

Supporting Information For:

Bonding and The Role of Electrostatics in Driving
C-C Bond Formation in High Valent
Organocopper Compounds

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Computational Methods. All hybrid density functional theory and post Hartree-Fock calculations were performed using the electronic structure package *ORCA* v. 4.2.1,¹ utilizing program defaults except for *ORCA*'s TightSCF (hybrid DFT) and VeryTightSCF (CCSD(T)) convergence criteria. Geometry optimizations, relaxed surface scans, and transition state searches were performed using the PBE0 hybrid density functional,² Ahlrichs' def2-tzvp basis set,³ and the Becke-Johnson damping dispersion correction.⁴ Transition state searches started from an estimate of the elimination transition state derived from a relaxed surface scan and subsequently followed the mode corresponding to the formation of the C-C bond involved in the elimination reaction. For all transition state searches an exact Hessian was recalculated after every three steps in the optimization. Elimination transition states could not be located for [Cu(CF₃)₄]⁻ and [Cu(CHF₂)(CF₃)₃]⁻, and were therefore estimated by restraining the Cu-C skeleton of the [Cu(CH₂F)(CF₃)⁻ elimination transition state and allowing the H and F atoms to optimize. CCSD(T) calculations employed Dunning's correlation consistent basis sets⁵ automatically extrapolated to the basis set limit using the cc-pVTZ and cc-pVQZ results with properties derived from the linearized densities. Valence bond calculations were performed using the *XMVB* v. 3.0 *ab initio* valence bond package⁶ using the Sapporo-DZP-2012 basis set.⁷ One and two electron integrals were generated using the PREINT utility with the basis-set files modified for the Sapporo-DZP-2012 basis set. Guess orbitals for the BOVB calculations were obtained from converged VBSCF calculations. Atomic charges for all calculations were derived through a Mulliken population analysis.

Cu-C bond dissociation energies (BDEs) and equilibrium bond lengths (r_e) were determined as follows. Initial Cu-C BDEs were calculated from the geometry optimized reactant structures and then employed one of two different methods. At the CCSD(T) level using the Boys and Bernardi counterpoise correction procedure comparing the [Cu(CR₃)(CR'₃)(CF₃)₂]⁻ vs [Cu(CR'₃)(CF₃)₂]⁻ and CR₃ energies. At the BOVB level the difference between the DFT determined optimized geometry for [Cu(CR₃)(CR'₃)(CF₃)₂]⁻ and the geometry optimized structure where the Cu-C bond length was restrained to 10.0 Å was calculated. A relaxed surface scan was then performed at the PBE0 level of theory by scanning the dissociated Cu-C bond from 1.85 to 5.00 Å. The energies of these structures were then calculated at the CCSD(T) or BOVB levels. These potential energy surfaces were then fit to a Morse potential to extract r_e and the corrected Cu-C BDEs. Transition state ΔE^\ddagger were obtained from the differences in CCSD(T) single point energies of the PBE0 geometry optimized structures.

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4) Grimme S., Ehrlich S., Goerigk L. *Comp. Chem.* **2011**, *32*, 1456.

- 5a) Dunning, T. H., *J. Chem. Phys.* **1989**, *90*, 1007. b) Balabanov, N.B. Peterson, K. A. *J. Chem. Phys.* **2005**, *123*, 064107. c) Balabanov, N.B., Peterson, K.A. *J. Chem. Phys.* **2006**, *125*, 074110.
- 6a) Chen, Z.; Ying, F.; Chen, X.; Song, J.; Su, P.; Song, L.; Mo, Y.; Zhang, Q.; Wu, W. *Int. J. Quantum Chem.* **2015**, *115*, 731. b) Song, L.; Mo, Y.; Zhang, Q.; Wu, W. *J. Comput. Chem.* **2005**, *26*, 514.
- 7a) Noro, T.; Sekiya, M.; Koga, T. *Theor. Chem. Acc.* **2012**, *131*, 1124. b) Sekiya, M.; Noro, T.; Koga, T.; Shimazaki, T. *Theor. Chem. Acc.* **2012**, *131*, 1247.

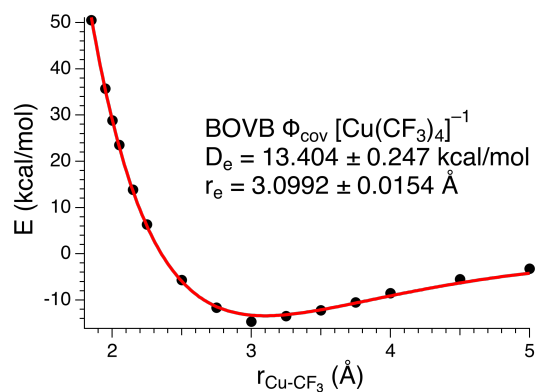
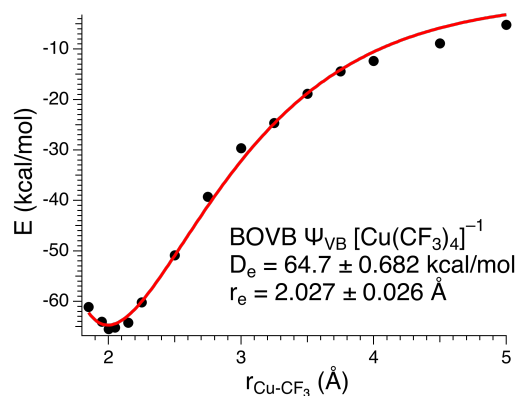
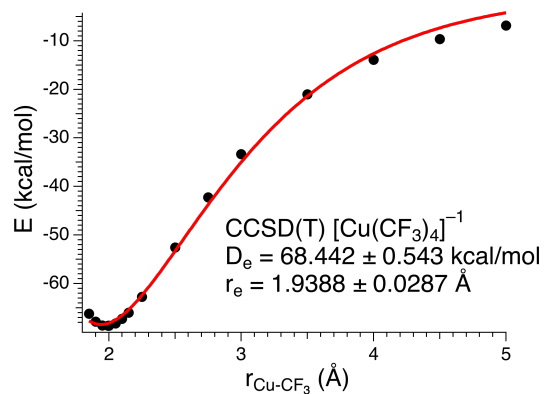


Figure S-1. Results from the Cu-CF₃ relaxed surface scan for $[\text{Cu}(\text{CF}_3)_4]^{-1}$ and Morse potential parameters at the CCSD(T) and BOVB levels. The dots represent the individual calculated single point energies relative to D_e and the red curve the fitted Morse potential.

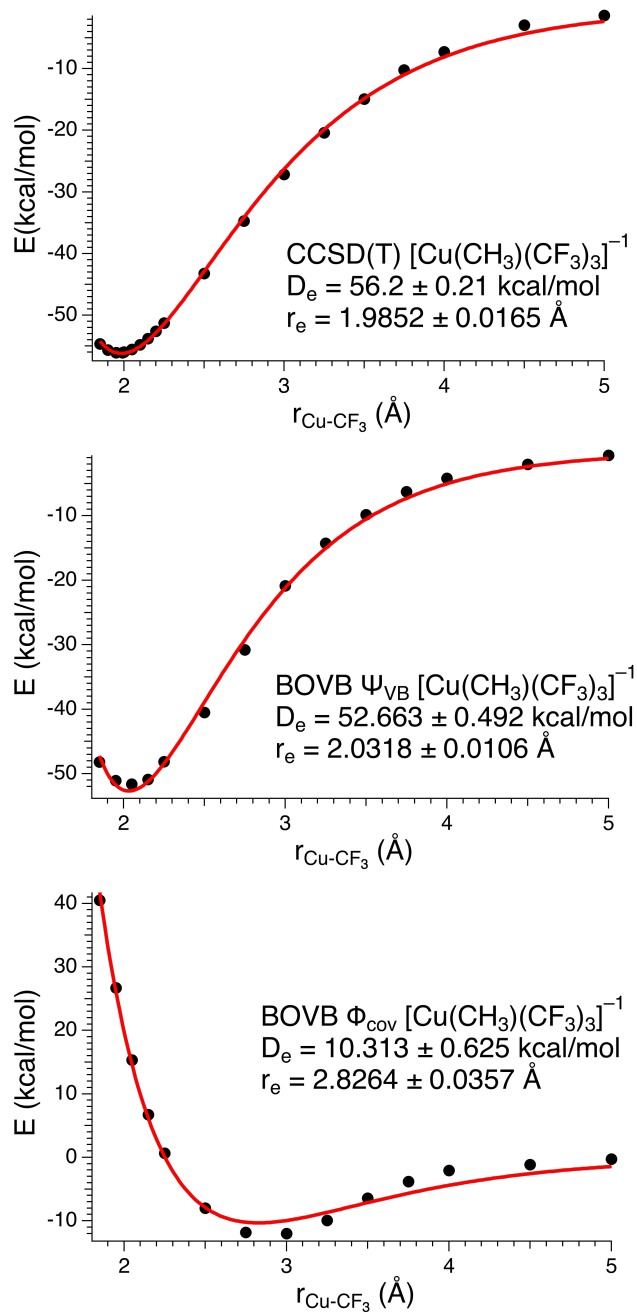


Figure S-2. Results from the Cu-CF₃ relaxed surface scan for [Cu(CH₃)(CF₃)₃]¹⁻ and Morse potential parameters at the CCSD(T) and BOVB levels. The dots represent the individual calculated single point energies relative to D_e and the red curve the fitted Morse potential.

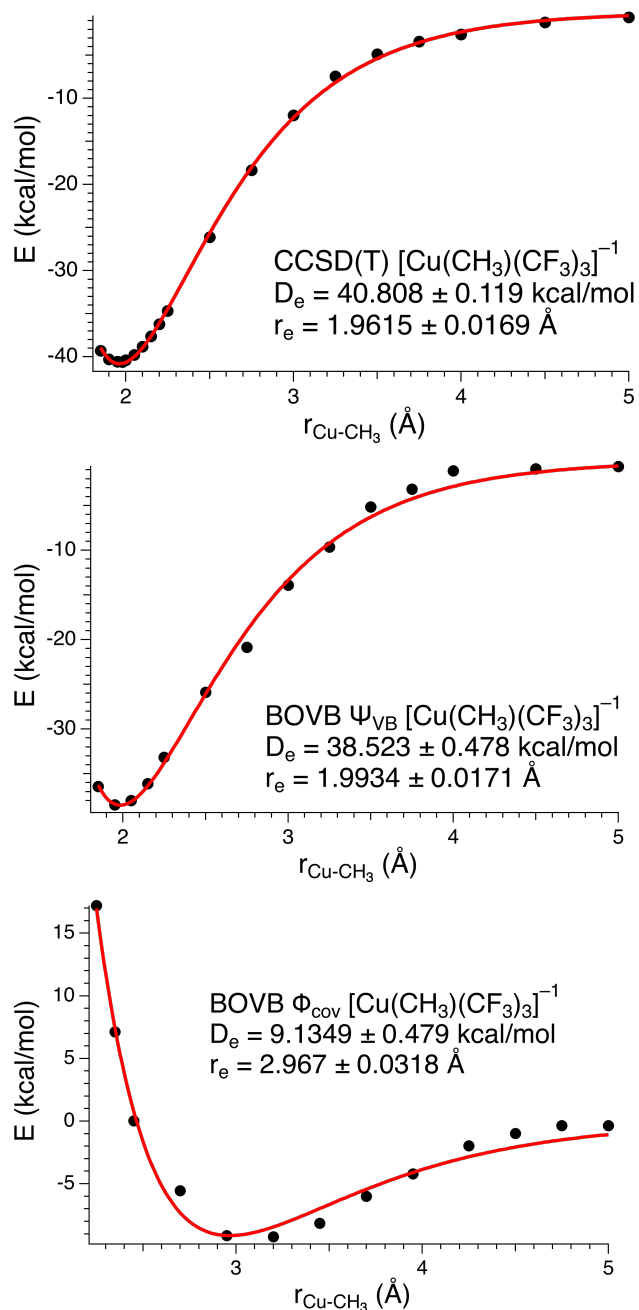


Figure S-3. Results from the Cu-CH₃ relaxed surface scan for [Cu(CH₃)(CF₃)₃]⁻¹ and Morse potential parameters at the CCSD(T) and BOVB levels. The dots represent the individual calculated single point energies relative to D_e and the red curve the fitted Morse potential.

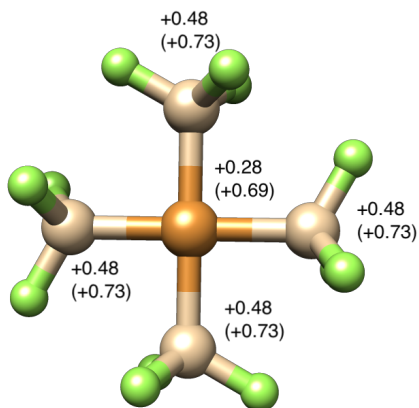


Figure S-4. Ball and stick structure for [Cu(CF₃)₄]⁻ and Mulliken charges at the CCSD(T) and BOVB level (in parentheses) for specific Cu and C atoms.

Table S-1. Cartesian coordinates for [Cu(CF₃)₄]⁻ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	-0.00000	-0.00001	-0.00028
C	-0.00901	2.01817	0.00182
F	-1.20953	2.67998	0.00304
F	0.64363	2.51778	-1.10716
F	0.64488	2.51893	1.10927
C	-2.01813	-0.00903	-0.01497
F	-2.67983	-1.20953	-0.02932
F	-2.51214	0.65319	-1.12055
F	-2.52457	0.63521	1.09577
C	0.00897	-2.01819	0.00243
F	1.20939	-2.67999	0.01944
F	-0.62995	-2.51972	-1.11347
F	-0.65852	-2.51705	1.10278
C	2.01815	0.00899	0.01202
F	2.68001	1.20948	0.00675
F	2.52735	-0.65311	-1.08668
F	2.50927	-0.63536	1.12961

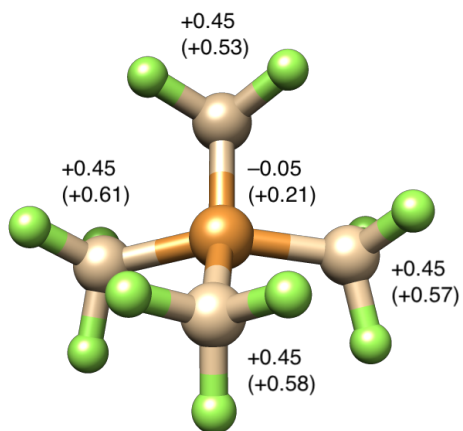


Figure S-5. Ball and stick structure for the isomerization transition state of $[\text{Cu}(\text{CF}_3)_4]^-$ and Mulliken charges at the CCSD(T) and BOVB level (in parentheses) for specific Cu and C atoms.

Table S-2. Cartesian coordinates for the isomerization transition state of $[\text{Cu}(\text{CF}_3)_4]^-$ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	0.274158	-0.188141	-0.026010
C	0.239723	1.736801	0.501638
F	-0.762070	1.957536	1.428327
F	0.075231	2.700608	-0.456062
F	1.400614	2.073117	1.172149
C	-1.692026	-0.285784	-0.356475
F	-2.554680	-0.305217	0.706193
F	-2.002653	-1.403665	-1.107315
F	-2.096389	0.775074	-1.145107
C	0.426613	-2.093439	0.545694
F	1.629650	-2.316645	1.187699
F	0.314716	-3.092332	-0.383217
F	-0.527573	-2.369226	1.507681
C	2.115760	-0.104752	-0.787717
F	3.194508	-0.029303	0.051230
F	2.229365	0.978247	-1.639312
F	2.351588	-1.199321	-1.598345

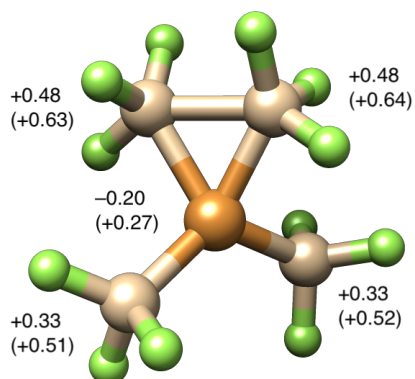


Figure S-6. Ball and stick structure for the estimated elimination transition state of $[\text{Cu}(\text{CF}_3)_4]^-$ and Mulliken charges at the CCSD(T) and BOVB level (in parentheses) for specific Cu and C atoms.

Table S-3. Cartesian coordinates for the estimated elimination transition state of $[\text{Cu}(\text{CF}_3)_4]^-$ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	0.202914	-0.318932	0.037807
C	-0.188754	1.555296	0.684860
F	-1.211715	2.133481	1.367718
F	0.323993	2.510141	-0.074808
F	0.672457	1.293673	1.711009
C	-1.663797	0.601200	-0.338592
F	-1.765150	-0.228023	-1.408337
F	-2.003663	1.791565	-0.863896
F	-2.608233	0.260163	0.527688
C	-0.254982	-2.250841	0.365362
F	0.280912	-2.699890	1.550789
F	0.218850	-3.136739	-0.564171
F	-1.585758	-2.581158	0.473116
C	2.047532	0.231599	-0.635235
F	1.971731	0.916945	-1.829118
F	2.848317	-0.838209	-0.934841
F	2.846254	1.022311	0.144222

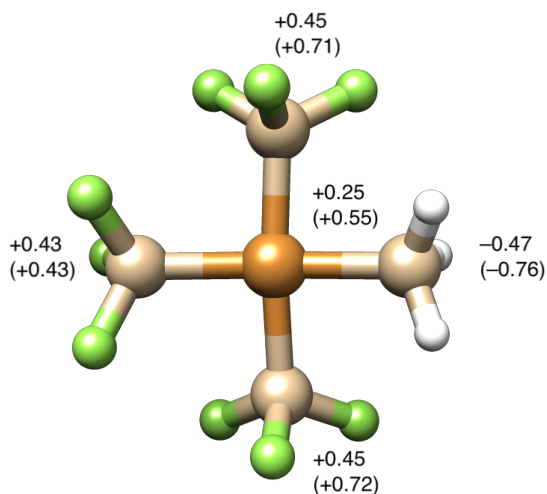


Figure S-7. Ball and stick structure for [Cu(CF₃)₃(CH₃)]⁻ and Mulliken charges at the CCSD(T) and BOVB level (in parentheses) for specific Cu and C atoms.

Table S-4. Cartesian coordinates for [Cu(CF₃)₃(CH₃)]⁻ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	0.000784	0.007552	-0.014902
C	0.021357	1.983879	0.170148
H	-0.878235	2.299245	0.709505
H	0.018973	2.407836	-0.842241
H	0.928106	2.289221	0.702654
C	-1.988230	0.105352	-0.165661
F	-2.553885	-0.913531	-0.903679
F	-2.499303	1.246088	-0.774663
F	-2.619457	0.063041	1.064816
C	-0.024596	-2.011674	0.122488
F	1.044949	-2.559077	0.815450
F	-0.020199	-2.658165	-1.101648
F	-1.123250	-2.530330	0.792600
C	1.995163	0.058732	-0.121157
F	2.548184	1.185677	-0.719587
F	2.550649	-0.975650	-0.846447
F	2.598959	0.001556	1.122834

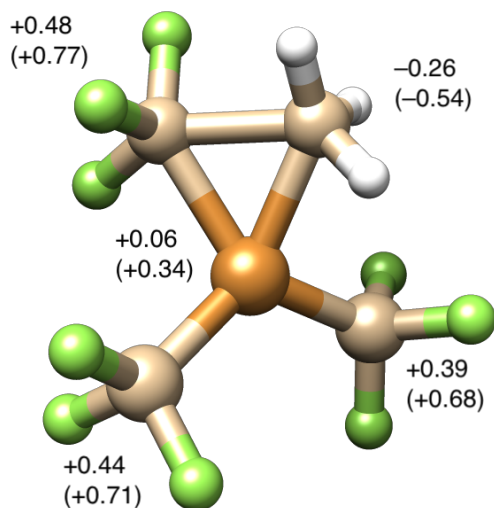


Figure S-8. Ball and stick structure for the elimination transition state of $[\text{Cu}(\text{CF}_3)_3(\text{CH}_3)]^-$ and Mulliken charges at the CCSD(T) and BOVB level (in parentheses) for specific Cu and C atoms.

Table S-5. Cartesian coordinates for the elimination transition state of $[\text{Cu}(\text{CF}_3)_3(\text{CH}_3)]^-$ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	0.23310	-0.30156	-0.02260
C	-0.29193	1.62239	0.56662
H	-1.14465	2.06770	1.08639
H	0.16393	2.31951	-0.13933
H	0.43022	1.26371	1.32153
C	-1.69746	0.58463	-0.36887
F	-1.78850	-0.24852	-1.47127
F	-2.22365	1.76751	-0.89180
F	-2.60891	0.17173	0.54663
C	-0.24074	-2.21671	0.36469
F	0.79726	-2.90889	1.00259
F	-0.52754	-3.01720	-0.74607
F	-1.33496	-2.45824	1.21752
C	2.13745	0.19681	-0.51487
F	2.25285	1.13931	-1.56516
F	3.00137	-0.81388	-0.91094
F	2.84212	0.83144	0.53544

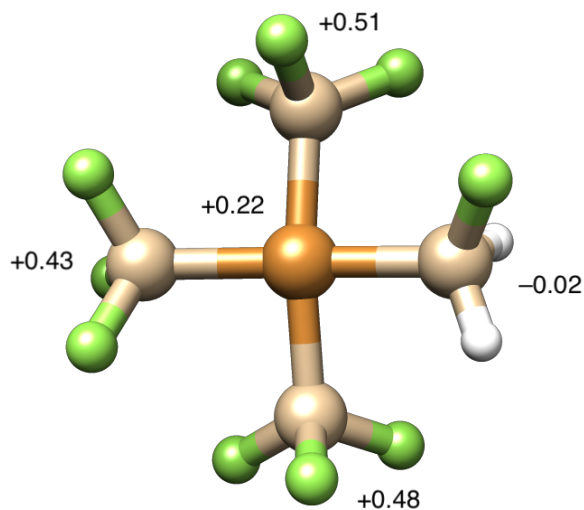


Figure S-9. Ball and stick structure for $[\text{Cu}(\text{CF}_3)_3(\text{CH}_2\text{F})]^-$ and Mulliken charges at the CCSD(T) level for specific Cu and C atoms.

Table S-6. Cartesian coordinates for $[\text{Cu}(\text{CF}_3)_3(\text{CH}_2\text{F})]^-$ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	0.397619	0.342614	0.403319
C	-1.094404	0.011533	1.673469
F	-2.104822	0.987281	1.548744
H	-0.697407	0.048132	2.698246
H	-1.569421	-0.952853	1.459086
C	0.490408	2.227700	1.042147
F	1.776186	2.735651	0.976203
F	0.144100	2.429313	2.371025
F	-0.292792	3.107196	0.334330
C	1.632207	0.701472	-1.147529
F	1.357230	-0.104650	-2.245412
F	2.972043	0.496755	-0.877269
F	1.568366	1.979547	-1.673045
C	0.485717	-1.629317	0.148269
F	0.345263	-2.340497	1.344327
F	1.661920	-2.118695	-0.366833
F	-0.507741	-2.132742	-0.672137

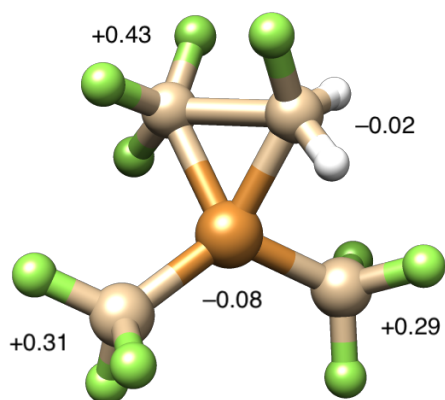


Figure S-10. Ball and stick structure for the elimination transition state of $[\text{Cu}(\text{CF}_3)_3(\text{CH}_2\text{F})]^-$ and Mulliken charges at the CCSD(T) level for specific Cu and C atoms.

Table S-7. Cartesian coordinates for the elimination transition state of $[\text{Cu}(\text{CF}_3)_3(\text{CH}_2\text{F})]^-$ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	0.202915	-0.318932	0.037809
C	-0.188754	1.555296	0.684860
F	-1.133440	2.025815	1.566797
H	0.082877	2.329250	-0.025837
H	0.656902	1.225087	1.300497
C	-1.663797	0.601200	-0.338592
F	-1.687032	-0.143167	-1.468043
F	-2.111647	1.808621	-0.766652
F	-2.588512	0.139280	0.491727
C	-0.254982	-2.250841	0.365361
F	0.296732	-2.733382	1.536979
F	0.213694	-3.123812	-0.587176
F	-1.582354	-2.604356	0.481472
C	2.047532	0.231599	-0.635235
F	2.037795	0.862981	-1.865005
F	2.967786	-0.762382	-0.798577
F	2.715971	1.147910	0.171252

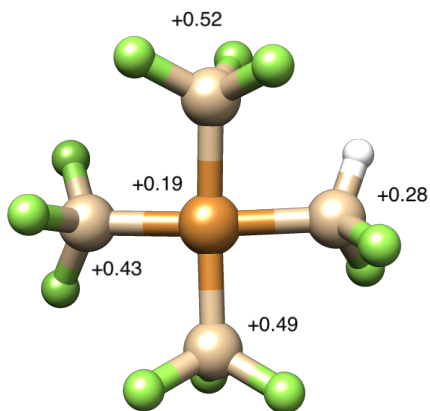


Figure S-11. Ball and stick structure for $[\text{Cu}(\text{CF}_3)_3(\text{CHF}_2)]^-$ and Mulliken charges at the CCSD(T) level for specific Cu and C atoms.

Table S-8. Cartesian coordinates for $[\text{Cu}(\text{CF}_3)_3(\text{CH}_2\text{F})]^-$ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	0.414722	0.354605	0.420468
C	-1.079355	-0.019343	1.690416
F	-2.100941	0.916960	1.557504
F	-0.695123	-0.016063	3.019626
H	-1.546396	-0.997126	1.497259
C	0.473602	2.261569	0.998194
F	1.765989	2.755295	0.994991
F	0.027546	2.542722	2.269709
F	-0.252120	3.094349	0.175510
C	1.657825	0.708268	-1.128205
F	1.333984	-0.053512	-2.241606
F	2.977889	0.412403	-0.850078
F	1.681107	1.995301	-1.622838
C	0.483864	-1.619610	0.109477
F	0.372592	-2.362075	1.283821
F	1.615811	-2.123565	-0.476158
F	-0.566527	-2.061738	-0.681152

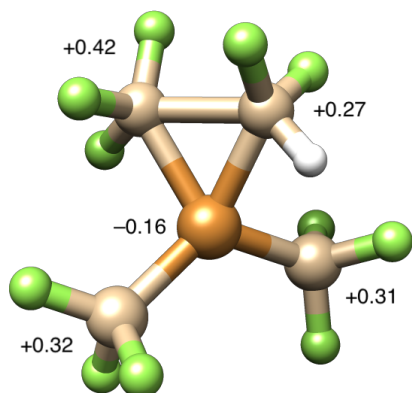


Figure S-12. Ball and stick structure for the estimated elimination transition state of $[\text{Cu}(\text{CF}_3)_3(\text{CHF}_2)]^-$ and Mulliken charges at the CCSD(T) level for specific Cu and C atoms.

Table S-9. Cartesian coordinates for the estimated elimination transition state of $[\text{Cu}(\text{CF}_3)_3(\text{CH}_2\text{F})]^-$ derived from the PBE0/def2-tzvp/D3 geometry optimization.

Cu	0.202915	-0.318931	0.037809
C	-0.188754	1.555296	0.684860
F	-1.116241	1.997474	1.575376
F	0.147919	2.577392	-0.093837
H	0.671205	1.231765	1.291660
C	-1.663797	0.601200	-0.338592
F	-1.665760	-0.131336	-1.474752
F	-2.140589	1.796219	-0.744057
F	-2.570913	0.105025	0.493577
C	-0.254982	-2.250841	0.365361
F	0.323238	-2.746387	1.516099
F	0.196427	-3.103979	-0.609886
F	-1.578620	-2.606159	0.502811
C	2.047532	0.231599	-0.635235
F	2.076274	0.864468	-1.856206
F	2.950382	-0.784258	-0.784043
F	2.715086	1.123349	0.199797