm^{-1})

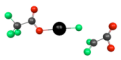
Ag	47.0	0.03061100	0.20030200	-0.14878900
O	8.0	-5.52811384	-0.63021398	0.19814900
O	8.0	-5.09134579	1.61718297	-0.30725101
C	6.0	-4.85560417	0.46827999	-0.05602000
C	6.0	-3.82194209	-0.55358201	0.15155900
F	9.0	-1.98715103	0.62707901	-0.13797900
F	9.0	-3.38541389	-0.90792900	1.33542001
F	9.0	-3.42279792	-1.37365794	-0.79024398
O	8.0	2.06602001	-0.40884700	-0.24782100
C	6.0	2.96383810	0.38927901	0.18735901
O	8.0	2.86862803	1.50586903	0.69062501
C	6.0	4.39355803	-0.22424901	0.01741500
F	9.0	4.67483902	-0.48695901	-1.28765297
F	9.0	4.52001286	-1.39914405	0.69208598
F	9.0	5.37392092	0.58900100	0.46854401

Sum of electronic and zero-point Energies= -1199.474886

(CF_2CO_2)

O	8.0	0.31390399	-0.00121500	1.13978899
O	8.0	2.07964206	0.00008400	-0.48517999
C	6.0	0.96919900	-0.00071400	-0.07084900
C	6.0	-0.48286301	-0.00040000	-0.06215400
F	9.0	-1.22713101	-1.08855700	-0.24735899
F	9.0	-1.22468996	1.09030497	-0.24584700

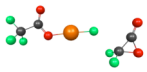
Sum of electronic and zero-point Energies= -426.272303



TS $[CF_3CO_2AuF_3CCO_2]^- \rightarrow [CF_3CO_2AuF]^- + CF_2CO_2$ (- 366 cm^{-1})

Au	79.0	0.01739600	0.18678600	0.05871100
O	8.0	-5.49220514	-0.69846100	-0.27515501
O	8.0	-4.91935301	1.52693403	-0.70711398
C	6.0	-4.77139807	0.38108000	-0.37847000
C	6.0	-3.76840091	-0.58967203	0.10878300
F	9.0	-1.94470704	0.63648200	0.26242399
F	9.0	-3.64061403	-0.90741903	1.36846495
F	9.0	-3.15001512	-1.42629099	-0.67931002
O	8.0	1.98133397	-0.37679100	-0.18510300
C	6.0	2.95697904	0.42243201	0.07177700
O	8.0	2.97145605	1.58489096	0.44864500
C	6.0	4.31924105	-0.31582901	-0.14036401
F	9.0	4.39231205	-0.93708599	-1.34457600
F	9.0	4.51014423	-1.27067602	0.81087399
F	9.0	5.37480211	0.52312702	-0.06884200

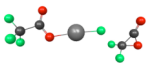
Sum of electronic and zero-point Energies= -1188.230813



$[CF_3CO_2CuF]^-(CF_2CO_2)$

Cu	29.0	-0.08447100	0.26129699	0.05792400
O	8.0	5.36962605	-0.52583897	-0.05283900
O	8.0	4.80768585	1.77519000	0.20113000
C	6.0	4.60778379	0.61150497	0.07092500
C	6.0	3.89640999	-0.64142698	-0.07026700
F	9.0	1.68378997	0.64668298	0.05445300
F	9.0	3.43104601	-1.10701704	-1.22016799
F	9.0	3.42407489	-1.34643495	0.94781703
O	8.0	-1.87922001	-0.26367399	0.09194100
C	6.0	-2.87368989	0.52029902	-0.09222300
O	8.0	-2.92441392	1.72271395	-0.33083299
C	6.0	-4.22300100	-0.26602200	0.01775300
F	9.0	-4.35730219	-0.87938398	1.22516501
F	9.0	-4.31724215	-1.23979199	-0.92931402
F	9.0	-5.30712080	0.52695698	-0.13485400

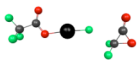
Sum of electronic and zero-point Energies= -1249.844212



$[CF_3CO_2AgF]^-(CF_2CO_2)$

Ag	47.0	0.08461100	0.18377700	-0.15679500
O	8.0	-5.61261702	-0.48708501	0.19080700
O	8.0	-5.01994085	1.76991999	-0.28398201
C	6.0	-4.83589315	0.61782700	-0.05931700
C	6.0	-4.13929176	-0.63147599	0.16375101
F	9.0	-1.92490399	0.56898099	-0.15301800
F	9.0	-3.64210105	-1.00927103	1.33236599
F	9.0	-3.72352004	-1.43375003	-0.80602801
O	8.0	2.13293409	-0.38865101	-0.24939600
C	6.0	3.03356290	0.39207301	0.20731100
O	8.0	2.94940996	1.49545801	0.74166697
C	6.0	4.46024179	-0.22662801	0.02120100
F	9.0	4.73834276	-0.46745700	-1.28925204
F	9.0	4.58304501	-1.41512895	0.67359501
F	9.0	5.44839001	0.57158101	0.48443800

Sum of electronic and zero-point Energies= -1199.477196

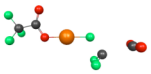


$[CF_3CO_2AuF]^-(CF_2CO_2)$

Au	79.0	-6.22285080	2.67548037	1.12800705
O	8.0	-0.48686504	2.37763834	1.62927306
O	8.0	-1.46502149	4.53755426	1.87575305
C	6.0	-1.43343151	3.37619352	1.63048518
C	6.0	-1.87043905	2.05061841	1.24327290
F	9.0	-4.25800180	2.98603153	0.87098438
F	9.0	-1.97600174	1.64080226	-0.01294586
F	9.0	-2.45012093	1.18984532	2.06726599
O	8.0	-8.21681309	2.24919534	1.43203032
C	6.0	-9.15616226	3.07962441	1.15082610
O	8.0	-9.12776852	4.21743536	0.70284063
C	6.0	-10.54943943	2.42703152	1.43648493
F	9.0	-10.61211681	1.83283937	2.65515709
F	9.0	-10.83623409	1.46671116	0.51369649
F	9.0	-11.55866337	3.32453346	1.38961232

Sum of electronic and zero-point Energies= -1188.235113

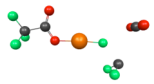
Figure S22. DFT Calculated Cartesian coordinates and energies (Hartrees) for species related to the fragmentation of $[CF_3CO_2MF_3CCO_2]^-$ M = Cu, Ag and Au.



TS $[CF_3CO_2CuF_3C\ CO_2]^-$→ $[CF_3CO_2CuF]^-$ + CF_2 + CO_2
(- 114 cm^{-1})

Cu	29.0	-0.00727700	0.10230900	0.04395700
C	6.0	2.71388102	0.55209398	-0.02065400
C	6.0	4.13712978	-0.09306300	0.00727100
O	8.0	1.80181801	-0.34869599	0.04864900
O	8.0	2.62570190	1.77227294	-0.09322300
F	9.0	4.37102222	-0.72488701	1.18904197
F	9.0	5.12257814	0.81614000	-0.15117900
F	9.0	4.29395294	-1.01827598	-0.97488201
C	6.0	-5.21364212	0.56874597	0.08693400
C	6.0	-3.07384396	-0.58779401	-0.09055600
O	8.0	-5.40724897	0.78367001	-1.05897403
O	8.0	-5.35421991	0.52535301	1.25956595
F	9.0	-2.67021108	-1.17433798	-1.25468504
F	9.0	-1.84793305	0.51737797	0.05553200
F	9.0	-2.65813303	-1.46798003	0.86718899

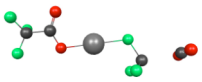
Sum of electronic and zero-point Energies= -1249.853243



$[CF_3CO_2CuF]^-(CF_2)(CO_2)$

Cu	29.0	0.18419400	0.09930200	0.09105500
C	6.0	-2.51817894	-0.57945400	-0.05497100
C	6.0	-3.97664809	-0.01555100	-0.00422100
O	8.0	-1.66374803	0.36236799	0.10137500
O	8.0	-2.36597490	-1.78414905	-0.22577700
F	9.0	-4.24781609	0.56873602	1.19443798
F	9.0	-4.91371012	-0.97096503	-0.19074699
F	9.0	-4.18636703	0.92930001	-0.95973402
C	6.0	4.27116919	-1.66906202	0.01846000
C	6.0	3.43209410	1.37393403	-0.09412500
O	8.0	4.22851801	-1.75528502	-1.14793801
O	8.0	4.37799406	-1.66056800	1.18397999
F	9.0	2.88654995	1.94248497	-1.18253100
F	9.0	2.01458406	-0.04034500	0.10389800
F	9.0	2.97936511	2.14435792	0.90972197

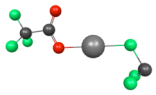
Sum of electronic and zero-point Energies= -1249.855398



TS $[CF_3CO_2AgF_3C\ CO_2]^-$→ $[CF_3CO_2AgF\ CF_2]^-$ + CO_2 (- 51 cm^{-1})

Ag	47.0	0.00467400	0.04250700	-0.03724100
C	6.0	3.15671611	-0.47053900	-0.02378100
F	9.0	2.11243391	0.66675699	-0.01427700
F	9.0	2.69616604	-1.16571295	-1.13650703
F	9.0	2.64320207	-1.22982299	1.02159297
O	8.0	-2.06018901	-0.55654401	-0.06874200
C	6.0	-2.86983705	0.42680201	0.02993200
O	8.0	-2.64217806	1.63137197	0.13177200
C	6.0	-4.35882616	-0.04805400	0.02235900
F	9.0	-4.63171911	-0.83509099	1.09752297
F	9.0	-4.65082884	-0.77659303	-1.08680499
F	9.0	-5.23659611	0.97767198	0.05719400
C	6.0	5.60474777	0.47317901	0.07018900
O	8.0	5.71442318	0.70242500	-1.07926500
O	8.0	5.76164484	0.34511700	1.22994304

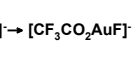
Sum of electronic and zero-point Energies= -1199.494026
(non-converged structure)



$[CF_3CO_2AgF\text{-}CF_2]^-$

Ag	47.0	-0.93017298	0.23809101	-0.00647100
C	6.0	2.00416708	0.38355100	-0.01789000
C	6.0	3.42536902	-0.26918700	0.01835100
O	8.0	1.08383703	-0.50056601	0.02650100
O	8.0	1.93006599	1.60968804	-0.07423800
F	9.0	3.64195204	-0.91863102	1.19453299
F	9.0	4.42254782	0.63287503	-0.11629100
F	9.0	3.58925009	-1.18341506	-0.97379500
C	6.0	-4.13382292	-0.11573200	-0.11819000
F	9.0	-3.48668408	-0.97059900	-1.02164900
F	9.0	-2.96978211	0.97668701	-0.01606800
F	9.0	-3.88254499	-0.76525301	1.08798301

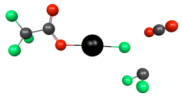
Sum of electronic and zero-point Energies= -1010.911608



TS $[CF_3CO_2AuF_3CCO_2]^-$→ $[CF_3CO_2AuF]^-$ + CF_2 + CO_2
(-130 cm^{-1})

Au	79.0	0.00246400	-0.02831400	-0.07619900
C	6.0	2.88189292	-0.52556598	0.01816700
C	6.0	4.32316208	0.07504200	0.07907400
O	8.0	2.00625205	0.42131200	0.05450600
O	8.0	2.74885511	-1.73593104	-0.07165100
F	9.0	4.62817621	0.71813703	-1.07984197
F	9.0	5.26297283	-0.87578601	0.26063001
F	9.0	4.46911716	0.97289598	1.08401000
C	6.0	-5.33596611	-0.63558400	0.08400300
C	6.0	-3.28768897	0.60318601	0.06540500
O	8.0	-5.42682791	-0.84528798	1.24512398
O	8.0	-5.59316015	-0.62695903	-1.07100499
F	9.0	-2.82456803	1.19126403	1.20035696
F	9.0	-2.05212593	-0.46122500	-0.18978600
F	9.0	-2.99068093	1.50241399	-0.91047299

Sum of electronic and zero-point Energies= -1188.241605



$[CF_3CO_2AuF]^-(CF_2)(CO_2)$

Au	79.0	0.12373500	0.06161600	-0.04983300
O	8.0	-1.89801002	0.33976200	0.22200900
C	6.0	-2.75409698	-0.51912802	-0.20955101
C	6.0	4.39344788	-1.70135903	0.25431001
C	6.0	3.60830498	1.34152198	0.02597200
O	8.0	4.64899778	-1.78163898	-0.88491601
O	8.0	4.20036697	-1.69434297	1.40861905
F	9.0	3.28813291	2.03823805	-1.06829500
F	9.0	2.13558197	-0.12370000	-0.26358899
F	9.0	2.95257092	1.97744095	1.00086904
O	8.0	-2.60647297	-1.57831597	-0.80168098
C	6.0	-4.20452595	-0.03816800	0.12188400
F	9.0	-4.38360405	0.15261100	1.45505905
F	9.0	-5.14298487	-0.92422199	-0.27494001
F	9.0	-4.49335003	1.14089799	-0.49034101

Sum of electronic and zero-point Energies= -1188.245106

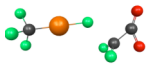
Figure S22. DFT Calculated Cartesian coordinates and energies (Hartrees) for species related to the fragmentation of $[CF_3CO_2MF_3CCO_2]^-$ M = Cu, Ag and Au.

[$CF_3CuF_3C\ CO_2$]$^-$

12may11_01b

Cu	29.0	0.96917403	0.24906600	-0.04430900
O	8.0	-4.39442778	-0.48766801	0.06961400
O	8.0	-3.47755504	1.59688699	-0.21061499
C	6.0	-3.49905992	0.36791301	-0.04559100
C	6.0	-2.06518888	-0.32506299	0.04802300
F	9.0	-0.98387903	0.62381601	-0.08894900
F	9.0	-1.81024504	-0.92517602	1.22812998
F	9.0	-1.81656206	-1.22894502	-0.92090499
C	6.0	2.85785294	-0.01323600	-0.01419100
F	9.0	3.34922290	-0.54504299	1.16758800
F	9.0	3.60249209	1.14298606	-0.19374400
F	9.0	3.33654308	-0.87219501	-0.99096799

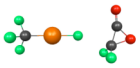
Sum of electronic and zero-point Energies= -1061.284400



TS [$CF_3CuF_3CCO_2$]$^-$→ [CF_3CuF]$^-$ + CF_2CO_2 (- 370 cm^{-1})

Cu	29.0	-1.10073400	0.33687499	-0.00215700
O	8.0	4.25107002	-0.60261500	0.00040000
O	8.0	3.81545496	1.70012105	0.00143900
C	6.0	3.57824302	0.52389801	0.00084500
C	6.0	2.53963590	-0.51413602	0.00000700
F	9.0	0.70036799	0.71875501	0.00076400
F	9.0	2.11938691	-1.10801697	-1.08827996
F	9.0	2.11880112	-1.10947299	1.08730197
C	6.0	-2.96588206	-0.05433800	0.00052600
F	9.0	-3.54932094	-0.19263899	1.26296496
F	9.0	-3.33347607	-1.23930299	-0.64295399
F	9.0	-3.78052711	0.89934701	-0.61540103

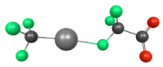
Sum of electronic and zero-point Energies= -1061.251777



[CF_3CuF]$^-$(CF_2CO_2)

Cu	29.0	-1.22815299	0.08376900	0.00006200
O	8.0	4.43786907	-0.02790800	-0.00012600
O	8.0	3.29850698	2.06277204	0.00000100
C	6.0	3.40632701	0.87948197	-0.00003300
C	6.0	3.04058290	-0.52110201	-0.00001800
F	9.0	0.59763598	0.13583300	0.00013300
F	9.0	2.74377394	-1.21165299	-1.09078896
F	9.0	2.74394608	-1.21167397	1.09078896
C	6.0	-3.13265705	0.01222500	-0.00002900
F	9.0	-3.76349902	0.61202502	1.09588003
F	9.0	-3.68690300	-1.27346301	-0.00649200
F	9.0	-3.76385307	0.62317002	-1.08955503

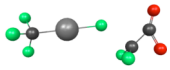
Sum of electronic and zero-point Energies= -1061.254126



[$CF_3AgF_3C\ CO_2$]$^-$

Ag	47.0	0.88450199	0.20859200	-0.03225300
O	8.0	-4.69101906	-0.58392799	-0.01111000
O	8.0	-3.86296010	1.55449295	0.03462000
C	6.0	-3.83033490	0.31392300	0.00665100
C	6.0	-2.36370897	-0.31466901	0.00791500
F	9.0	-1.33597803	0.66290098	-0.09603900
F	9.0	-2.05856705	-0.98521000	1.14521599
F	9.0	-2.11383891	-1.15705001	-1.02061999
C	6.0	2.97918701	-0.06903600	0.01841900
F	9.0	3.43079996	-1.15921998	-0.70097798
F	9.0	3.49898791	-0.26060501	1.28506303
F	9.0	3.70630288	0.99366802	-0.48709801

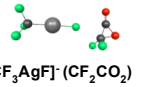
Sum of electronic and zero-point Energies= -1010.928699



TS [$CF_3AgF_3CCO_2$]$^-$→ [CF_3AgF]$^-$ + CF_2CO_2 (-369 cm^{-1})

Ag	47.0	-1.00768399	0.26028100	-0.00422000
O	8.0	4.59148407	-0.57425302	0.00845100
O	8.0	4.10712481	1.72193694	0.00722600
C	6.0	3.89236808	0.54238802	0.00549700
C	6.0	2.90622401	-0.54066902	-0.00025300
F	9.0	1.02717197	0.62845302	-0.00940700
F	9.0	2.50525188	-1.14684606	-1.09222496
F	9.0	2.49385810	-1.14822900	1.08669698
C	6.0	-3.07354689	-0.10899900	0.00336500
F	9.0	-3.65101504	-0.23455299	1.26563394
F	9.0	-3.47249103	-1.27735603	-0.64336300
F	9.0	-3.85588789	0.87064201	-0.60497397

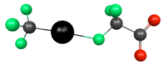
Sum of electronic and zero-point Energies= -1010.887964



[CF_3AgF]$^-$ (CF_2CO_2)

Ag	47.0	1.10006201	0.10576600	-0.02246900
O	8.0	-4.75895977	-0.11617000	0.04356700
O	8.0	-3.72034311	2.02455997	0.01313900
C	6.0	-3.77251506	0.83705401	0.01692600
C	6.0	-3.33529496	-0.54296601	0.00852600
F	9.0	-0.94869101	0.21349099	-0.05161700
F	9.0	-2.98459005	-1.21861506	1.09229398
F	9.0	-3.03957391	-1.22227502	-1.08939898
C	6.0	3.19347501	-0.02648100	0.01668400
F	9.0	3.73264503	-1.15176797	-0.60879201
F	9.0	3.76484299	-0.07392100	1.28907895
F	9.0	3.87731290	1.02600300	-0.59272301

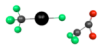
Sum of electronic and zero-point Energies= -1010.889448



[$CF_3AuF_3C\ CO_2$]$^-$

Au	79.0	-0.74088401	-0.16596000	-0.02425700
O	8.0	4.85396004	0.55388802	-0.10502100
O	8.0	3.96930599	-1.55702698	0.04325400
C	6.0	3.97082591	-0.31823900	-0.02271100
C	6.0	2.52579594	0.35895100	0.03298900
F	9.0	1.46391594	-0.60290402	-0.07851300
F	9.0	2.26780701	0.99188000	1.19802201
F	9.0	2.27158904	1.23463202	-0.95946801
C	6.0	-2.73655605	0.12613399	0.01790600
F	9.0	-3.14299989	1.26948798	-0.62280899
F	9.0	-3.25277710	0.22855200	1.28587699
F	9.0	-3.45383501	-0.88444102	-0.57407397

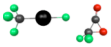
Sum of electronic and zero-point Energies= -999.703283



TS [$CF_3AuF_3C\ CO_2$]$^-$→ [CF_3AuF]$^-$ + CF_2CO_2 (- 374 cm^{-1})

Au	79.0	0.82136202	-0.22324200	-0.00353000
O	8.0	-4.74014711	0.65697700	0.01141200
O	8.0	-4.29931879	-1.64371705	0.01226900
C	6.0	-4.06560421	-0.46654201	0.00854800
C	6.0	-3.01967597	0.56652600	-0.00099300
F	9.0	-1.18966901	-0.67543203	-0.01250100
F	9.0	-2.60826492	1.15880406	-1.09243703
F	9.0	-2.59221601	1.16300297	1.08193398
C	6.0	2.78895903	0.20509601	0.00554400
F	9.0	3.35259700	0.33785099	1.26608002
F	9.0	3.13274598	1.38924897	-0.62982100
F	9.0	3.59436703	-0.74019301	-0.61205101

Sum of electronic and zero-point Energies= -999.670050

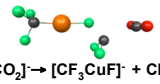


[CF_3AuF]$^-$ (CF_2CO_2)

Au	79.0	-0.88809699	0.17157499	0.00103900
O	8.0	4.87308884	-0.40097201	-0.00432400
O	8.0	4.15173912	1.86782598	-0.00307800
C	6.0	4.03307581	0.68544799	-0.00244400
C	6.0	3.40802789	-0.62081897	-0.00032300
F	9.0	1.12769794	0.50744700	0.00570700
F	9.0	2.98179889	-1.24160004	-1.08979106
F	9.0	2.98767996	-1.24083996	1.09188998
C	6.0	-2.87415195	-0.15976800	-0.00190600
F	9.0	-3.45263696	-0.28527400	1.25560296
F	9.0	-3.27805805	-1.31751704	-0.65600997
F	9.0	-3.63766599	0.83129197	-0.60682499

Sum of electronic and zero-point Energies= -999.672655

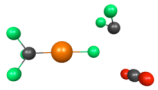
Figure S23. DFT Calculated Cartesian coordinates and energies (Hartrees) for species related to the fragmentation of [$CF_3MF_3CCO_2$]$^-$ M = Cu, Ag and Au.



TS $[CF_3CuF_3CCO_2]^- \rightarrow [CF_3CuF]^- + CF_2 + CO_2$ (- 79 cm^{-1})

Cu	29.0	-1.06760800	-0.24374600	0.00003000
C	6.0	-2.97182393	-0.11567300	0.00016500
F	9.0	-3.60236812	-0.70782101	1.09331405
F	9.0	-3.60271192	-0.71063203	-1.09126306
F	9.0	-3.48288894	1.17827404	-0.00142100
C	6.0	4.28135204	-0.59882098	0.00053000
C	6.0	2.03783703	0.64403301	-0.00051200
O	8.0	4.41794014	-0.67255098	-1.16744995
O	8.0	4.41819000	-0.67003202	1.16863799
F	9.0	1.60859096	1.38011503	-1.07247496
F	9.0	0.82513601	-0.49538600	-0.00002600
F	9.0	1.60839605	1.38123596	1.07059705

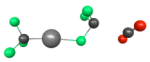
Sum of electronic and zero-point Energies= -1061.265368



$[CF_3CuF]\cdot(CF_2)(CO_2)$

Cu	29.0	0.84103698	-0.11870800	-0.03167500
C	6.0	2.74486399	-0.23744400	0.00426000
F	9.0	3.28056908	-1.37406397	-0.60631698
F	9.0	3.31633806	-0.26787800	1.27757597
F	9.0	3.42795110	0.80564702	-0.62145501
C	6.0	-3.47503090	-1.43856800	0.01212100
C	6.0	-2.27820897	1.40897298	0.02477700
O	8.0	-3.46719098	-1.49652100	1.18117404
O	8.0	-3.55550098	-1.46079302	-1.15542805
F	9.0	-1.70345199	2.01220798	1.08622396
F	9.0	-1.02062404	-0.07316500	-0.06218700
F	9.0	-1.76281500	2.08650303	-1.02210104

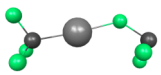
Sum of electronic and zero-point Energies= -1061.266040



TS $[CF_3AgF_3CCO_2]^- \rightarrow [CF_3AgFCF_2]^- + CO_2$ (- 25 cm^{-1})

Ag	47.0	0.94919199	-0.11075300	-0.19539000
C	6.0	-2.26076388	0.35349101	0.40540299
F	9.0	-1.20414197	-0.22035401	-0.61387002
F	9.0	-1.84327996	1.68354797	0.41780201
F	9.0	-1.70108294	-0.14541900	1.58454800
C	6.0	3.05404305	-0.06040000	0.01819700
F	9.0	3.49797893	0.92414498	0.94859701
F	9.0	3.76272297	0.24044500	-1.19574797
F	9.0	3.64992690	-1.28162003	0.46896201
C	6.0	-4.66214800	-0.30843601	-0.30794501
O	8.0	-5.07537699	0.85760301	-0.63266200
O	8.0	-4.54686594	-1.55750895	-0.07024200

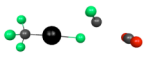
Sum of electronic and zero-point Energies= -1010.906611
(non-converged structure)



$[CF_3AgF\text{-}CF_2]^-$

Ag	47.0	-0.56201297	1.55085683	-1.50032365
C	6.0	-2.61213493	2.03548908	-1.35350859
F	9.0	-3.17691779	1.82240748	-0.10016766
F	9.0	-3.44665885	1.31736946	-2.20594954
F	9.0	-2.93328977	3.35841870	-1.63019073
C	6.0	2.78344417	1.84412658	-1.55941463
F	9.0	2.23424911	2.94703007	-2.21320343
F	9.0	1.47389472	0.87195063	-1.66362464
F	9.0	2.62808704	2.21284890	-0.22809057

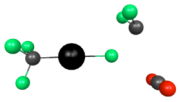
Sum of electronic and zero-point Energies= -822.323568



TS $[CF_3AuF_3CCO_2]^- \rightarrow [CF_3AuF]^- + CF_2 + CO_2$ (- 70 cm^{-1})

Au	79.0	-0.80469400	-0.16764100	-0.00932300
C	6.0	-2.81504703	-0.00293400	0.01151800
F	9.0	-3.36764503	0.09196600	1.27398801
F	9.0	-3.48121405	-1.06757200	-0.56612903
F	9.0	-3.30631590	1.10156298	-0.65477097
C	6.0	4.77881622	-0.58328497	0.01066100
C	6.0	2.52016306	0.69880801	0.00134000
O	8.0	4.91455889	-0.65315700	-1.15685296
O	8.0	4.90073490	-0.65359402	1.17970204
F	9.0	2.10154796	1.45703006	-1.05964005
F	9.0	1.31969595	-0.44142500	-0.03043100
F	9.0	2.08336592	1.41645205	1.08282399

Sum of electronic and zero-point Energies= -999.683560

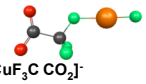


$[CF_3AuF]^- (CF_2)(CO_2)$

Au	79.0	-0.64235502	-0.08448000	-0.02685800
C	6.0	-2.65528488	-0.16816600	0.02578300
F	9.0	-3.23330212	0.43766201	1.12870002
F	9.0	-3.17962599	-1.45095897	0.04377900
F	9.0	-3.29138088	0.43053401	-1.04893005
C	6.0	3.86718702	-1.45109499	0.02448000
C	6.0	2.71055388	1.43121696	0.02476400
O	8.0	3.95707893	-1.48401797	-1.14210200
O	8.0	3.84932709	-1.49771500	1.19391203
F	9.0	2.19342303	2.13333392	-1.00301397
F	9.0	1.44460106	-0.04910600	-0.08316400
F	9.0	2.15073299	2.01587200	1.10230899

Sum of electronic and zero-point Energies= -999.684139

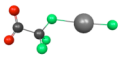
Figure S23. DFT Calculated Cartesian coordinates and energies (Hartrees) for species related to the fragmentation of $[CF_3MF_3CCO_2]^-$ M = Cu, Ag and Au.



[FCuF$_3$C CO$_2$]$^-$

Cu	29.0	-1.86584902	0.19155701	-0.01722800
O	8.0	3.46441698	-0.47141501	-0.10384200
O	8.0	2.53391099	1.62233901	0.01192200
C	6.0	2.56326199	0.38327500	-0.03360400
C	6.0	1.13659000	-0.32803601	0.02795700
F	9.0	0.04609200	0.62050402	-0.03558300
F	9.0	0.88045400	-1.17274296	-0.98871899
F	9.0	0.90677297	-0.99963701	1.17436802
F	9.0	-3.61955595	-0.12523200	-0.00908000

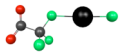
Sum of electronic and zero-point Energies= -823.510729



[FAgF$_3$C CO$_2$]$^-$

Ag	47.0	1.66729105	0.13348800	-0.01374300
O	8.0	-3.89159989	-0.55480301	-0.10965100
O	8.0	-3.05996895	1.57947397	0.00500100
C	6.0	-3.02988601	0.33929601	-0.03825500
C	6.0	-1.56640697	-0.29441100	0.03080000
F	9.0	-0.53130502	0.67566597	-0.04749000
F	9.0	-1.31196404	-0.94822299	1.19004095
F	9.0	-1.27886903	-1.15495801	-0.97296101
F	9.0	3.65854192	-0.21033201	0.00016800

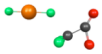
Sum of electronic and zero-point Energies= -773.148727



[FAuF$_3$C CO$_2$]$^-$

Au	79.0	1.28338397	0.09157800	-0.02138400
O	8.0	-4.26859617	-0.45209900	-0.00638400
O	8.0	-3.30156708	1.62752402	0.04129400
C	6.0	-3.35327291	0.38954499	0.00782600
C	6.0	-1.93384695	-0.34685099	0.00801300
F	9.0	-0.83936501	0.58339000	-0.17794000
F	9.0	-1.63929403	-0.96099502	1.17051005
F	9.0	-1.75682294	-1.24512804	-0.97666502
F	9.0	3.22400308	-0.25440499	0.13020501

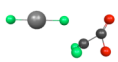
Sum of electronic and zero-point Energies= -761.896958



TS [FCuF$_3$C CO$_2$]$^-$→ [FCuF]$^-$ + CF$_2$CO$_2$ (- 358 cm^{-1})

Cu	29.0	-2.02693200	0.21963400	0.00001900
O	8.0	3.27229500	-0.58566201	-0.00010300
O	8.0	2.85138392	1.72217500	-0.00006400
C	6.0	2.60368991	0.54880899	-0.00005200
C	6.0	1.58490896	-0.50418901	0.00001200
F	9.0	-0.26865301	0.73427999	0.00015800
F	9.0	1.15955198	-1.09564102	-1.08905900
F	9.0	1.15970302	-1.09565496	1.08913505
F	9.0	-3.75504589	-0.29067600	-0.00012200

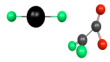
Sum of electronic and zero-point Energies= -823.475613



TS [FAgF$_3$C CO$_2$]$^-$→ [FAgF]$^-$ + CF$_2$CO$_2$ (-354 cm^{-1})

Ag	47.0	1.79744804	0.16272800	0.00001700
O	8.0	-3.72604990	-0.58769703	-0.00012400
O	8.0	-3.31599593	1.72496104	-0.00008000
C	6.0	-3.06121397	0.55397397	-0.00006400
C	6.0	-2.06106997	-0.51315397	0.00001300
F	9.0	-0.19991100	0.70788401	0.00018100
F	9.0	-1.63395095	-1.10643995	1.09049797
F	9.0	-1.63377202	-1.10642695	-1.09040904
F	9.0	3.75541496	-0.38293701	-0.00014500

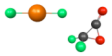
Sum of electronic and zero-point Energies= -773.105614



TS [FAuF$_3$C CO$_2$]$^-$→ [FAuF]$^-$ + CF$_2$CO$_2$ (-369 cm^{-1})

Au	79.0	-1.39551198	0.09038900	0.02162500
O	8.0	4.18060589	-0.43628100	-0.22831599
O	8.0	3.52600694	1.80922902	-0.10189200
C	6.0	3.40794992	0.61498600	-0.10293900
C	6.0	2.47703099	-0.51743799	0.01248500
F	9.0	0.56219798	0.54563701	0.32494500
F	9.0	1.96536696	-1.13294995	-1.02107298
F	9.0	2.27333498	-1.16539097	1.13068604
F	9.0	-3.32505012	-0.32613701	-0.27055901

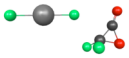
Sum of electronic and zero-point Energies= -761.865536



[FCuF]$^-$(CF$_2$CO$_2$)

Cu	29.0	2.10233498	0.20394000	0.00002600
O	8.0	-3.29143405	-0.48476401	-0.00057600
O	8.0	-2.76888895	1.83477795	-0.00047000
C	6.0	-2.54877806	0.66602200	-0.00035700
C	6.0	-1.80284703	-0.57520300	0.00006700
F	9.0	0.35264900	0.71471399	0.00152300
F	9.0	-1.33652306	-1.16036499	1.09147000
F	9.0	-1.33568001	-1.16005504	-1.09121704
F	9.0	3.83340096	-0.31199300	-0.00073700

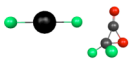
Sum of electronic and zero-point Energies= -823.476917



[FAgF]$^-$(CF$_2$CO$_2$)

Ag	47.0	-1.85570395	0.15218601	0.00064500
O	8.0	3.76336908	-0.49404499	-0.00479200
O	8.0	3.24871492	1.82683396	-0.00329900
C	6.0	3.02509093	0.65860599	-0.00252500
C	6.0	2.27215409	-0.57840002	-0.00007500
F	9.0	0.12988600	0.69448501	0.00782800
F	9.0	1.80315101	-1.16467500	-1.09022701
F	9.0	1.81013298	-1.16488397	1.09292996
F	9.0	-3.81673002	-0.39784300	-0.00497300

Sum of electronic and zero-point Energies= -773.106433



[FAuF]$^-$(CF$_2$CO$_2$)

Au	79.0	-1.46920002	0.06848500	0.02366400
O	8.0	4.25870419	-0.24824300	-0.20580100
O	8.0	3.40009499	1.96830904	-0.07993300
C	6.0	3.35817695	0.78070998	-0.08125600
C	6.0	2.82298589	-0.56382900	-0.01706100
F	9.0	0.49862599	0.41014901	0.31807601
F	9.0	2.30113292	-1.20583701	-1.05018401
F	9.0	2.58862209	-1.21503401	1.11238205
F	9.0	-3.42067003	-0.26396200	-0.26846299

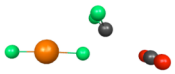
Sum of electronic and zero-point Energies= -761.867886

Figure S24. DFT Calculated Cartesian coordinates and energies (Hartrees) for species related to the fragmentation of [FMF$_3$CCO$_2$]$^-$ M = Cu, Ag and Au.

TS [FCuF$_3$C CO$_2$]$^-$→ [FCuF]$^-$ + CF$_2$ + CO$_2$ (- 38 cm^{-1})

Cu	29.0	-1.99669302	-0.32082900	-0.00016200
F	9.0	-3.79157996	-0.30465299	-0.00024500
C	6.0	3.36333799	-0.61332297	-0.00028600
C	6.0	1.06357205	0.73667997	0.00039800
O	8.0	3.47542310	-0.67562300	-1.16908002
O	8.0	3.47499204	-0.67760903	1.16843998
F	9.0	0.60436398	1.45847404	-1.07000005
F	9.0	-0.11274400	-0.45699400	-0.00011800
F	9.0	0.60433000	1.45759106	1.07138097

Sum of electronic and zero-point Energies= -823.490607



[FCuF]$^-$(CF$_2$)(CO$_2$)

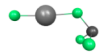
Cu	29.0	-1.99428499	-0.33959299	-0.00278600
F	9.0	-3.79003191	-0.34444699	-0.00468000
C	6.0	3.40606809	-0.64719498	-0.00464600
C	6.0	1.05375898	0.80260402	0.00674700
O	8.0	3.50086689	-0.68339300	-1.17418206
O	8.0	3.49071288	-0.71829098	1.16398096
F	9.0	0.57101703	1.51545799	-1.05806696
F	9.0	-0.11392400	-0.43747899	-0.00037000
F	9.0	0.57101202	1.50304794	1.07975996

Sum of electronic and zero-point Energies= -823.490577

TS [FAgF$_3$C CO$_2$]$^-$→ [FAgFCF$_2$]$^-$ + CO$_2$ (- 28 cm^{-1})

Ag	47.0	1.75955296	-0.21776301	-0.02896400
F	9.0	3.79017210	-0.19865200	-0.10845900
C	6.0	-3.86002707	-0.59413999	-0.11540400
C	6.0	-1.46604395	0.70560598	0.11994000
O	8.0	-3.89245510	-0.98361999	0.99316603
O	8.0	-4.03931904	-0.32323200	-1.24514306
F	9.0	-1.04296196	1.35777605	1.26892698
F	9.0	-0.39974800	-0.44255599	0.09241600
F	9.0	-0.93506002	1.50797606	-0.88067198

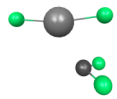
Sum of electronic and zero-point Energies= -773.125948
(non-converged structure)



[FAgF-CF$_2$]$^-$

Ag	47.0	-0.84391701	-0.09696400	-0.07247200
F	9.0	-2.74540591	0.45905200	0.40108600
C	6.0	2.48026109	-0.12888899	-0.19505300
F	9.0	2.10248494	1.19823694	-0.40817499
F	9.0	1.10961401	-0.81742501	-0.66536200
F	9.0	2.28692007	-0.24757200	1.18095303

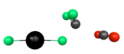
Sum of electronic and zero-point Energies= -584.542750



TS [FAgF-CF$_2$]- → [FAgF(CF$_2$)]-

Ag	47.0	0.72839397	0.16075900	0.00005500
F	9.0	-0.59323800	1.75753200	0.00044800
C	6.0	-1.56093800	-0.68255699	-0.00008100
F	9.0	2.33465195	-1.12563205	-0.00029400
F	9.0	-2.27814007	-0.28406101	1.04940903
F	9.0	-2.27806091	-0.28372401	-1.04950094

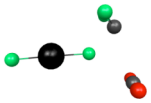
Sum of electronic and zero-point Energies= -584.528941



TS [FAuF$_3$C CO$_2$]$^-$→ [FAuF]$^-$ + CF$_2$ + CO$_2$ (- 82 cm^{-1})

Au	79.0	1.37178898	-0.14747100	-0.04745800
F	9.0	3.34695101	0.05836400	0.09118100
C	6.0	-4.16000414	-0.54159498	-0.10123100
C	6.0	-1.91110897	0.63984698	0.15481199
O	8.0	-4.23677683	-0.97213000	0.99315798
O	8.0	-4.36582088	-0.25058001	-1.22472894
F	9.0	-1.45949495	1.05052197	1.37596798
F	9.0	-0.70773798	-0.44429600	-0.20253900
F	9.0	-1.52681303	1.65123403	-0.67791897

Sum of electronic and zero-point Energies= -761.878938

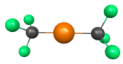


[FAuF]$^-$(CF$_2$)(CO$_2$)

Au	79.0	-1.16442394	-0.14688900	-0.05077200
F	9.0	-3.12985611	-0.37973300	0.19185400
C	6.0	3.20626712	-1.45019698	0.06425700
C	6.0	2.11727190	1.48320496	0.15297800
O	8.0	3.48042107	-1.38122594	-1.07172799
O	8.0	3.00304794	-1.59834802	1.20726502
F	9.0	1.77815700	2.28782797	-0.87150699
F	9.0	0.86311400	0.03358100	-0.31622699
F	9.0	1.39752698	1.97418702	1.17624605

Sum of electronic and zero-point Energies= -761.879649

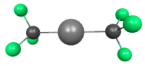
Figure S24. DFT Calculated Cartesian coordinates and energies (Hartrees) for species related to the fragmentation of [FMF$_3$CCO$_2$]$^-$ M = Cu, Ag and Au.



$[CF_3CuCF_3]^-$

Cu	29.0	-0.00003100	0.00072700	-0.00099400
C	6.0	-1.95050395	0.00030000	-0.00016300
F	9.0	-2.55768204	1.17889094	0.44992301
F	9.0	-2.55722904	-0.20127600	-1.24546397
F	9.0	-2.55368209	-0.97955400	0.79738098
C	6.0	1.95043004	0.00005700	0.00006800
F	9.0	2.55615401	-1.15968001	-0.49862501
F	9.0	2.55726194	1.01184201	-0.75390899
F	9.0	2.55532789	0.14719801	1.25396204

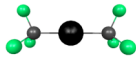
Sum of electronic and zero-point Energies= -872.734923
Zero-point correction= 0.024244



$[CF_3AgCF_3]^-$

Ag	47.0	-0.00000800	-0.00176500	0.00193900
C	6.0	-2.14146304	0.00042000	-0.00069000
F	9.0	-2.74462104	-0.53677499	-1.14143705
F	9.0	-2.74718904	-0.71586901	1.03555095
F	9.0	-2.73998904	1.25919795	0.10200100
C	6.0	2.14173794	0.00137900	-0.00053700
F	9.0	2.74781203	0.40084499	1.19330394
F	9.0	2.74068308	-1.23582697	-0.25312501
F	9.0	2.74316001	0.83644700	-0.94559997

Sum of electronic and zero-point Energies= -822.376753
Zero-point correction= 0.023906



$[CF_3AuCF_3]^-$

Au	79.0	0.00000000	0.00028000	-0.00003400
C	6.0	-2.08800411	-0.00008300	-0.00006700
F	9.0	-2.68125606	-0.67542303	-1.06325996
F	9.0	-2.68080592	-0.58391303	1.11632895
F	9.0	-2.68199396	1.25809097	-0.05277400
C	6.0	2.08799696	-0.00015700	0.00002900
F	9.0	2.68118000	-0.58725101	1.11440396
F	9.0	2.68111300	-0.67212403	-1.06543398
F	9.0	2.68176603	1.25832105	-0.04894300

Sum of electronic and zero-point Energies= -811.172007
Zero-point correction= 0.024867

$[FCuCF_3]^-$

Cu	29.0	-0.88754898	-0.00009200	-0.00012200
C	6.0	1.01823604	0.00002900	-0.00006300
F	9.0	1.62790704	1.24405599	-0.21252300
F	9.0	1.62790406	-0.43778101	1.18360901
F	9.0	1.62830496	-0.80609399	-0.97079498
F	9.0	-2.70305991	0.00009600	0.00014400

Sum of electronic and zero-point Energies= -634.967555
Zero-point correction= 0.013975

$[FAgCF_3]^-$

Ag	47.0	0.75497597	-0.00026800	-0.00012700
C	6.0	-1.34164596	-0.00003400	0.00000900
F	9.0	-1.94607198	-0.27626300	1.22976100
F	9.0	-1.94541502	1.20360696	-0.37519401
F	9.0	-1.94687796	-0.92639798	-0.85419399
F	9.0	2.79014492	0.00047700	0.00028400

Sum of electronic and zero-point Energies= -584.602350
Zero-point correction= 0.013469

$[FAuCF_3]^-$

Au	79.0	0.53109300	-0.00007500	0.00016100
C	6.0	-1.48357105	0.00009200	0.00001200
F	9.0	-2.07825208	1.25866306	-0.00163700
F	9.0	-2.07813001	-0.63031298	-1.08934903
F	9.0	-2.07927394	-0.62799299	1.09009194
F	9.0	2.56288695	0.00024000	-0.00052700

Sum of electronic and zero-point Energies= -573.38677
Zero-point correction= 0.014204

Figure S25: Calculated Cartesian coordinates and energies (Hartrees) of $[CF_3MF]^-$ and $[CF_3MCF_3]^-$, M = Cu, Ag and Au.

TS $[CF_3CuCF_3]^-$ → $[CF_2(F)CuCF_3]^-$ (- 78 cm^{-1})

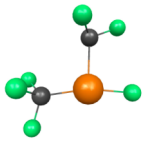
Cu	29.0	0.16618700	0.06177400	0.00003100
C	6.0	-1.80659997	-0.12945201	-0.00008500
F	9.0	-2.30684710	-1.44363999	-0.00544700
F	9.0	-2.46537495	0.43678701	1.09634197
F	9.0	-2.46646810	0.44607100	-1.09094298
C	6.0	1.93340099	-0.54571497	-0.00018500
F	9.0	1.12826896	1.77340496	0.00041700
F	9.0	2.74519396	-0.48127899	1.05485106
F	9.0	2.74520111	-0.48028100	-1.05514002

Sum of electronic and zero-point Energies= -872.679579

$[CF_2(F)CuCF_3]^-$

Cu	29.0	0.18980999	0.76795101	-0.00313200
C	6.0	-1.25583005	-0.60511500	-0.00665900
F	9.0	-0.88228101	-1.92661798	-0.25935799
F	9.0	-1.93176496	-0.69140899	1.20418704
F	9.0	-2.25840211	-0.37672400	-0.93413401
C	6.0	1.80975497	-0.08278200	0.00285200
F	9.0	-0.51143998	2.49405408	0.00345700
F	9.0	2.29487109	-0.76867503	1.06366706
F	9.0	2.30812311	-0.74654001	-1.06518698

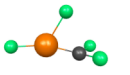
Sum of electronic and zero-point Energies= -872.688420



TS $[CF_2(F)CuCF_3]^-$ → CF_2 + $[FCuCF_3]^-$ (-33 cm^{-1})

Cu	29.0	0.17549101	0.74638700	-0.01955900
C	6.0	-1.55392897	-0.14583100	0.04396900
F	9.0	-1.78810406	-1.09955394	-0.94412702
F	9.0	-1.83930004	-0.83071798	1.22084403
F	9.0	-2.64950705	0.71924502	-0.08845400
C	6.0	1.49012804	-0.93882501	0.42909601
F	9.0	1.55155897	1.91018605	-0.25790200
F	9.0	1.41505599	-1.78114200	-0.62866700
F	9.0	2.78735900	-0.59994102	0.44595301

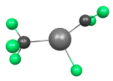
Sum of electronic and zero-point Energies=-872.678844



TS $[FCuCF_3]^-$ → $[CF_2(F)CuF]^-$ (-167 cm^{-1})

Cu	29.0	-0.69001102	-0.12810101	0.00000000
F	9.0	-2.52525496	-0.34794199	0.00000000
C	6.0	1.10340405	-0.46987501	0.00000000
F	9.0	0.20490099	1.68477905	-0.00000100
F	9.0	1.90406001	-0.30540699	1.05762398
F	9.0	1.90406001	-0.30540901	-1.05762398

Sum of electronic and zero-point Energies= -634.908855



TS $[CF_3AgCF_3]^-$ → $[CF_2(F)AgCF_3]^-$ (-58 cm^{-1})

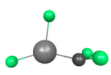
Ag	47.0	-0.19509900	0.13639300	-0.00693600
C	6.0	1.93972802	-0.26901701	-0.00389700
F	9.0	2.71255898	0.48832500	-0.87646800
F	9.0	2.56697989	-0.07644100	1.22845304
F	9.0	2.30547905	-1.58537495	-0.33239099
C	6.0	-2.10935998	-0.56447703	-0.00203900
F	9.0	-2.91588712	-0.62011701	1.05931103
F	9.0	-0.60294998	2.23689890	0.01134200
F	9.0	-2.93424201	-0.59990400	-1.05006695

Sum of electronic and zero-point Energies= -822.300813

$[CF_2(F)AgCF_3]^-$

Ag	47.0	0.18393700	0.73700899	-0.00216400
C	6.0	-1.36545205	-0.79749697	-0.00373700
F	9.0	-0.94671798	-2.10582805	-0.22884400
F	9.0	-2.06343198	-0.88274300	1.19174898
F	9.0	-2.35233998	-0.60654098	-0.95529097
C	6.0	1.92671704	-0.33707500	0.00243500
F	9.0	-0.46585199	2.71773601	0.00364600
F	9.0	2.24231601	-1.11287606	1.06140804
F	9.0	2.25128794	-1.10219204	-1.06050003

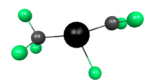
Sum of electronic and zero-point Energies= -822.306856



TS $[FAgCF_3]^-$ → $[CF_2(F)AgF]^-$ (- 51 cm^{-1})

Ag	47.0	-0.50994599	-0.09522800	0.00000000
F	9.0	-2.48449302	-0.74314803	0.00000000
C	6.0	1.46353900	-0.50175798	0.00000000
F	9.0	-0.30507201	2.01917911	-0.00000100
F	9.0	2.23846197	-0.22211300	1.05677903
F	9.0	2.23846197	-0.22211300	-1.05677903

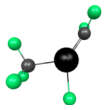
Sum of electronic and zero-point Energies= -584.526793



TS $[CF_3AuCF_3]^-$ → $[CF_2(F)AuCF_3]^-$ (-115 cm^{-1})

Au	79.0	0.11899900	-0.04945600	0.00000500
C	6.0	-1.97942102	-0.12986100	-0.00003100
F	9.0	-2.54478192	-1.40453696	-0.00051300
F	9.0	-2.58081603	0.48068699	1.09181499
F	9.0	-2.58081102	0.48151100	-1.09141505
C	6.0	2.05992794	-0.45052600	-0.00009400
F	9.0	0.88316602	2.12616992	0.00030400
F	9.0	2.86249995	-0.43175301	1.05392599
F	9.0	2.86252403	-0.43103999	-1.05407500

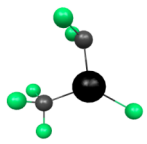
Sum of electronic and zero-point Energies= -811.079806



$[CF_2(F)AuCF_3]^-$

Au	79.0	0.21178500	0.32520199	-0.00241000
C	6.0	-1.69394302	-0.65315098	-0.00176400
F	9.0	-1.61545503	-2.03463793	-0.16302601
F	9.0	-2.40738392	-0.49973401	1.16697705
F	9.0	-2.55551410	-0.25659901	-0.99620801
C	6.0	2.01286888	-0.30667499	0.00153700
F	9.0	-0.89620298	2.12169909	0.00705700
F	9.0	2.69648600	-0.77629000	1.07134795
F	9.0	2.70644689	-0.76910901	-1.06484497

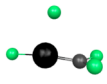
Sum of electronic and zero-point Energies= -811.092571



TS $[CF_2(F)AuCF_3]^-$ → CF_2 + $[FAuCF_3]^-$ (-108 cm^{-1})

Au	79.0	0.22852699	0.51158100	-0.00115900
C	6.0	-1.55602801	-0.57043099	-0.00100000
C	6.0	1.69767201	-0.91560799	0.00026600
F	9.0	0.51691800	2.61222506	0.00222900
F	9.0	1.75884700	-1.75978100	1.06616497
F	9.0	1.76152396	-1.75791395	-1.06569397
F	9.0	-1.81221402	-1.23141301	1.18424904
F	9.0	-1.63696897	-1.55594897	-0.96475101
F	9.0	-2.68849611	0.19297899	-0.21153300

Sum of electronic and zero-point Energies= -811.083512



TS $[FAuCF_3]^-$ → $[CF_2(F)AuF]^-$ (-125 cm^{-1})

Au	79.0	-0.37800601	-0.15091699	0.00000000
F	9.0	-2.39921999	-0.23234899	0.00000100
C	6.0	1.51052701	-0.31080300	0.00000000
F	9.0	0.09370700	2.17542911	0.00000000
F	9.0	2.30827188	-0.20558099	1.05459499
F	9.0	2.30827308	-0.20558199	-1.05459499

Sum of electronic and zero-point Energies= -573.293538

Figure S26: Calculated Cartesian coordinates and energies (Hartrees) relevant to the fragmentation of $[CF_3MF]^-$ and $[CF_3MCF_3]^-$, M = Cu, Ag and Au.

[$CF_2(F)CuF$]$^-$

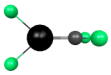
Cu	29.0	-0.53847200	-0.05177500	-0.00100600
F	9.0	-1.96928895	-1.26014996	0.02234200
C	6.0	1.25323200	-0.17157701	0.00442400
F	9.0	-1.28708899	1.67333806	-0.02605600
F	9.0	2.07642508	-0.03187400	1.06255698
F	9.0	2.07954001	-0.10010000	-1.05855095

Sum of electronic and zero-point Energies= -634.913377

[$CF_2(F)AgF$]$^-$

Ag	47.0	0.45246601	-0.07587800	-0.00007000
F	9.0	2.22140503	-1.17062497	0.00051000
C	6.0	-1.52244401	-0.27730399	0.00000200
F	9.0	1.08342898	1.92781997	-0.00074500
F	9.0	-2.32695699	-0.08901000	-1.05699205
F	9.0	-2.32579303	-0.08706400	1.05758905

Sum of electronic and zero-point Energies= -584.526309



[$CF_2(F)AuF$]$^-$

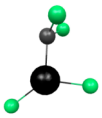
Au	79.0	-0.26356801	0.00000200	-0.00000500
F	9.0	-1.81318998	-1.38858604	-0.00006000
C	6.0	1.60533404	-0.00030800	-0.00004500
F	9.0	-1.81109905	1.38929904	0.00003100
F	9.0	2.43367600	-0.00032200	1.06413901
F	9.0	2.43393111	-0.00020300	-1.06403506

Sum of electronic and zero-point Energies= -573.306183

TS [$CF_2(F)CuF$]$^-$ → CF_2 + [$FCuF$]$^-$ (-40 cm^{-1})

Cu	29.0	-0.66540200	0.28584501	0.08089400
F	9.0	-1.87748003	-1.00489295	-0.43668100
C	6.0	1.11538196	-0.68633997	0.26027000
F	9.0	-0.07259100	1.97344303	0.43078399
F	9.0	2.13637710	0.06214200	0.73041099
F	9.0	1.53675497	-1.00769103	-0.99639201

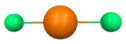
Sum of electronic and zero-point Energies= -634.907978



TS [$CF_2(F)AuF$]$^-$ → CF_2 + [$FAuF$]$^-$ (-161 cm^{-1})

Au	79.0	0.40404600	0.02768200	-0.00001200
F	9.0	-0.21998200	2.02095890	0.00032000
C	6.0	-1.51425695	-0.72713900	-0.00018200
F	9.0	2.25719500	-0.98076302	-0.00010300
F	9.0	-2.28707695	-0.39960000	1.06246805
F	9.0	-2.28725600	-0.39882100	-1.06245601

Sum of electronic and zero-point Energies= -573.283137



[$FCuF$]-

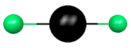
Cu	29.0	0.00000000	0.00000000	0.00008000
F	9.0	0.00000000	0.00000000	-1.81214595
F	9.0	0.00000000	0.00000000	1.81188703

Sum of electronic and zero-point Energies= -397.189505

[$FAgF$]$^-$

Ag	47.0	0.00000000	0.00431800	0.00000000
F	9.0	2.04459310	0.02034200	0.00000000
F	9.0	-2.04459310	-0.04288900	0.00000000

Sum of electronic and zero-point Energies= -346.819169



[$FAuF$]$^-$

Au	79.0	0.00000000	0.00000000	0.00000300
F	9.0	0.00000000	0.00000000	-2.01486397
F	9.0	0.00000000	0.00000000	2.01484108

Sum of electronic and zero-point Energies= -335.581873

Figure S27: Calculated Cartesian coordinates and energies (Hartrees) of $[CF_2M(F)_2]^-$ and $[FMF]^-$, M = Cu, Ag and Au.

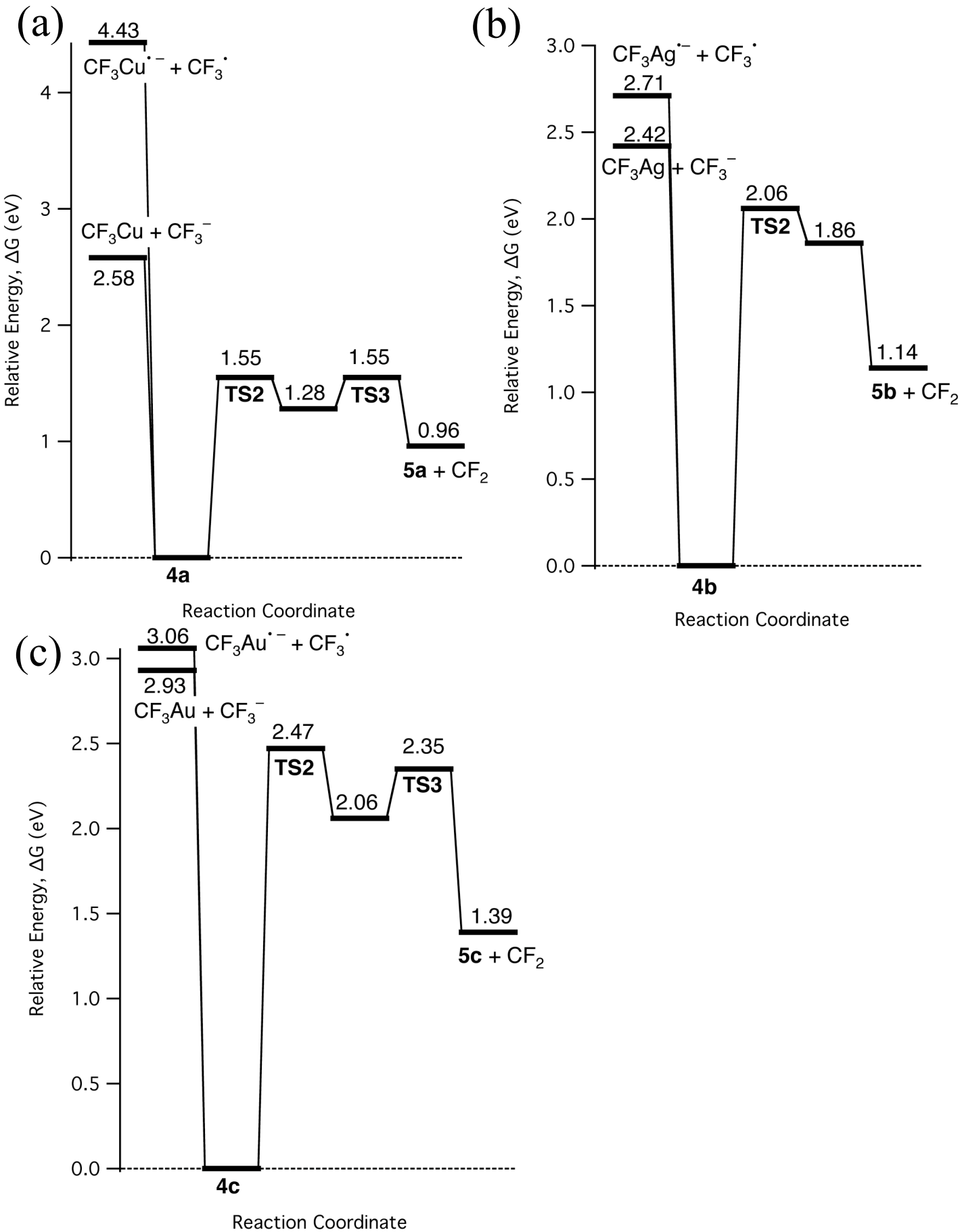


Figure S28: B3LYP/Def2-QZVP//B3LYP/SDD6-31+G(d) calculated Potential Energy Surfaces (ΔG, eV) for fragmentation of $[CF_3MCF_3]$-; M = (a) Cu; (b) Ag and (c) Au.

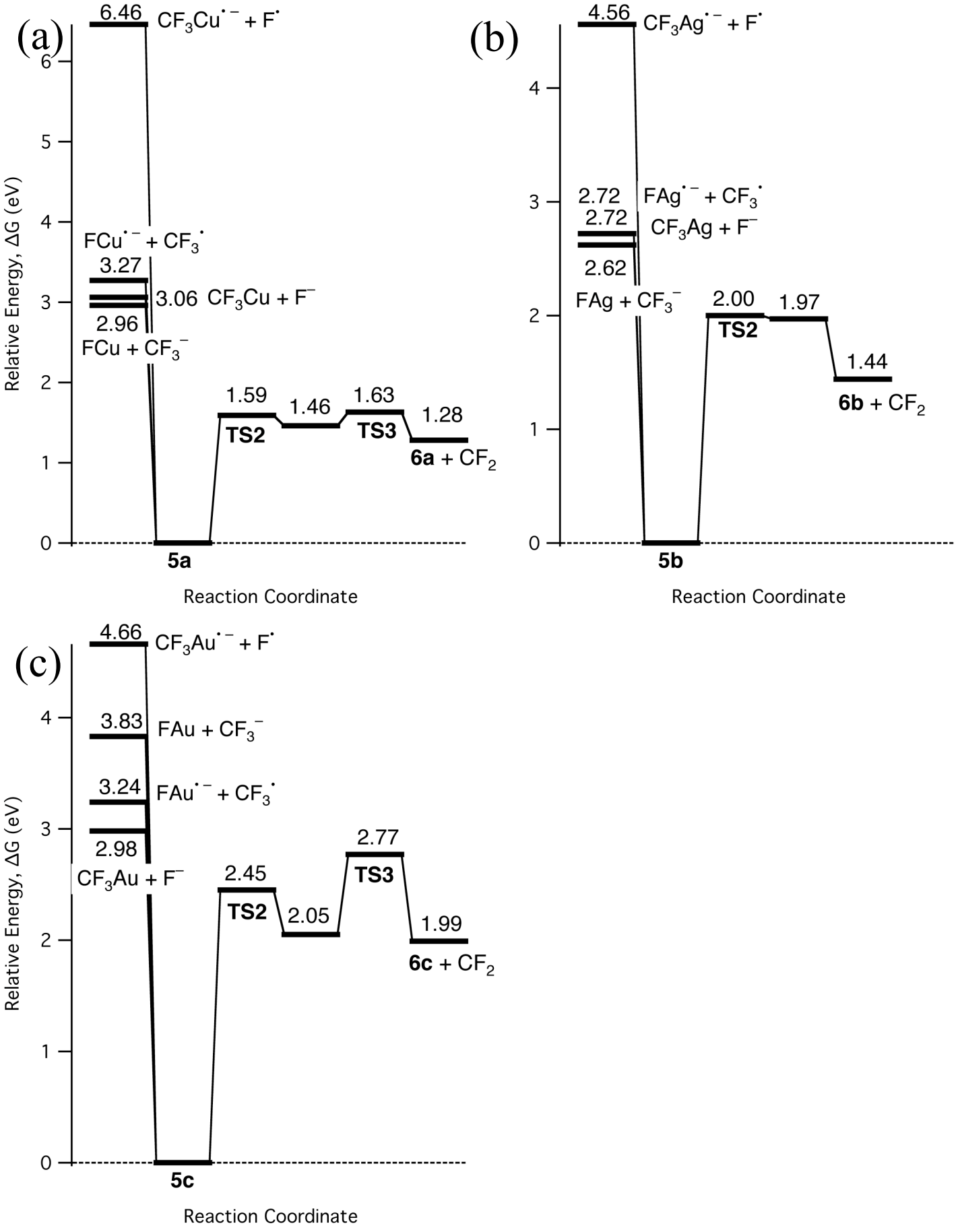


Figure S29: B3LYP/Def2-QZVP//B3LYP/SDD6-31+G(d) calculated Potential Energy Surfaces (ΔG, eV) for fragmentation of $[FMCF_3]^-$; M = (a) Cu; (b) Ag and (c) Au.

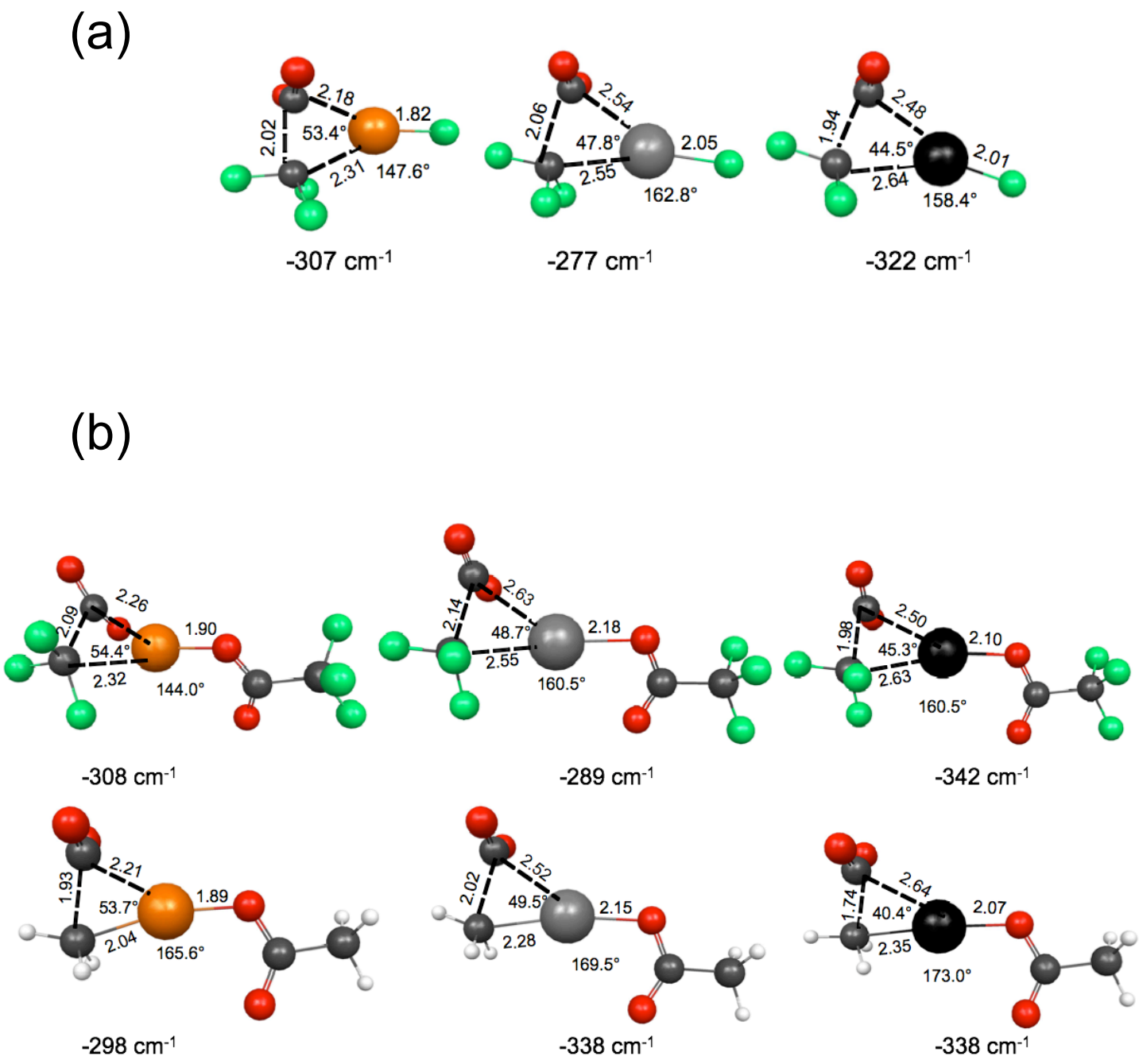


Figure S30: Decarboxylation TS comparison: (a) $[CF_3CO_2MF]^-$, M = Cu, Ag and Au; (b) $[CX_3CO_2MO_2CCX_3]^-$, X = F and H, M = Cu, Ag and Au.

	Cu	Ag	Au
$[CF_3CO_2MO_2CCF_3]^-$	1.98	1.77	2.20
$[CH_3CO_2MO_2CCH_3]^-$	1.67	1.61	1.80
$[CF_3CO_2MCF_3]^-$	1.96	1.79	2.07
$[CH_3CO_2MCH_3]^-$	1.67	1.66	1.65
$[CF_3CO_2MF]^-$	1.97	1.74	2.16
$[CH_3CO_2MH]^-$	1.66	1.68	1.64

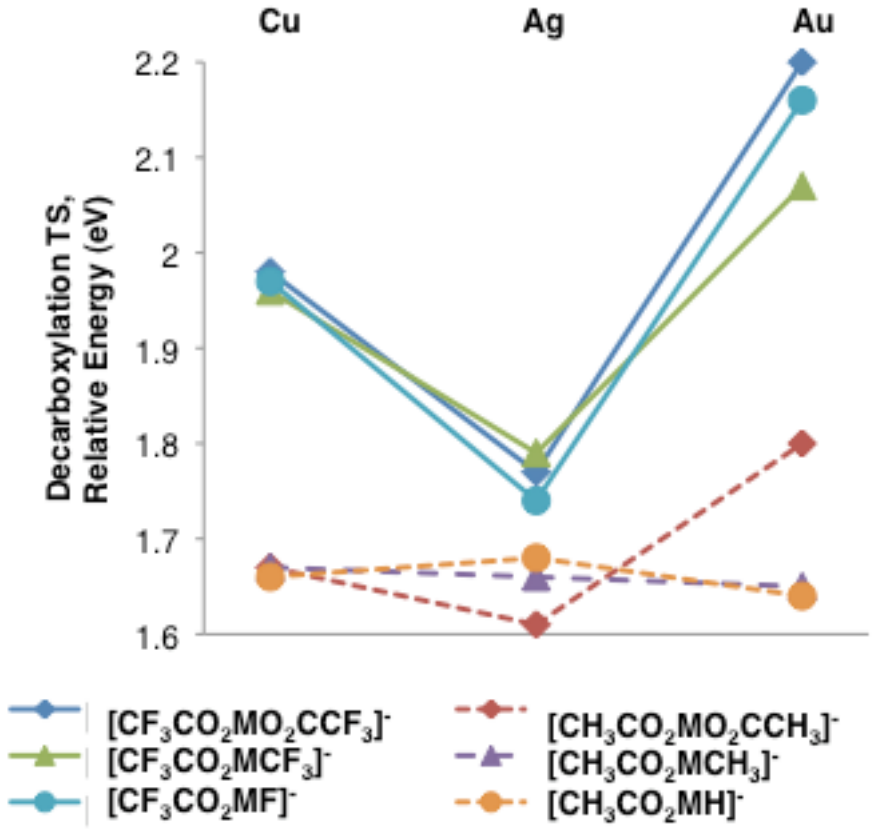


Figure S31: Decarboxylation energy comparison, B3LYP/SDD6-31+G(d), E0, in eV. Energies for hydrocarbon analogues are taken from Ref 21c, d and g.