

Supporting Information for *Organic Letters* Paper: "Dimethyl cuprate undergoes C-C bond coupling with methyl iodide in the gas phase but dimethyl argenate does not." by Patrick F. James and Richard A.J. O'Hair*

Index of Supporting Information:

Supplementary Figure S1: Mass spectra for ion-molecule reactions of organocuprate ions with methyl iodide

- (a) $(\text{CH}_3)_2\text{Cu}^- + \text{CH}_3\text{I}$
- (b) $(\text{CD}_3)_2\text{Cu}^- + \text{CH}_3\text{I}$
- (c) $(\text{CD}_3)_2\text{Cu}^- + \text{CD}_3\text{I}$
- (d) $\text{CH}_3\text{CuCD}_3^- + \text{CH}_3\text{I}$
- (e) $\text{CH}_3\text{CuCD}_3^- + \text{CD}_3\text{I}$
- (f) $\text{CH}_3\text{CuO}_2\text{CCH}_3^- + \text{CH}_3\text{I}$

Supplementary Figure S2: Structures and cartesian coordinates for all species associated with Figure 2.

- (a) Reactant Anion: $(\text{CH}_3)_2\text{Cu}^-$
- (b) Reactant Neutral: CH_3I
- (c) Pre Complex for "T shaped" transition state
- (d) "T shaped" transition state
- (e) Post complex for both the T shaped and side on TS.
- (f) Pre Complex for "Side On" transition state
- (g) Side On - TS
- (h) Product Neutral: CuCH_3
- (i) Product Neutral: CH_3CH_3
- (j) Product Ion: CH_3CuI^-

Supplementary Figure S3: Structures and cartesian coordinates for all species associated with Figure 3.

- (a) Reactant Anion: $(\text{CH}_3)_2\text{Ag}^-$
- (b) Pre Complex for "T shaped" transition state
- (c) "T shaped" transition state
- (d) Post complex for the T shaped TS
- (e) Pre Complex for "Side On" transition state
- (f) Side On - TS

(g) Post complex for the Side On TS

(h) Product Neutral: AgCH₃

(i) Product Ion: CH₃AgI⁻

Supplementary Figure S4: Imaginary vibrational frequencies and their vectors for all transition states shown in Figures 2 and 3.

(a) Cu "T shaped" transition state (see Supplementary Figure S2(d) for cartesian coordinates)

(b) Cu Side On - TS (see Supplementary Figure S2(g) for cartesian coordinates)

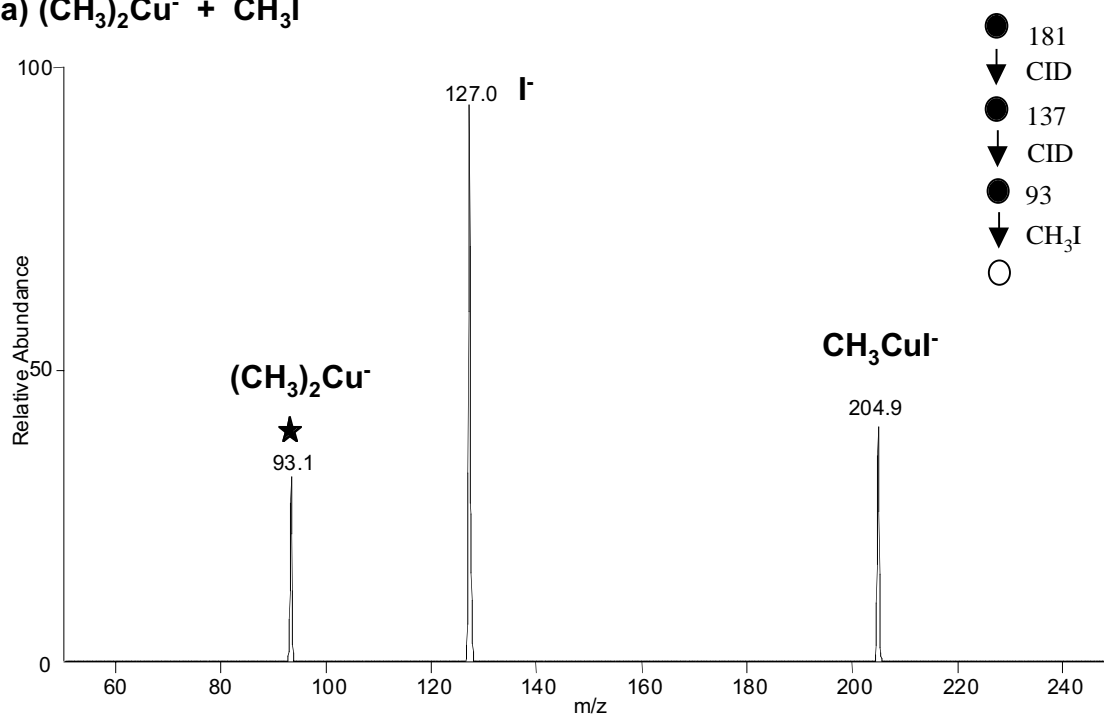
(c) Ag "T shaped" transition state (see Supplementary Figure S3(c) for cartesian coordinates)

(d) Ag Side On - TS (see Supplementary Figure S3(f) for cartesian coordinates)

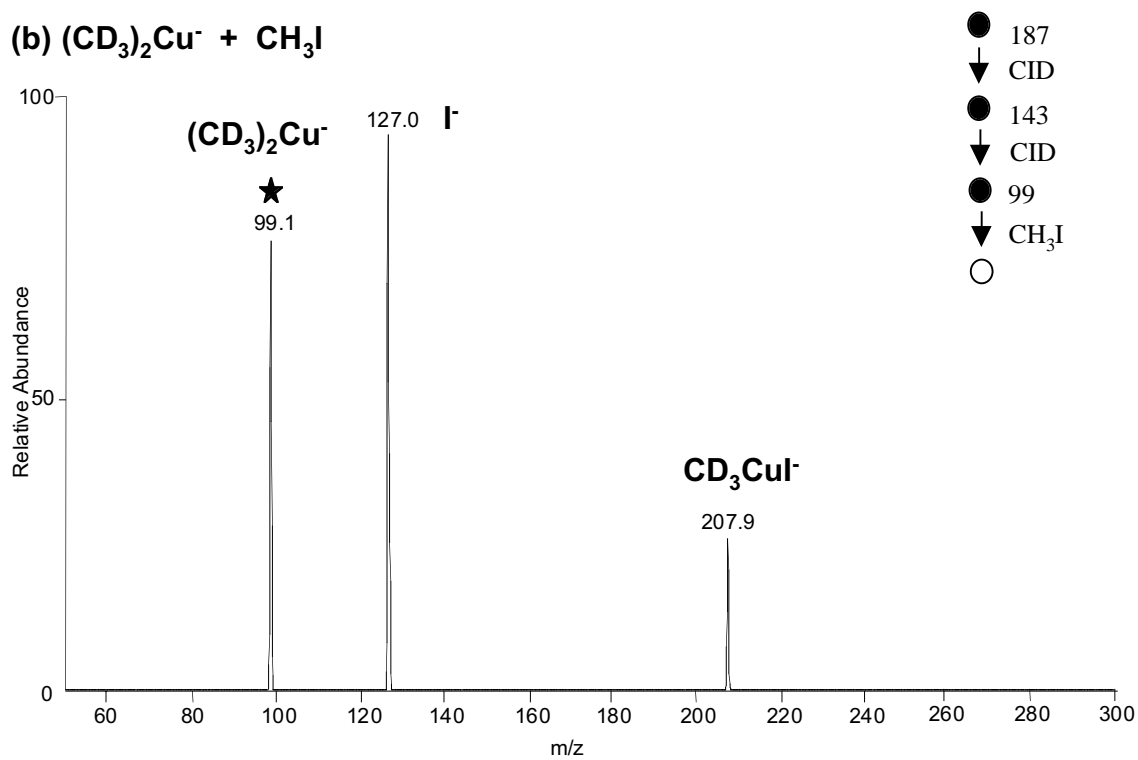
Supplementary Table S1: Energies for all species associated with Figures 2 and 3.

Supplementary Figure S1: Mass spectra for ion-molecule reactions of organocuprate ions with methyl iodide

(a) $(\text{CH}_3)_2\text{Cu}^- + \text{CH}_3\text{I}$

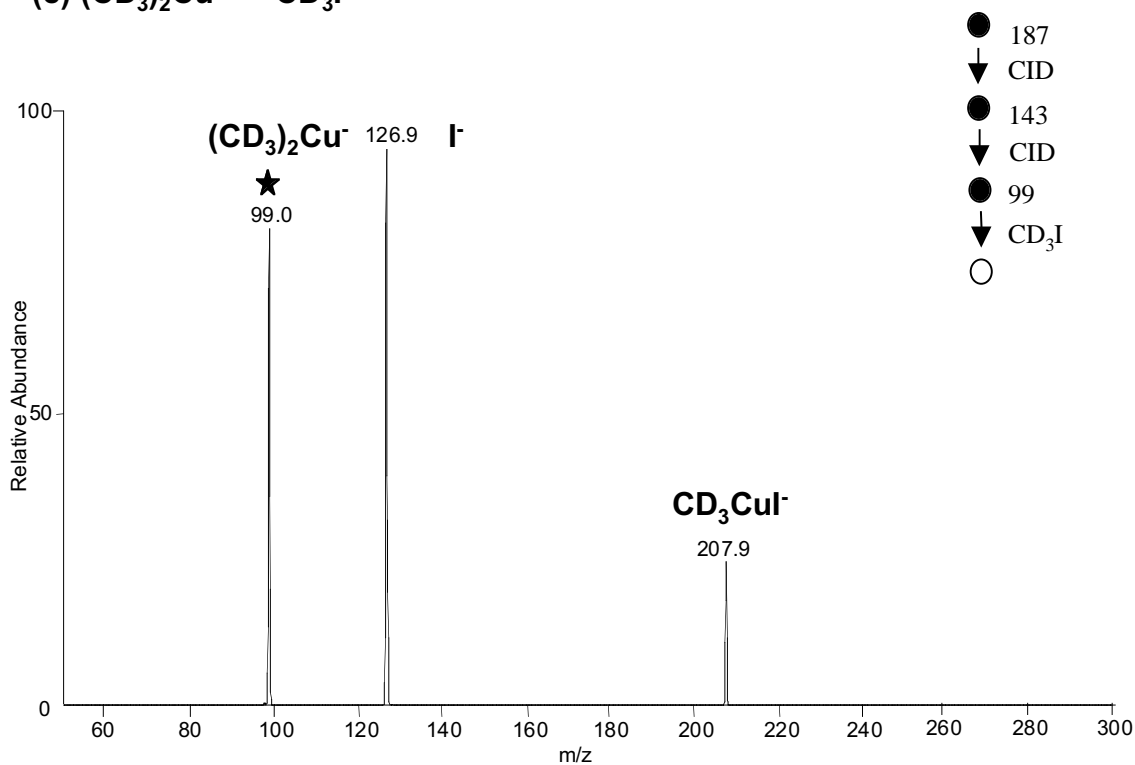


(b) $(\text{CD}_3)_2\text{Cu}^- + \text{CH}_3\text{I}$

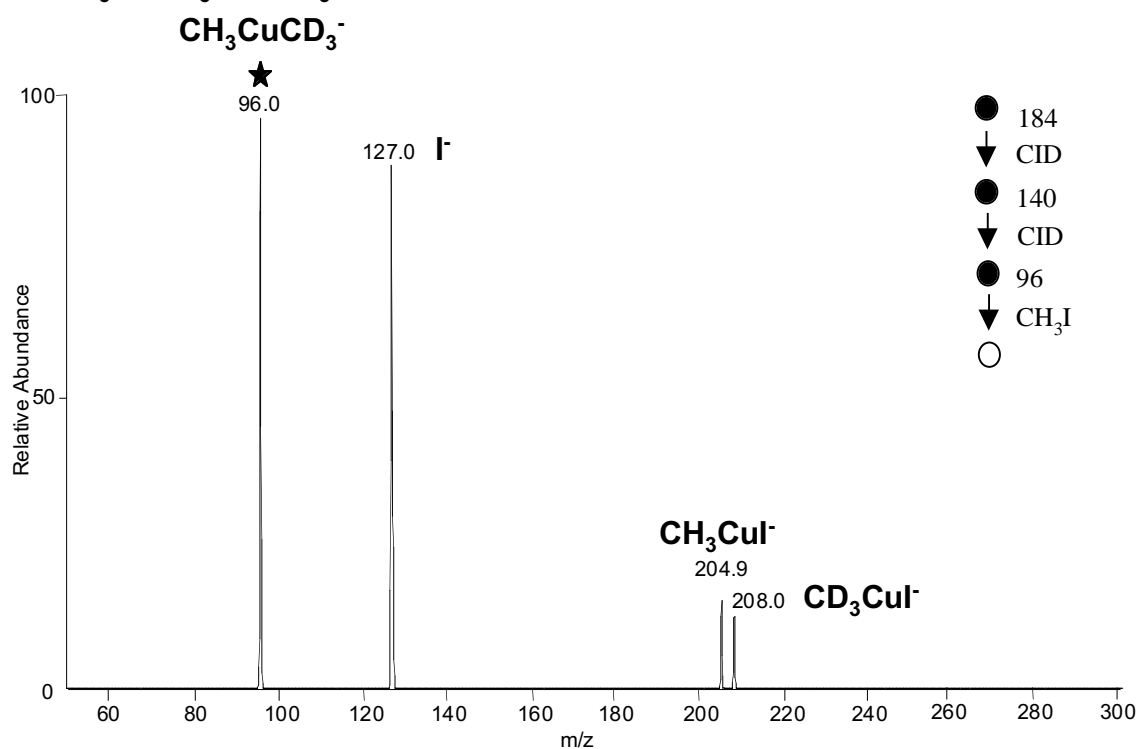


Supplementary Figure S1: Mass spectra for ion-molecule reactions of organocuprate ions with methyl iodide

(c) $(\text{CD}_3)_2\text{Cu}^- + \text{CD}_3\text{I}$

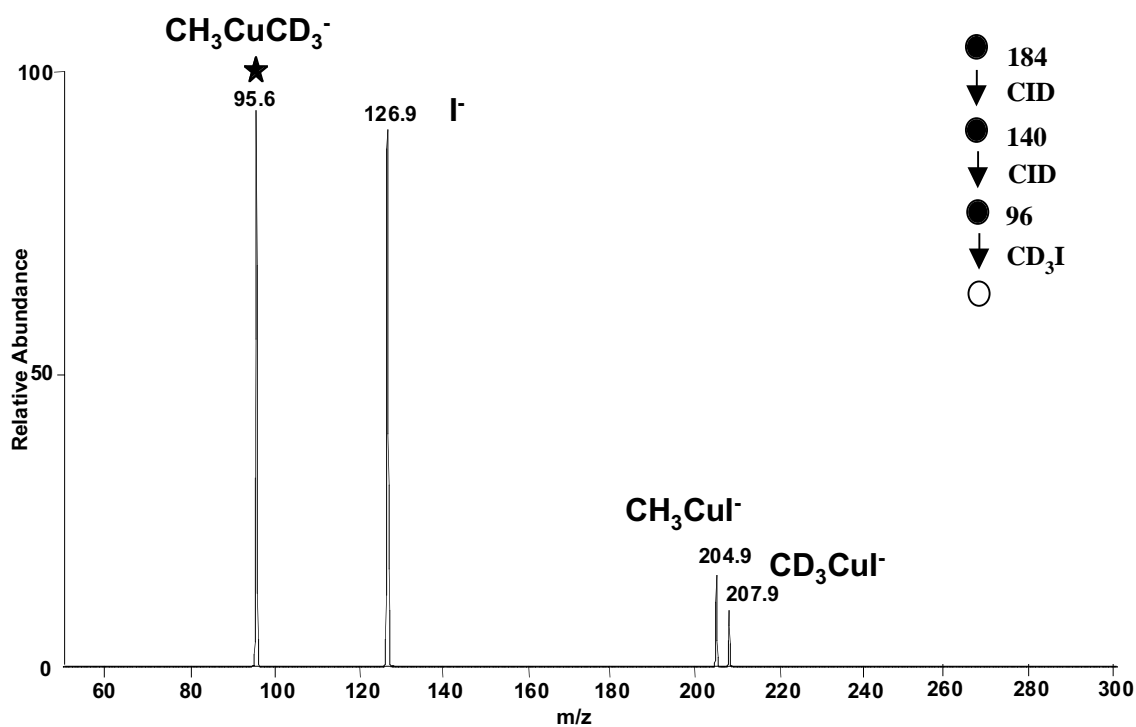


(d) $\text{CH}_3\text{CuCD}_3^- + \text{CH}_3\text{I}$

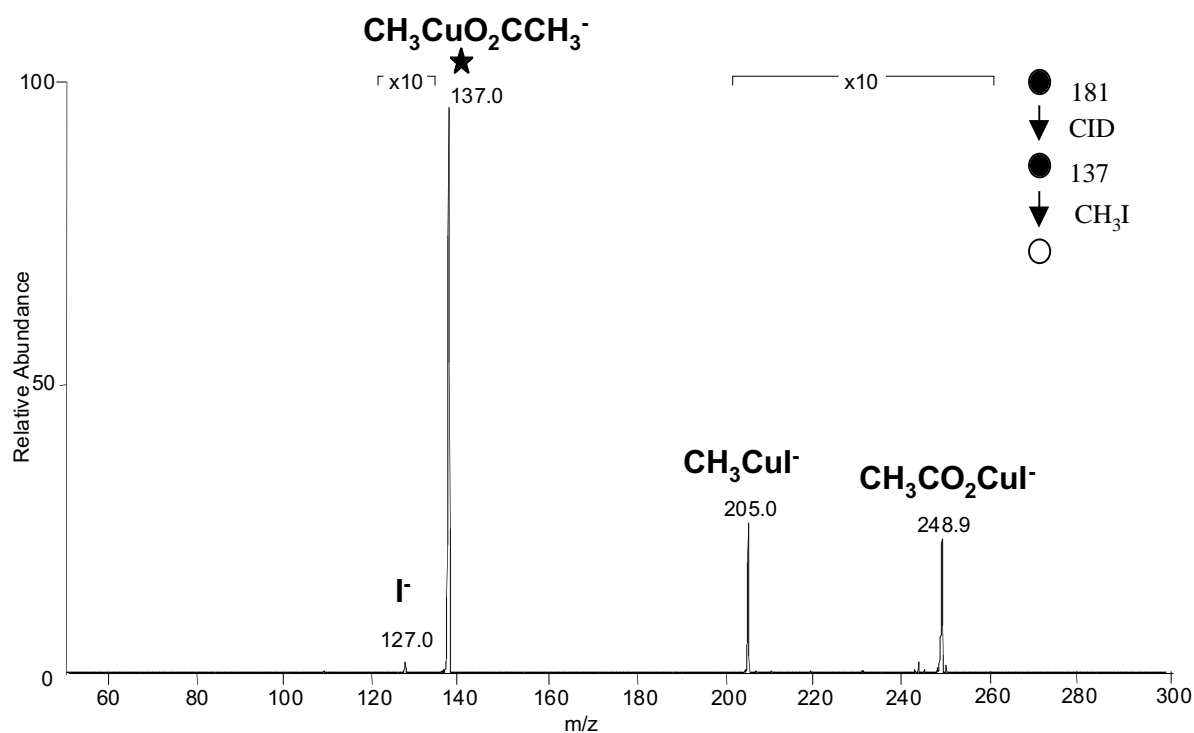


Supplementary Figure S1: Mass spectra for ion-molecule reactions of organocuprate ions with methyl iodide

(e) $\text{CH}_3\text{CuCD}_3^- + \text{CD}_3\text{I}$

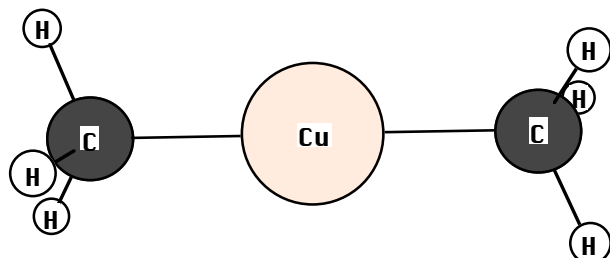


(f) $\text{CH}_3\text{CuO}_2\text{CCH}_3^- + \text{CH}_3\text{I}$



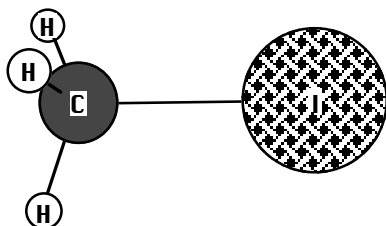
Supplementary FigureS2:
Structures and cartesian coordinates for all species associated with
Figure 2.

(a) Reactant Anion: $(\text{CH}_3)_2\text{Cu}^-$

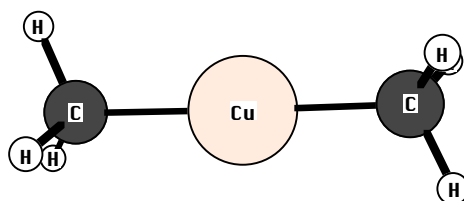
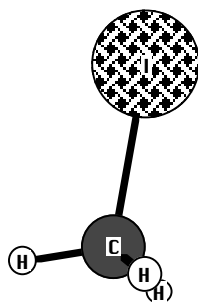


Cu	0.681607	1.082735	-0.032530
C	0.384461	3.022195	-0.303877
C	0.978683	-0.856745	0.238764
H	0.257513	3.565533	0.650804
H	-0.520808	3.228134	-0.904616
H	1.227374	3.506606	-0.830778
H	1.884067	-1.062729	0.839314
H	1.105393	-1.400091	-0.715944
H	0.135859	-1.341108	0.765853

(b) Reactant Neutral: CH_3I

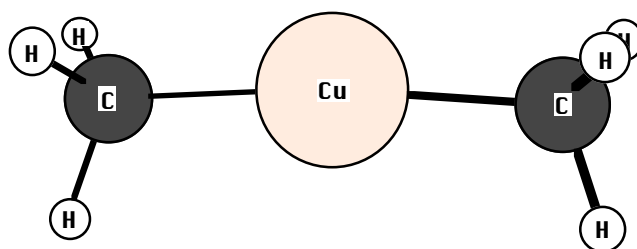
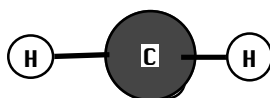
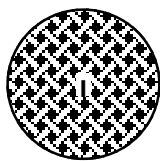


I	1.744010	0.592185	-0.281535
C	-0.365891	0.204672	-0.098219
H	-0.537429	-0.855156	-0.248285
H	-0.687312	0.501131	0.893739
H	-0.890378	0.781168	-0.851700

(c) Pre Complex for "T shaped" transition state

C	-1.175281	-1.172828	0.112532
H	-1.123324	-1.881948	-0.728848
H	-2.225394	-0.848278	0.158800
H	-1.014277	-1.778242	1.018635
Cu	0.110651	0.302431	-0.055279
I	3.453016	-3.847752	-0.016806
C	1.451127	1.726960	-0.223469
C	2.157158	-2.090480	-0.040649
H	1.420112	2.436335	0.617388
H	1.311075	2.332425	-1.131771
H	2.487700	1.359177	-0.266238
H	2.790611	-1.218296	-0.131903
H	1.485237	-2.177815	-0.883332
H	1.595114	-2.072813	0.882938

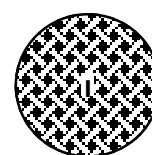
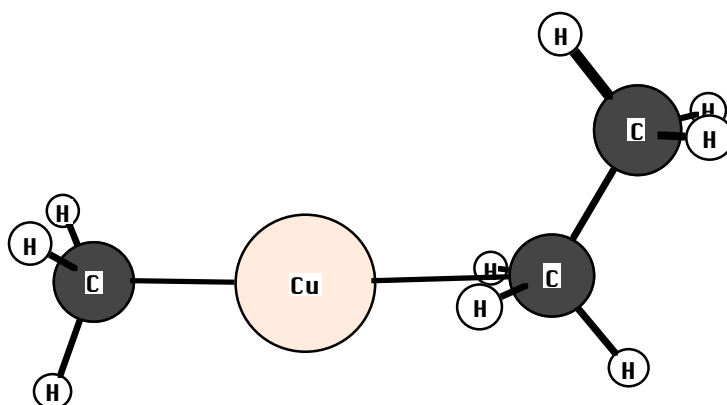
(d) "T shaped" transition state



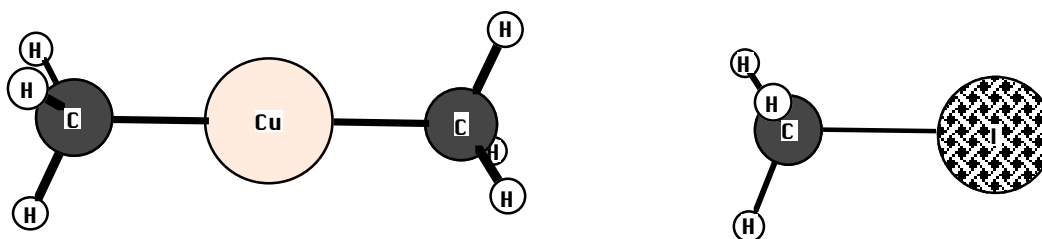
Vibrational Frequency = -463.7312

C	1.873385	-1.463488	-0.434944
H	2.205014	-0.752852	-1.203117
H	2.267131	-2.447267	-0.729083
H	2.395221	-1.187743	0.491155
Cu	-0.071093	-1.505964	-0.228919
I	-0.365064	3.299511	0.429906
C	-2.006228	-1.748591	-0.081564
C	-0.202970	0.767249	0.160271
H	-2.387588	-1.538982	0.926714
H	-2.299599	-2.782895	-0.312912
H	-2.569890	-1.103862	-0.768347
H	-1.071197	0.570962	0.760176
H	-0.302142	0.776550	-0.910591
H	0.778841	0.707542	0.590065

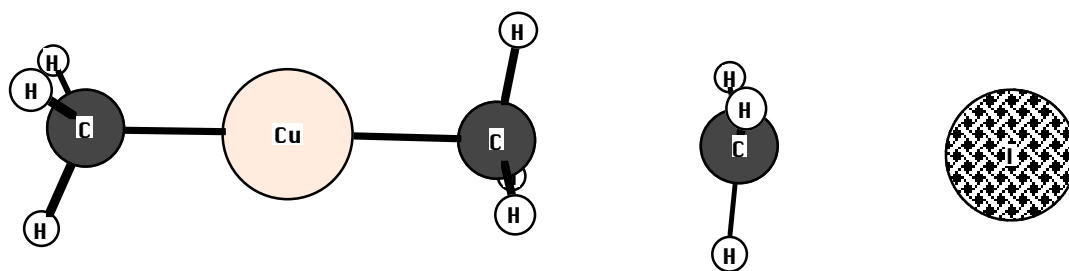
(e) Post complex for both the T shaped and side on TS.



C	0.600449	0.067798	-0.141091
H	1.682458	0.147054	-0.236364
H	0.256458	-0.452267	-1.058373
H	0.423269	-0.506368	0.791196
Cu	-0.613540	-1.805399	-0.086456
I	4.086570	1.778348	-0.405492
C	-1.724265	-3.380006	-0.032326
C	-0.041481	1.446248	-0.042889
H	-2.290155	-3.448170	0.902259
H	-1.122703	-4.290878	-0.114481
H	-2.450115	-3.395615	-0.851610
H	-1.126722	1.386335	0.053241
H	0.203302	2.031247	-0.927663
H	0.360597	1.980252	0.816260

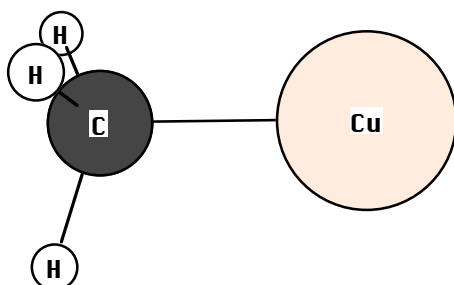
(f) Pre Complex for "Side On" transition state

C	-4.665023	-0.262961	-0.377417
H	-4.995578	-1.127971	-0.971727
H	-5.093832	0.624305	-0.866904
H	-5.173126	-0.349606	0.594713
Cu	-2.710799	-0.163682	-0.205247
I	4.769648	0.216342	0.453790
C	-0.761387	-0.064648	-0.033501
C	2.611077	0.106682	0.263616
H	-0.436011	0.801879	0.561500
H	-0.258093	0.021848	-1.008169
H	-0.337557	-0.954040	0.456513
H	2.262506	1.007474	-0.223513
H	2.361780	-0.763032	-0.329402
H	2.182384	0.023453	1.253322

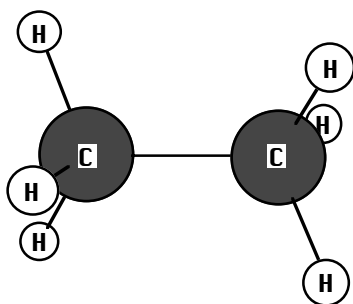
(g) Side On - TS

Vibrational Frequency = -637.7969

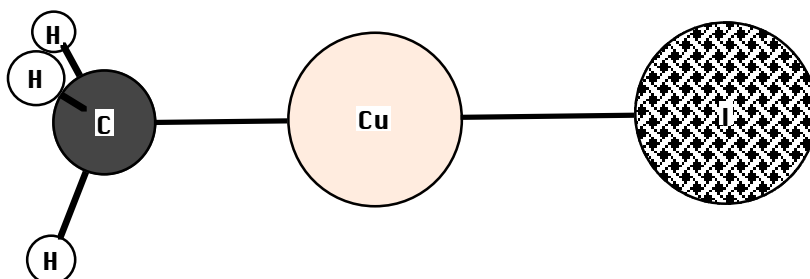
C	-4.383783	-0.248673	-0.352640
H	-4.707154	-1.113855	-0.946402
H	-4.805423	0.639296	-0.841918
H	-4.884791	-0.334760	0.620623
Cu	-2.442848	-0.150069	-0.181640
I	4.514286	0.203369	0.431291
C	-0.447363	-0.048694	-0.005835
C	1.893009	0.070202	0.200354
H	-0.366633	0.849769	0.597395
H	-0.179410	0.029218	-1.054534
H	-0.263001	-0.997990	0.486596
H	1.848077	1.026637	-0.279950
H	1.951704	-0.821341	-0.390563
H	1.764459	-0.000520	1.261462

(h) Product Neutral: CuCH₃

C	0.650324	-2.095223	3.242662
H	1.412809	-2.221232	2.468243
H	-0.283042	-2.579292	2.940208
H	1.001827	-2.506661	4.193527
Cu	0.321432	-0.235863	3.472230

(i) Product Neutral: CH₃CH₃

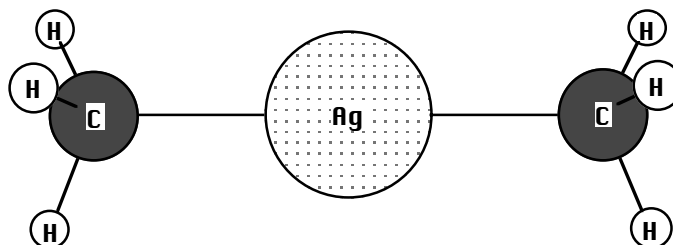
C	-0.030710	0.082165	-0.675867
C	0.020710	0.124334	0.848366
H	0.897458	-0.311772	-1.090323
H	-0.845610	-0.552337	-1.024866
H	-0.183781	1.077962	-1.092296
H	0.173773	-0.871464	1.264796
H	0.835615	0.758831	1.197366
H	-0.907454	0.518279	1.262823

(j) Product Ion: CH₃CuI

C	0.644371	-2.062150	3.246615
H	1.404736	-2.258220	2.479278
H	-0.256999	-2.609836	2.941693
H	1.001693	-2.536283	4.170154
Cu	0.306018	-0.157183	3.479287
I	-0.135429	2.327981	3.783073

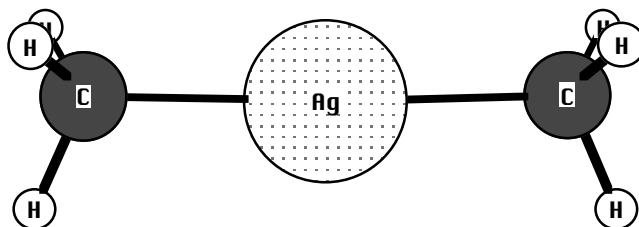
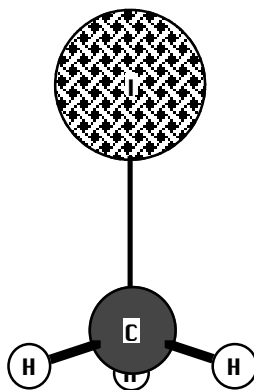
Supplementary FigureS3:
Structures and cartesian coordinates for all species associated with
Figure 3.

(a) Reactant Anion: $(\text{CH}_3)_2\text{Ag}^-$



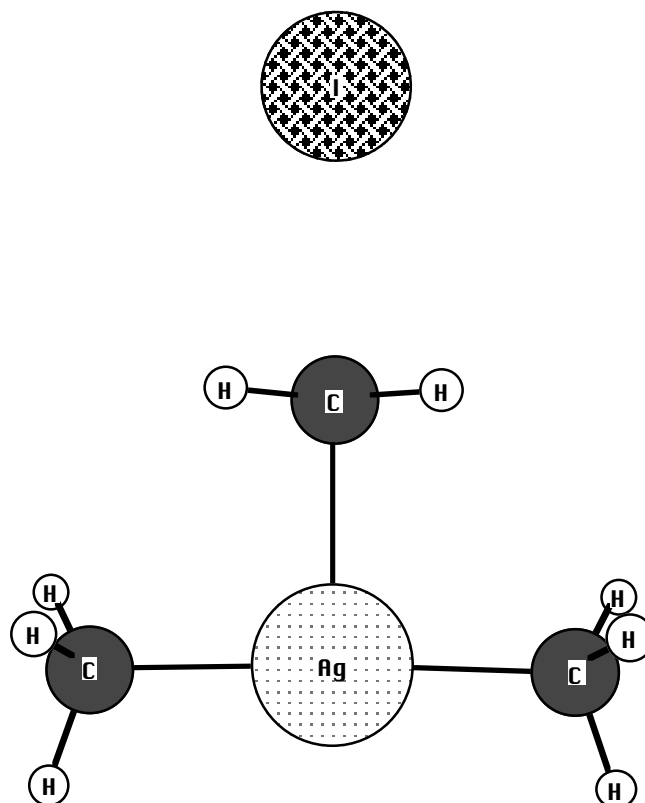
Ag	0.681551	1.082720	-0.032567
C	0.360154	3.180125	-0.326098
C	1.002992	-1.014675	0.260973
H	0.743945	3.772700	0.514733
H	-0.706740	3.418507	-0.427818
H	0.859880	3.545923	-1.232686
H	1.515246	-1.219396	1.210249
H	1.619199	-1.448133	-0.537673
H	0.057923	-1.573241	0.277877

(b) Pre Complex for "T shaped" transition state



C	2.069159	-1.643003	-0.467718
H	2.338008	-0.924995	-1.253925
H	2.553948	-2.593787	-0.723247
H	2.530788	-1.289736	0.464047
Ag	-0.052346	-1.843077	-0.282006
I	-0.364392	3.485279	0.547509
C	-2.180461	-1.949366	-0.094551
C	-0.238035	1.333227	0.212398
H	-2.519070	-1.653653	0.907438
H	-2.561838	-2.962629	-0.273874
H	-2.680988	-1.286938	-0.813299
H	-1.057281	0.863466	0.741228
H	-0.318064	1.152346	-0.851773
H	0.718832	0.991966	0.585823

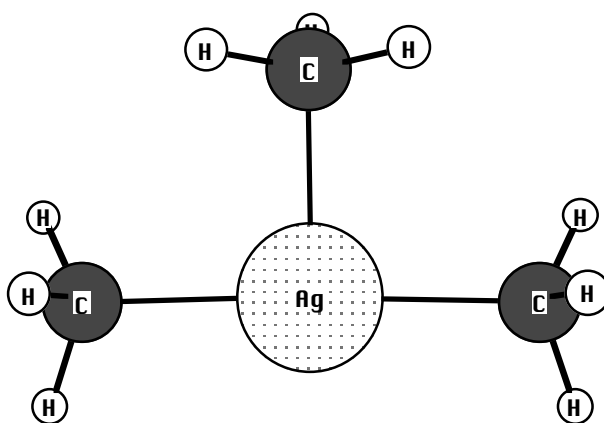
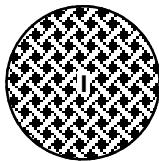
(c) "T shaped" transition state



Vibrational Frequency = -315.8822

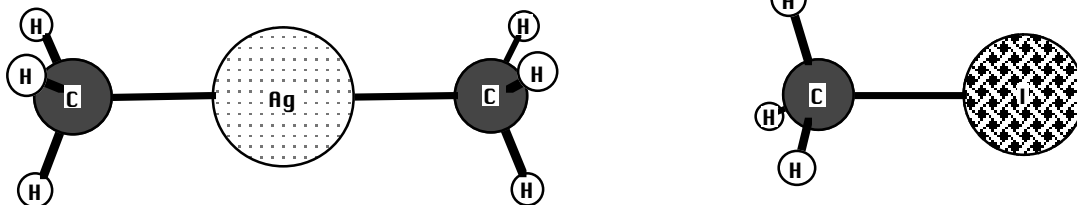
C	2.040027	-1.485728	-0.426469
H	2.338891	-0.701217	-1.128709
H	2.437711	-2.438985	-0.795535
H	2.515898	-1.273386	0.536799
Ag	-0.066203	-1.588111	-0.230614
I	-0.369782	3.420114	0.427196
C	-2.167269	-1.789128	-0.056992
C	-0.200826	0.687922	0.107484
H	-2.494420	-1.633446	0.976522
H	-2.482798	-2.794312	-0.362139
H	-2.692013	-1.064935	-0.687943
H	-1.081370	0.627222	0.720220
H	-0.305856	0.863365	-0.949186
H	0.771831	0.760794	0.558175

(d) Post complex for the T shaped TS



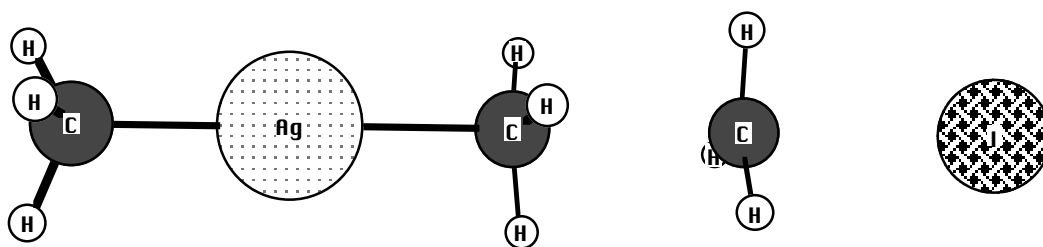
C	2.030420	-1.502417	-0.423725
H	2.328041	-0.704587	-1.107483
H	2.404214	-2.456938	-0.814436
H	2.496446	-1.316024	0.547325
Ag	-0.065040	-1.607188	-0.233216
I	-0.388819	3.694283	0.437858
C	-2.155068	-1.804139	-0.056500
C	-0.188755	0.492499	0.083355
H	-2.467384	-1.674944	0.983034
H	-2.451270	-2.806582	-0.389454
H	-2.677169	-1.064720	-0.667485
H	-1.063605	0.615922	0.706006
H	-0.304358	0.846387	-0.933804
H	0.754698	0.747367	0.545115

(e) Pre Complex for "Side On" transition state



C	-4.911974	-0.275506	-0.399174
H	-5.274842	-1.308920	-0.326668
H	-5.256113	0.120341	-1.363409
H	-5.419346	0.300368	0.385567
Ag	-2.784339	-0.167418	-0.211726
I	4.896091	0.222766	0.464930
C	-0.654302	-0.059208	-0.024067
C	2.737847	0.113122	0.274786
H	-0.357494	0.567316	0.827077
H	-0.193166	0.368773	-0.923656
H	-0.213771	-1.052828	0.129964
H	2.355027	1.113269	0.120690
H	2.498846	-0.516723	-0.571832
H	2.333522	-0.309309	1.185094

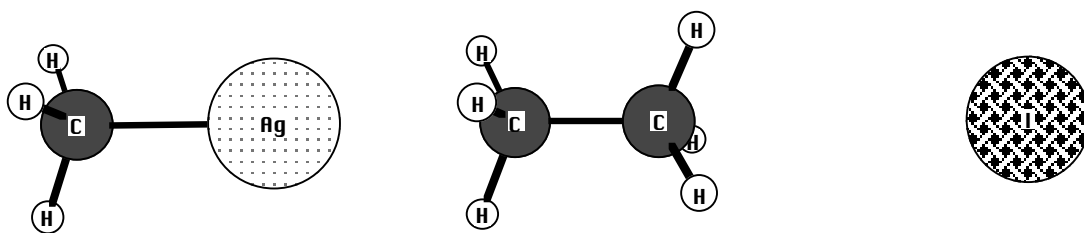
(f) Side On - TS



Vibrational Frequency = -629.2598

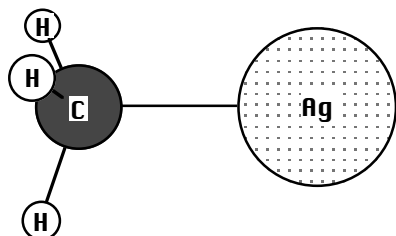
C	-4.643574	-0.261871	-0.375528
H	-4.999298	-1.292511	-0.271572
H	-4.975191	0.106793	-1.352094
H	-5.140755	0.339929	0.392726
Ag	-2.530316	-0.154513	-0.189347
I	4.635528	0.209528	0.441974
C	-0.321720	-0.042311	0.005233
C	2.019103	0.076608	0.211463
H	-0.268479	0.617789	0.862583
H	-0.094789	0.374515	-0.968611
H	-0.119948	-1.094754	0.164188
H	1.935751	1.134569	0.063007
H	2.084212	-0.577172	-0.635059
H	1.910604	-0.334012	1.195276

(g) Post complex for the Side On TS



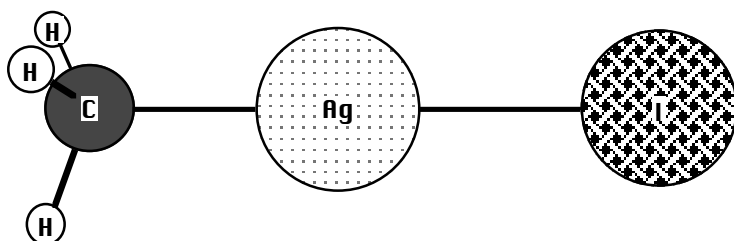
C	-4.653391	-0.262452	-0.376291
H	-4.920347	-0.601034	-1.378371
H	-5.091011	0.721857	-0.203972
H	-5.054638	-0.964378	0.356081
Ag	-2.564359	-0.156277	-0.192301
I	5.393122	0.247785	0.509078
C	-0.011643	-0.026426	0.032365
C	1.512852	0.050915	0.166833
H	-0.446763	0.955710	0.253317
H	-0.272187	-0.321615	-0.991215
H	-0.402115	-0.768492	0.739208
H	1.934551	0.779068	-0.521223
H	1.978239	-0.908040	-0.045954
H	1.807419	0.341673	1.171894

(h) Product Neutral: AgCH₃



C	0.658315	-2.140508	3.237106
H	1.417070	-2.259827	2.466136
H	-0.272881	-2.616764	2.936447
H	1.007536	-2.544437	4.185381
Ag	0.293309	-0.076734	3.491801

(i) Product Ion: CH₃AgI⁻

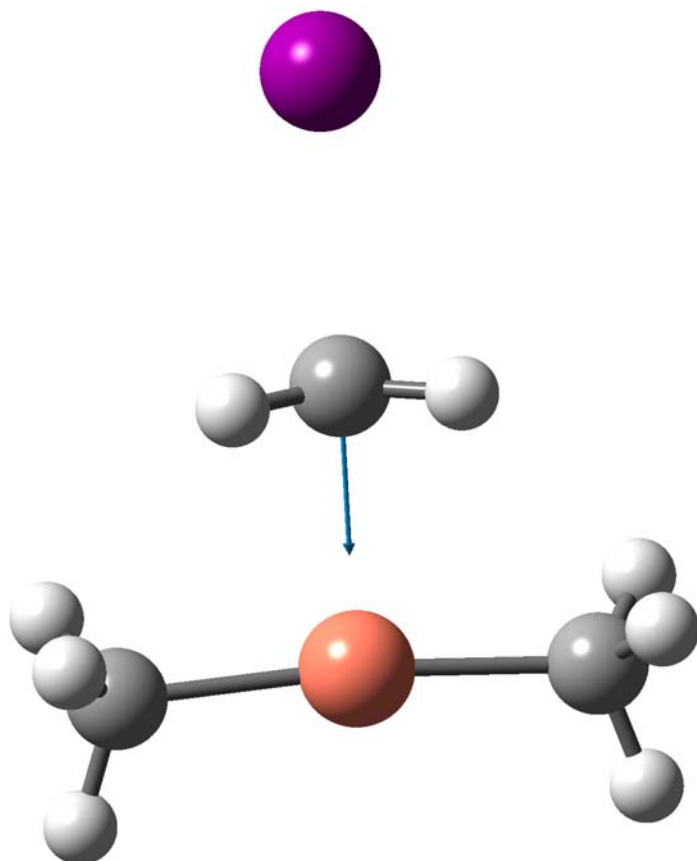


C	0.660870	-2.154979	3.235307
H	1.420903	-2.329200	2.466957
H	-0.248952	-2.682587	2.931629
H	1.015921	-2.608809	4.166083
Ag	0.293156	-0.084938	3.488280
I	-0.177508	2.564824	3.811844

Supplementary FigureS4:
Imaginary vibrational frequencies and their vectors for all transition states shown in Figures 2 and 3.

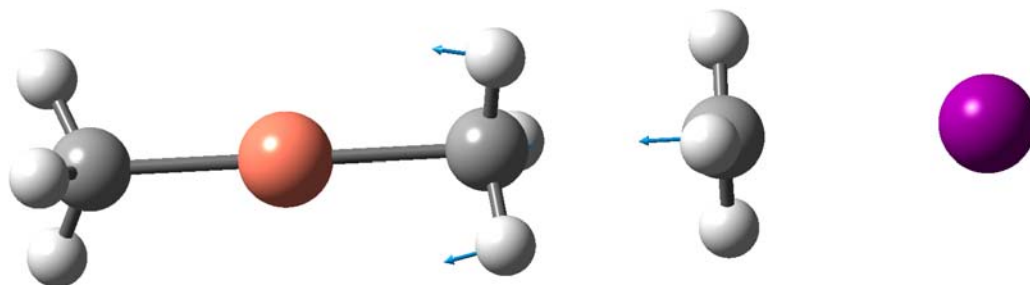
(a) Cu "T shaped" transition state (see Supplementary Figure S2(d) for cartesian coordinates)

Vibrational Frequency = -463.7312



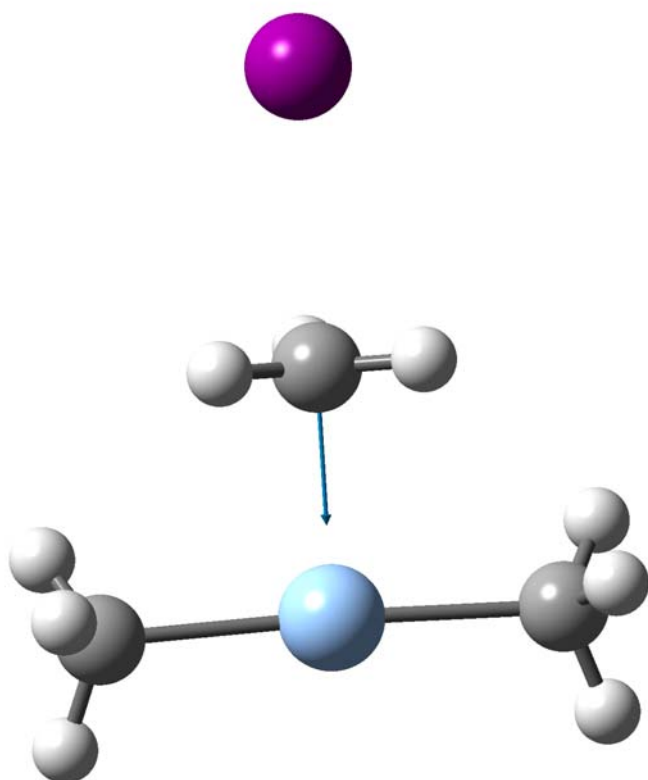
(b) Cu Side On - TS (see Supplementary Figure S2(g) for cartesian coordinates)

Vibrational Frequency = -637.7969



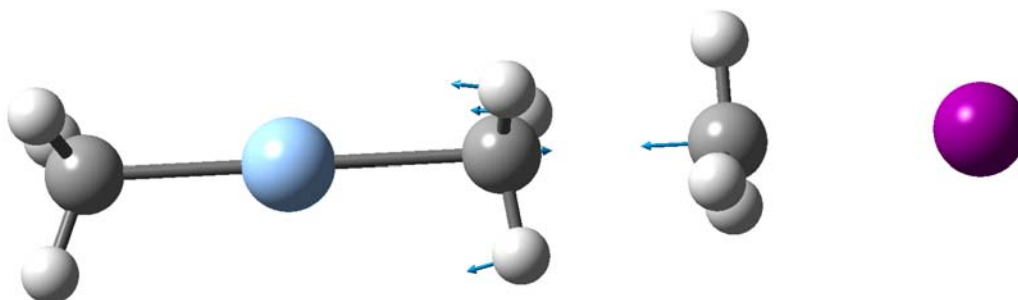
(c) Ag "T shaped" transition state (see Supplementary Figure S3(c) for cartesian coordinates)

Vibrational Frequency = -315.8822



(d) Ag Side On - TS (see Supplementary Figure S3(f) for cartesian coordinates)

Vibrational Frequency = -629.2598



Supplementary Table S1: Energies for all species associated with Figures 2 and 3.

Species	Structure Shown in Supplementary Figure	MP2 Energy (Hartrees)	Uncorrected Zero Point Energy (ZPE, Hartrees)	Relative energies (kJ mol ⁻¹) ^(a)
Organocopper System (Fig. 2)				
(CH ₃) ₂ Cu ⁻	Figure S2(a)	-1718.4618689	0.0689	0.0
CH ₃ I	Figure S2(b)	-50.9648283	0.037789	
Pre complex for T shaped TS	Figure S2(c)	-1769.442144	0.107741	-9.0
T shaped TS	Figure S2(d)	-1769.431083	0.107091	-2.5
Post complex for T shaped and side on TS	Figure S2(e)	-1769.513973	0.113819	-50.3
Pre complex for side on TS	Figure S2(f)	-1769.436815	0.106903	-6.2
side on TS	Figure S2(g)	-1769.410996	0.107315	+10.2
I ⁻		-11.2791816	-	
CuCH ₃	Figure S2(h)	-1678.6482563	0.035272	-24.4
CH ₃ CH ₃	Figure S2(i)	-79.5436166	0.076916	
CH ₃ CuI ⁻	Figure S2(j)	-1689.9952357	0.03535	-66.9
Organosilver System (Fig. 3)				
(CH ₃) ₂ Ag ⁻	Figure S3(a)	-225.7699069	0.069599	0.0
Pre complex for T shaped TS	Figure S3(b)	-276.748863	0.107977	-8.5
T shaped TS	Figure S3(c)	-276.7285025	0.10799	+4.3
Post complex for T shaped TS	Figure S3(d)	-276.7306078	0.108871	+3.5
Pre complex for side on TS	Figure S3(e)	-276.7441484	0.107788	-5.7
side on TS	Figure S3(f)	-276.7190959	0.108396	+10.4
Post complex for side on TS	Figure S3(g)	-276.8085668	0.113046	-42.8
AgCH ₃	Figure S3(h)	-185.9632739	0.035598	-29.0
CH ₃ AgI ⁻	Figure S3(i)	-197.3116475	0.035672	-72.4

(a) Calculated from MP2 Energy + 0.9882 ZPE. Scaling factor from: Scott, A. P.; Radom, L. *J. Phys. Chem.* 1996, 100, 16502.