Supporting Information

The Fate of Copper Catalysts in Atom Transfer Radical Chemistry

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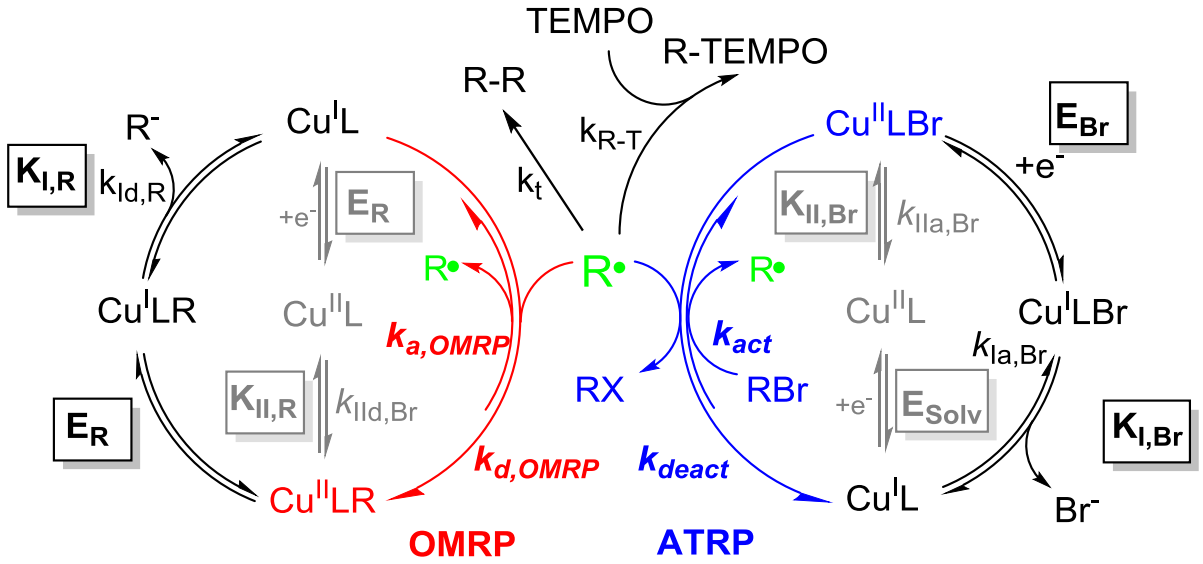
S1. Electrochemistry Simulations

A detailed protocol for measuring and simulating the full complement of thermodynamic and kinetic parameters from Scheme S1 (which includes the 'solvent pathway') has been described in previous work.[1] The same method was employed here and many of the parameters from Scheme 2 ($K_{II,Br}$, k_t, k_{R-T}) are identical to those used in this, and other, earlier studies.[2] The rate and equilibrium constants for the ATRP and OMRP reactions were determined as described in the main-text. The full complement of thermodynamic and kinetic parameters (excluding those reported in the main-text) are collected in Table S1 below.



Scheme S1. Complete mechanism used to simulate the voltammetry of Cu/Me_6tren with bromo-ester initiators in DMSO.

Table S1. Kinetic and thermodynamic parameters used in the simulation of the voltammetry of Cu/Me_6tren with added bromo-ester initiators in DMSO.

$\mathbf{E_{Br}}$ (mV *vs.* $Fc^{+/0}$)	-817
$\boldsymbol{k_0}$ ($cm^2\ s^{-1}$)	0.0096
$\mathbf{E_{Solv}}$ (mV *vs.* $Fc^{+/0}$)	-737
$\boldsymbol{k_0}$ ($cm^2\ s^{-1}$)	0.005
$\mathbf{E_R}$ **– EtBrP** (mV *vs.* $Fc^{+/0}$)	-1232
$\mathbf{E_R}$ **– EtBrA** (mV *vs.* $Fc^{+/0}$)	-997
***D* – Cu/Me_6tren** ($cm^2\ s^{-1}$)	6.15×10^{-6}
D* – *RBr ($cm^2\ s^{-1}$)	1.44×10^{-5}
$\boldsymbol{K_{II,Br}}$ (M^{-1})	7.6×10^3
$\boldsymbol{k_{IIa,Br}}$ ($M^{-1}\ s^{-1}$)	1.2×10^3
$\boldsymbol{K_{I,Br}}$ (M^{-1})	3.4×10^2
$\boldsymbol{k_{Ia,Br}}$ ($M^{-1}\ s^{-1}$)	3.3×10^6
$\boldsymbol{k_{R-T}}$ ($M^{-1}\ s^{-1}$)	3.0×10^8
$\boldsymbol{k_{R-R}}$ ($M^{-1}\ s^{-1}$)	3.0×10^8

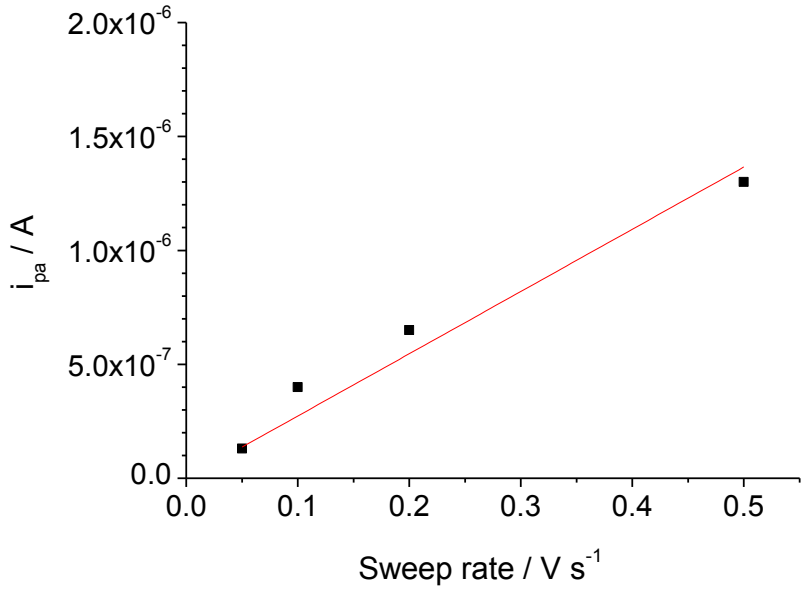


Figure S1. Sweep-rate dependence of the peak anodic current (i_{pa}) for the wave at -300 mV (*vs.* $Fc^{+/0}$) in experiment Figure 1F. Current is directly proportional to the sweep rate as expected for an eletro-adsorbed species.[3]

S2. Spectroelectrochemistry

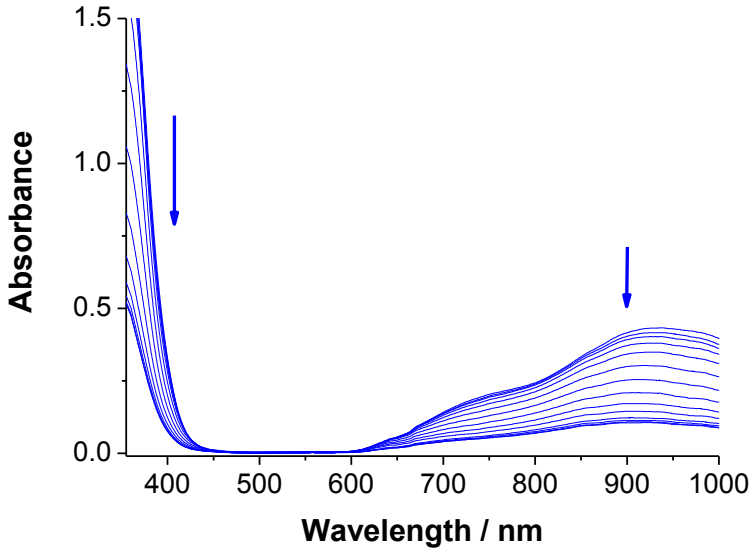


Figure S2. UV-vis spectra measured every 120 s during the electrochemical reduction of a 6.0 mM solution of [Cu^{II}(Me_6tren)Br]Br and 36.0 mM EtBrP in DMSO (0.1 M (Et_4N)(ClO_4)) at a potential of -1000 mV *vs.* $Fc^{+/0}$. The loss of spectral features is due to the reduction of all Cu^{II} complexes to their Cu^{I} form.

S3. Computational Chemistry

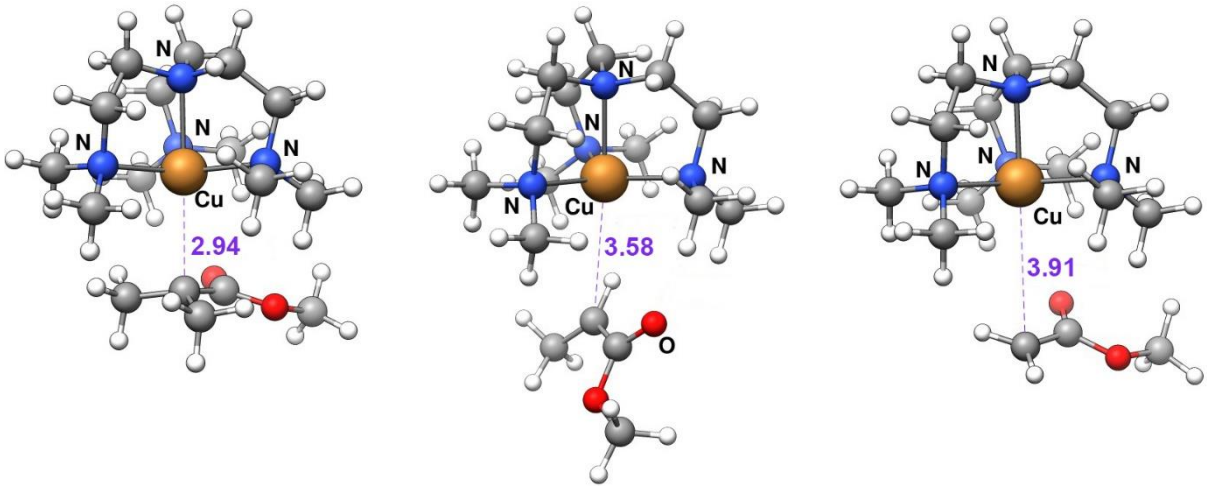


Figure S3. Transition-state structures along the potential energy surface for the OMRP pathway with (left to right) initiators EBriB, EtBrp and EtBrAc.

Computations

The Cartesian coordinates for the optimized geometries for are listed below, together with the following energies (in Hartree):

BP86 electronic potential energy in the gas phase (E_{gas}),

BP86 Gibbs free energy in the gas phase at 298.15 K and 1 atm (G_{gas}),

BP86 single-point electronic potential energy plus solvation energy in SMD DMSO at 0 K (E_{DMSO})

BP86-D3 electronic potential energy in the gas phase ($E_{BP86\text{-}D3}$)

Total Gibbs free energy, including dispersion, in DMSO at 298.15 K and 1 mol L^{-1} (G_{tot})

$[Cu(Me_6tren)]^+$

E_{gas} = -890.582508

G_{gas} = -890.211239

E_{DMSO} = -890.659668

$E_{BP86\text{-}D3}$ = -890.663417

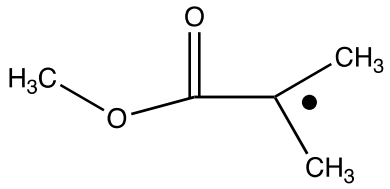
G_{tot} = -890.366289

N	0.015541	0.085619	1.613996
C	-1.193984	0.864352	1.970144
C	-2.274181	0.881925	0.865274
H	-0.883019	1.897008	2.190455
H	-1.662808	0.480758	2.898154
C	1.305869	0.743153	1.936021
C	2.404159	0.416052	0.908029
H	1.679176	0.464573	2.942190
H	1.134452	1.829718	1.960763
N	-1.753448	1.264638	-0.481686
H	-3.083842	1.574406	1.178339
H	-2.731706	-0.113218	0.763550
N	2.037086	0.769782	-0.498665
H	2.621425	-0.663988	0.925893
H	3.340060	0.932402	1.206115
C	-1.468583	2.722140	-0.524952
H	-0.733643	2.994015	0.243935
H	-2.390730	3.313383	-0.354627
H	-1.057210	2.985783	-1.508798

C	-2.780148	0.970128	-1.515196
H	-2.385204	1.233336	-2.506340
H	-3.709729	1.547337	-1.339912
H	-3.023757	-0.100789	-1.508601
C	2.979660	0.108613	-1.440317
H	2.930336	-0.981191	-1.317465
H	4.022657	0.440953	-1.268064
H	2.698450	0.360362	-2.472399
C	2.145966	2.238135	-0.703286
H	3.187315	2.585074	-0.548931
H	1.490625	2.775363	-0.006038
H	1.839430	2.486854	-1.728546
Cu	0.022375	0.046510	-0.613095
C	-0.026647	-1.344001	1.998410
C	-0.801733	-2.228653	1.004868
H	1.011202	-1.704128	2.075162
H	-0.476723	-1.476110	3.003802
N	-0.314072	-2.115688	-0.403191
H	-1.866685	-1.952792	1.009203
H	-0.747902	-3.282057	1.349679
C	0.928943	-2.910207	-0.575475
H	0.746944	-3.985775	-0.377124
H	1.710806	-2.559241	0.111537
H	1.293008	-2.801433	-1.606539
C	-1.336249	-2.668271	-1.329330
H	-1.525806	-3.742457	-1.133101
H	-0.988720	-2.557374	-2.366054
H	-2.281443	-2.120217	-1.214775

Radical Substrates

1a



E_{gas} = -346.462188

G_{gas} = -346.370220

E_{DMSO} = -346.468334

$E_{BP86\text{-}D3}$ = -346.473637

G_{tot} = -346.384795

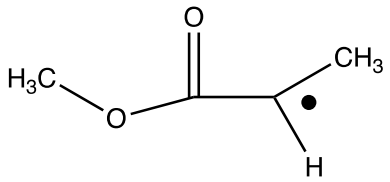
C	-2.576741	0.242868	-0.000008
O	-1.200248	0.675487	0.000001
H	-3.172117	1.164165	-0.000056
H	-2.795546	-0.361461	0.893772
H	-2.795511	-0.361540	-0.893742
C	-0.283175	-0.355131	0.000010
O	-0.624359	-1.538566	0.000000
C	1.096038	0.120760	0.000033
C	2.183960	-0.901176	-0.000013
H	1.767054	-1.916557	-0.000124
H	2.839790	-0.781004	0.883658
H	2.839878	-0.780832	-0.883594
C	1.449093	1.572549	0.000007

H 2.069142 1.823740 0.882361

H 0.560993 2.214948 0.000549

H 2.068124 1.823944 -0.883017

1b



E_{gas} = -307.132968

G_{gas} = -307.064236

E_{DMSO} = -307.139276

$E_{BP86\text{-}D3}$ = -307.140891

G_{tot} = -307.075448

C 2.385028 -0.049950 0.000023

O 1.117119 -0.740175 -0.000022

H 3.146759 -0.838907 -0.000084

H 2.482795 0.585217 0.893992

H 2.482787 0.585373 -0.893845

C 0.019279 0.091801 -0.000010

O 0.106142 1.318782 -0.000008

C -1.215933 -0.671116 -0.000007

C -2.534468 0.007675 0.000005

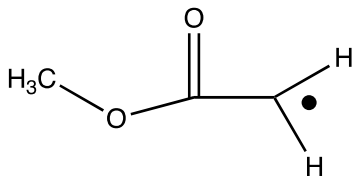
H -2.406192 1.099052 -0.000003

H -3.135834 -0.284241 0.882211

H -3.135922 -0.284257 -0.882128

H -1.143918 -1.761549 0.000035

1c



E_{gas} = -267.799797

G_{gas} = -267.755868

E_{DMSO} = -276.805275

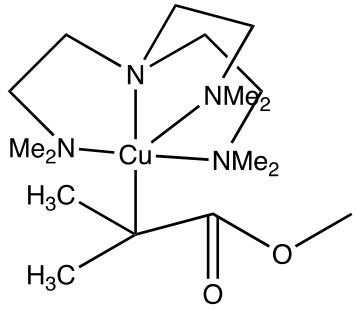
$E_{BP86\text{-}D3}$ = -267.805250

G_{tot} = -267.763780

C	1.827780	-0.100473	0.000001
O	0.534267	-0.743413	0.000000
H	2.559623	-0.916998	-0.000230
H	1.947005	0.531180	0.893812
H	1.946826	0.531553	-0.893567
C	-0.530388	0.128285	-0.000019
O	-0.402573	1.350170	0.000005
C	-1.792511	-0.582874	0.000003
H	-2.710612	0.003031	0.000007
H	-1.825689	-1.672451	0.000025

Organometallic Products

2a



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G_{gas} = -1236.562917

E_{DMSO} = -1237.136199

$E_{BP86\text{-}D3}$ = -1237.173133

G_{tot} = -1236.762049

C	-1.500699	2.742398	-0.347339
N	-0.131918	2.219273	-0.578867
C	0.791939	2.902748	0.363465
C	2.164132	2.245282	0.409034
N	2.069447	0.815826	0.812222
C	1.953386	0.706567	2.293140
C	1.330091	-0.620127	2.704929
N	-0.028403	-0.811684	2.136467
C	-0.432991	-2.224035	2.359497
C	0.260553	2.516443	-1.978624
Cu	0.154290	-0.070214	-0.085692
N	2.012274	-1.217883	-1.399073
C	1.851714	-1.332422	-2.866231
C	-1.575888	-0.970124	-1.070783

C	-2.741183	-0.684654	-0.186191
C	2.283176	-2.566419	-0.846957
C	3.160250	-0.319925	-1.128979
C	3.270436	0.074047	0.338582
C	-1.005764	0.065025	2.833836
H	3.390278	-0.825344	0.959409
H	4.184434	0.681642	0.491981
H	4.113236	-0.795259	-1.446291
H	3.036454	0.577744	-1.756811
H	2.946155	0.821448	2.771739
H	1.333927	1.539876	2.655717
H	1.297401	-0.682664	3.812397
H	1.955408	-1.460541	2.362346
H	2.825219	2.803943	1.100881
H	2.638284	2.296471	-0.581971
H	0.903901	3.972410	0.089655
H	0.323447	2.881423	1.360620
H	-2.213335	2.239031	-1.009972
H	-1.541049	3.835736	-0.524341
H	-1.800798	2.540774	0.690802
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H	1.016824	-2.005222	-3.103847
H	2.767337	-1.737795	-3.343748
H	2.367381	-2.531105	0.247768
H	3.222585	-2.989036	-1.259392
H	1.457394	-3.243391	-1.098206
C	-1.267909	-2.465047	-1.085890
C	-1.671919	-0.389275	-2.475897
O	-3.526411	0.344133	-0.638041
O	-3.037323	-1.315416	0.828676
C	-4.726943	0.595981	0.139161
H	-5.286503	1.347009	-0.430288
H	-5.311930	-0.327173	0.249379
H	-4.471840	0.979430	1.138533
H	-2.142521	-3.023159	-1.475885
H	-0.429144	-2.688788	-1.758278
H	-1.054546	-2.877894	-0.092977
H	-2.414778	-0.959729	-3.069156
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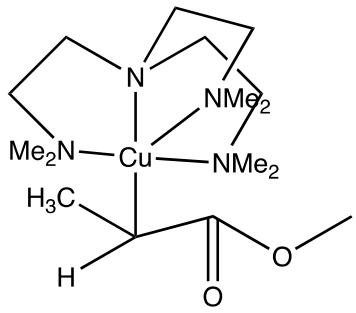
2b



E_{gas} = -1197.740524

G_{gas} = -1197.275083

E_{DMSO} = -1197.823702

$E_{BP86\text{-}D3}$ = -1197.852046

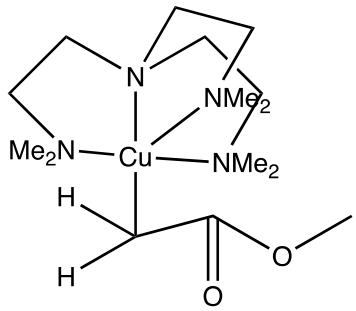
G_{tot} = -1197.466764

C	1.578224	-1.414582	2.171175
N	0.197555	-1.486294	1.630294
C	-0.762659	-1.031628	2.672124
C	-2.138482	-0.729529	2.087031
N	-2.055622	0.298139	1.011288
C	-1.973012	1.668117	1.595133
C	-1.376766	2.656345	0.598260
N	-0.022485	2.247832	0.145348
C	0.334898	3.007207	-1.082505
C	-0.092784	-2.887418	1.237337
Cu	-0.149848	-0.058969	-0.094646
N	-1.858866	-0.711882	-1.791439
C	-1.665872	-1.931048	-2.607951
C	1.534500	-0.454983	-1.317313
C	2.760563	0.216414	-0.832868
C	-2.023507	0.433891	-2.714088

C	-3.063928	-0.897842	-0.948724
C	-3.231971	0.196325	0.100488
C	0.981768	2.553314	1.197841
H	-3.369582	1.168486	-0.393789
H	-4.155708	0.011041	0.682995
H	-3.982694	-0.937517	-1.572581
H	-2.975445	-1.883434	-0.462167
H	-2.973576	2.014399	1.920988
H	-1.346673	1.621799	2.498168
H	-1.347980	3.667698	1.052677
H	-2.018983	2.735079	-0.293427
H	-2.826410	-0.401955	2.891002
H	-2.573241	-1.643612	1.656159
H	-0.857918	-1.791151	3.474589
H	-0.339244	-0.128944	3.140577
H	2.297927	-1.700285	1.394448
H	1.695564	-2.082562	3.046962
H	1.799210	-0.382949	2.479949
H	0.635312	-3.213131	0.485156
H	-1.098949	-2.969043	0.803334
H	-0.028648	-3.564258	2.112366
H	1.341511	2.706995	-1.400503
H	0.320258	4.097698	-0.887209
H	-0.387947	2.784611	-1.880064
H	1.979104	2.292503	0.822938
H	0.772827	1.978685	2.111996
H	0.966220	3.632390	1.450992
H	-1.507663	-2.803369	-1.957324

H	-0.790032	-1.808436	-3.258974
H	-2.548521	-2.128598	-3.250221
H	-2.179666	1.366564	-2.156313
H	-2.883651	0.284878	-3.398805
H	-1.112808	0.547004	-3.319228
H	1.104787	0.149899	-2.132430
C	1.682273	-1.930698	-1.656007
O	3.648718	-0.654174	-0.251457
O	3.018530	1.416999	-0.931477
C	4.907219	-0.066673	0.170994
H	5.524432	-0.911772	0.496940
H	5.381673	0.464104	-0.665670
H	4.749192	0.639835	0.999514
H	2.278925	-2.061058	-2.580015
H	2.220747	-2.476014	-0.869207
H	0.718399	-2.425896	-1.829624

2c



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G_{gas} = -1157.988121

E_{DMSO} = -1158.513500

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G_{tot} = -1158.177034

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C	-0.665000	1.697746	-2.255939
C	-2.052115	1.330931	-1.731956
N	-2.024552	0.057785	-0.953365
C	-2.028739	-1.130259	-1.858901
C	-1.430807	-2.355421	-1.168765
N	-0.050698	-2.098073	-0.682030
C	0.345123	-3.131951	0.309109
C	0.193327	3.027870	-0.385264
Cu	-0.159085	-0.000125	0.169132
N	-1.651485	0.373630	1.954777
C	-1.216144	1.407076	2.922203
C	1.454402	-0.030191	1.437870
C	2.765835	-0.357127	0.857140
C	-1.870333	-0.896676	2.684616
C	-2.890997	0.814078	1.267589
C	-3.167260	-0.001427	0.005347
C	0.923080	-2.128386	-1.803836
H	-3.336641	-1.055489	0.269666
H	-4.098020	0.355635	-0.476496
H	-3.768513	0.750843	1.943899
H	-2.767994	1.879436	1.014253
H	-3.055917	-1.352280	-2.207240
H	-1.439445	-0.879756	-2.753190
H	-1.449681	-3.217779	-1.865780
H	-2.043148	-2.642410	-0.298540

H	-2.767408	1.259358	-2.573981
H	-2.425354	2.126746	-1.070479
H	-0.721729	2.655043	-2.813296
H	-0.314439	0.937820	-2.972558
H	2.442879	1.781422	-0.925412
H	1.874028	2.584023	-2.430778
H	1.852293	0.794437	-2.290170
H	0.927919	3.032371	0.431300
H	-0.813651	3.099552	0.049163
H	0.364881	3.917787	-1.022960
H	1.372579	-2.923729	0.637501
H	0.303523	-4.143913	-0.139066
H	-0.334476	-3.100255	1.172773
H	1.926668	-1.936751	-1.401723
H	0.676338	-1.362230	-2.552777
H	0.916423	-3.118741	-2.301057
H	-1.014058	2.351869	2.398392
H	-0.294502	1.078456	3.421262
H	-1.987931	1.586179	3.696691
H	-2.200148	-1.689263	1.999007
H	-2.634652	-0.777920	3.478607
H	-0.928744	-1.215861	3.152467
H	1.113070	-0.846420	2.089980
H	1.442886	0.946034	1.938531
O	3.584603	0.746824	0.781672
O	3.139072	-1.464303	0.469847
C	4.922719	0.486547	0.279734
H	5.457150	1.438657	0.375800

H 5.409676 -0.295541 0.878401

H 4.890043 0.162305 -0.771375

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van der Waals complexes of $[Cu(Me_6tren)]^+$ and Radicals

VDW-1a

E_{gas} = -1237.047194

G_{gas} = -1236.564138

E_{DMSO} = -1237.132811

$E_{BP86\text{-}D3}$ = -1237.157139

G_{tot} = -1236.756681

C 4.436712 -2.150406 0.382813

O 3.601011 -1.128227 -0.218418

H 3.917163 -3.099387 0.202509

H 4.562428 -1.969331 1.460434

H 5.429568 -2.160490 -0.089698

C 4.116785 0.158130 -0.094680

O 5.132757 0.391265 0.554141

C 3.324126 1.150317 -0.809804

C 3.770617 2.574216 -0.750393

H 4.571101 2.706118 -0.010941

H 2.932108 3.255018 -0.513904

H 4.158605 2.902371 -1.734851

C 2.141121 0.761340 -1.626371

H	1.213068	0.619579	-0.991807
H	2.300204	-0.203286	-2.131424
H	1.895926	1.530518	-2.375033
Cu	-0.754751	0.084990	-0.157007
N	-2.080050	1.726418	-0.814534
N	-0.834952	-1.760970	-1.283053
N	0.062232	0.343720	1.832197
N	-2.564985	-0.687758	0.906299
C	-2.234570	-2.227622	-1.046595
C	-2.694364	-2.081273	0.412693
H	-2.080696	-2.725953	1.059354
H	-3.733680	-2.459300	0.491730
H	-2.890511	-1.637478	-1.706878
H	-2.347784	-3.287560	-1.354613
C	0.141825	-2.755211	-0.764052
C	-2.249740	-0.573870	2.351147
C	-1.165485	0.476454	2.669712
H	-3.153080	-0.326498	2.943179
H	-1.913613	-1.560255	2.704987
H	-0.908836	0.400113	3.747174
H	-1.557213	1.492141	2.510676
C	0.911896	1.548820	2.010380
C	-3.213683	1.636866	0.153785
C	-2.576684	1.535959	-2.200714
C	-3.661920	0.194006	0.442349
H	-4.086425	2.213078	-0.217539
H	-2.891793	2.124055	1.086042

H	-4.086286	-0.246547	-0.473307
H	-4.487797	0.227674	1.182210
C	0.856297	-0.840821	2.252426
C	-1.464074	3.075107	-0.732812
C	-0.608891	-1.618173	-2.744640
H	0.245209	-1.751361	2.194457
H	1.218075	-0.726564	3.293855
H	1.717845	-0.955205	1.580192
H	-0.751965	-2.583303	-3.269821
H	0.418853	-1.274518	-2.922599
H	-1.306009	-0.880404	-3.163627
H	-1.093559	3.256960	0.285303
H	-2.190054	3.871331	-0.992303
H	-0.617173	3.133095	-1.430654
H	-0.041281	-2.952575	0.300084
H	1.160252	-2.355703	-0.868844
H	0.065284	-3.712114	-1.318241
H	-3.072715	0.561421	-2.303422
H	-1.730591	1.573424	-2.900825
H	-3.301250	2.327696	-2.479079
H	0.358485	2.447653	1.705330
H	1.812202	1.456541	1.385891
H	1.228047	1.667115	3.065595

VDW-1b

E_{gas} = -1197.7167246

G_{gas} = -1197.258906

E_{DMSO} = -1197.805923

$E_{BP86\text{-}D3}$ = -1197.822258

G_{tot} = -1197.450619

C	5.065413	1.426970	-0.175805
O	3.981672	0.649922	0.396965
H	4.810159	2.475608	0.018385
H	5.154639	1.236475	-1.255467
H	6.018338	1.167243	0.307380
C	4.147619	-0.723896	0.266399
O	5.076419	-1.217666	-0.364980
C	3.119925	-1.477523	0.955311
C	2.022209	-0.888342	1.747775
H	1.125281	-0.617132	1.089714
H	2.319669	0.055016	2.229016
H	1.639399	-1.588638	2.505344
Cu	-0.596871	-0.054388	0.156070
N	-2.030819	-0.147742	1.844050
N	0.186688	1.886464	-0.392924
N	-0.573538	-1.851383	-1.080188
N	-2.377204	0.513200	-1.060391
C	-1.045242	2.621164	-0.808059
C	-1.976517	1.790878	-1.704231

H	-1.462482	1.548676	-2.646244
H	-2.852451	2.412518	-1.977286
H	-1.574331	2.919675	0.111471
H	-0.777063	3.558717	-1.337334
C	1.148613	1.801825	-1.524232
C	-2.585453	-0.610278	-2.007622
C	-1.996579	-1.948729	-1.519318
H	-3.661637	-0.764005	-2.221391
H	-2.118905	-0.337484	-2.966216
H	-2.099841	-2.695939	-2.333759
H	-2.573227	-2.332471	-0.664737
C	-0.192901	-3.096920	-0.366893
C	-3.349003	-0.241223	1.149029
C	-1.981611	1.073118	2.688201
C	-3.465118	0.691304	-0.067775
H	-4.175448	-0.012303	1.853213
H	-3.485471	-1.287268	0.837089
H	-3.443687	1.738352	0.272180
H	-4.459142	0.536104	-0.534255
C	0.326213	-1.707168	-2.254450
C	-1.856658	-1.323657	2.733716
C	0.855772	2.623644	0.712072
H	0.063198	-0.812995	-2.834492
H	0.257117	-2.591115	-2.919276
H	1.364067	-1.606230	-1.908136
H	1.114660	3.655755	0.402995
H	1.781230	2.097607	0.983367

H 0.194200 2.672636 1.587449

H -1.894541 -2.249598 2.143654

H -2.645842 -1.367161 3.510367

H -0.879405 -1.263553 3.232491

H 0.702263 1.270565 -2.374587

H 2.041532 1.256062 -1.190703

H 1.451590 2.813792 -1.860222

H -2.135624 1.972985 2.077664

H -0.997606 1.143403 3.172198

H -2.761613 1.046928 3.475493

H -0.834150 -3.238611 0.513822

H 0.852338 -3.020359 -0.036532

H -0.289365 -3.983945 -1.023391

H 3.220723 -2.560879 0.860296

Transition States for Hydrogen Atom Transfer

TS-3a

E_{gas} = -1237.016758

G_{gas} = -1236.535949

E_{DMSO} = -1237.104457

$E_{BP86\text{-}D3}$ = -1237.126334

G_{tot} = -1236.730206

C 4.657705 2.054013 -0.577954

O 3.769952 1.159263 0.143271

H	4.212217	3.050874	-0.477581
H	4.732237	1.760493	-1.635191
H	5.663224	2.034873	-0.133923
C	4.182038	-0.156082	0.144683
O	5.146501	-0.543689	-0.496109
C	3.342361	-1.037251	0.997688
C	3.681776	-2.501880	0.933053
H	3.601436	-2.894327	-0.094870
H	3.029141	-3.090846	1.593214
H	4.729500	-2.668069	1.232467
C	2.357128	-0.527632	1.798893
H	0.624154	-0.448206	0.925048
H	2.262577	0.550177	1.926667
H	1.863240	-1.167161	2.533597
Cu	-0.724143	-0.059181	0.185788
N	-2.066618	-1.819908	0.756454
N	-1.040231	1.846009	1.304789
N	0.094284	-0.316151	-1.855415
N	-2.520670	0.597034	-0.909167
C	-2.442514	2.230939	0.989885
C	-2.782071	2.005998	-0.486613
H	-2.159289	2.663693	-1.110591
H	-3.833926	2.298787	-0.671692
H	-3.103153	1.626434	1.632589
H	-2.633844	3.292121	1.250435
C	-0.078525	2.865221	0.817607
C	-2.225014	0.493887	-2.372190
C	-1.110434	-0.511507	-2.700902

H	-3.134266	0.222826	-2.941040
H	-1.927197	1.492233	-2.725538
H	-0.860363	-0.424216	-3.779161
H	-1.458034	-1.543270	-2.541121
C	1.005020	-1.479022	-1.969663
C	-3.183680	-1.743214	-0.220286
C	-2.560637	-1.665460	2.144417
C	-3.631688	-0.300011	-0.474698
H	-4.057907	-2.334153	0.123746
H	-2.842838	-2.207622	-1.157661
H	-4.055688	0.117256	0.451260
H	-4.448940	-0.296752	-1.222407
C	0.841876	0.906987	-2.234427
C	-1.371526	-3.123407	0.650196
C	-0.863990	1.689797	2.767828
H	0.193846	1.792029	-2.169971
H	1.232343	0.831470	-3.268885
H	1.681945	1.038134	-1.538026
H	-1.060259	2.640710	3.301046
H	0.166844	1.374210	2.976006
H	-1.548598	0.919892	3.148196
H	-1.007785	-3.271235	-0.375887
H	-2.041626	-3.965971	0.912932
H	-0.507184	-3.129870	1.328132
H	-0.227316	3.057755	-0.253360
H	0.945530	2.493537	0.958157
H	-0.199414	3.820269	1.366413
H	-3.108898	-0.720091	2.260451

H -1.704973 -1.657124 2.833780

H -3.237956 -2.496925 2.426104

H 0.475524 -2.399296 -1.688749

H 1.847464 -1.339745 -1.280005

H 1.392460 -1.588383 -3.001452

TS-3b

E_{gas} = -1197.689407

G_{gas} = -1197.232974

E_{DMSO} = -1197.778945

$E_{BP86\text{-}D3}$ = -1197.793695

G_{tot} = -1197.423782

C -5.169902 1.398567 0.263611

O -4.128929 0.659760 -0.428676

H -4.987410 2.452985 0.024927

H -5.115962 1.224465 1.348324

H -6.161283 1.088256 -0.095787

C -4.219183 -0.707664 -0.282094

O -5.036974 -1.244194 0.448939

C -3.233490 -1.439519 -1.096067

C -2.335915 -0.867677 -1.948708

H -0.686137 -0.423465 -1.051947

H -2.401684 0.194309 -2.187361

H -1.733993 -1.489469 -2.614051

Cu 0.591234 -0.050030 -0.198034

N	2.238037	-0.282842	-1.764442
N	-0.083864	2.017320	0.255729
N	0.493141	-1.840861	1.126977
N	2.279635	0.481856	1.099343
C	1.125053	2.686655	0.806030
C	1.910185	1.774484	1.753037
H	1.293853	1.541377	2.634099
H	2.804020	2.311241	2.125977
H	1.754384	2.988717	-0.047007
H	0.854426	3.619766	1.341542
C	-1.174773	1.953461	1.260418
C	2.465370	-0.620964	2.092729
C	1.887594	-1.964698	1.622498
H	3.535454	-0.755097	2.337923
H	1.970833	-0.321170	3.028501
H	1.951354	-2.691629	2.459370
H	2.488149	-2.376636	0.798287
C	0.086871	-3.074269	0.413663
C	3.491524	-0.326935	-0.966458
C	2.230357	0.885058	-2.676405
C	3.462178	0.660954	0.204341
H	4.376363	-0.106878	-1.598921
H	3.621814	-1.355351	-0.597166
H	3.430813	1.688402	-0.188206
H	4.402915	0.573700	0.782258
C	-0.461488	-1.603464	2.236410
C	2.096312	-1.512374	-2.577909
C	-0.584115	2.751593	-0.931161

H	-0.195302	-0.691715	2.788357
H	-0.469281	-2.454887	2.945556
H	-1.470524	-1.477745	1.821492
H	-0.856488	3.793281	-0.671040
H	-1.475724	2.240793	-1.317158
H	0.184555	2.769168	-1.715333
H	2.101055	-2.396961	-1.926011
H	2.918000	-1.611935	-3.314693
H	1.139612	-1.481462	-3.116757
H	-0.839385	1.427482	2.164235
H	-2.023460	1.406095	0.827269
H	-1.506770	2.970981	1.547844
H	2.371766	1.817646	-2.112716
H	1.261808	0.933664	-3.193014
H	3.036735	0.810004	-3.433371
H	0.781594	-3.276716	-0.412854
H	-0.919428	-2.931298	-0.001299
H	0.077078	-3.948117	1.094010
H	-3.280433	-2.523029	-0.961263

$[Cu(Me_6tren)H]^+$

E_{gas} = -891.140512

G_{gas} = -890.764117

E_{DMSO} = -891.225195

$E_{BP86\text{-}D3}$ = -891.224573

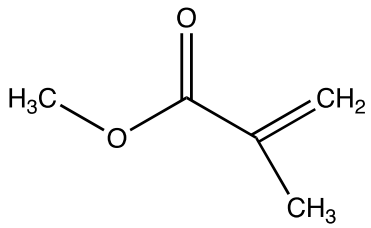
G_{tot} = -890.929842

N	-0.056679	-0.098938	1.503581
C	1.086221	-0.953448	1.964959
C	2.196069	-1.102335	0.913059
H	0.685247	-1.946548	2.216203
H	1.522703	-0.552187	2.897940
C	-1.381836	-0.671554	1.903365
C	-2.506976	-0.204682	0.974547
H	-1.633230	-0.415346	2.950614
H	-1.298341	-1.767460	1.857641
N	1.660806	-1.478273	-0.419341
H	2.932855	-1.849471	1.276145
H	2.741228	-0.154899	0.788187
N	-2.207504	-0.505276	-0.451139
H	-2.650411	0.884379	1.059927
H	-3.460328	-0.673446	1.292786
C	1.194102	-2.884197	-0.445889
H	0.426726	-3.056407	0.321350
H	2.032056	-3.587068	-0.267361
H	0.755509	-3.097627	-1.430124
C	2.692359	-1.302896	-1.469508
H	2.246387	-1.519034	-2.449223
H	3.554496	-1.977722	-1.302850
H	3.047251	-0.263864	-1.476561
C	-3.051183	0.313944	-1.355024
H	-2.898110	1.381236	-1.146729
H	-4.124543	0.073111	-1.228945
H	-2.755997	0.116771	-2.394126

C	-2.431060	-1.937746	-0.765570
H	-3.500798	-2.204939	-0.659312
H	-1.841105	-2.580006	-0.098021
H	-2.113292	-2.128983	-1.799487
Cu	-0.046437	-0.055552	-0.665854
C	0.062725	1.319365	1.963818
C	1.017805	2.149853	1.101804
H	-0.941636	1.767446	1.928081
H	0.387670	1.355993	3.021599
N	0.642052	2.100859	-0.334498
H	2.046298	1.769945	1.196490
H	1.031717	3.192657	1.480369
C	-0.489242	3.012024	-0.625971
H	-0.205448	4.070584	-0.460114
H	-1.350225	2.779962	0.016507
H	-0.792400	2.883912	-1.674231
C	1.784646	2.481287	-1.196623
H	2.084258	3.535415	-1.033939
H	1.501308	2.346386	-2.249349
H	2.647963	1.835878	-0.982265
H	-0.043640	-0.053956	-2.209445

Alkenes

3a



E_{gas} = -345.8792301=

G_{gas} = -345.792947

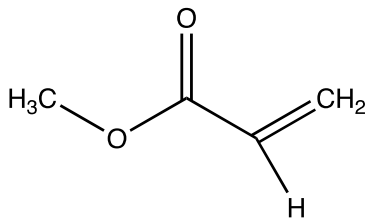
E_{DMSO} = -345.884696

$E_{BP86\text{-}D3}$ = -345.890125

G_{tot} = -345.806289

C	-2.493623	0.337283	0.000132
O	-1.085713	0.673510	0.000251
H	-2.749295	-0.249743	0.894676
H	-2.749169	-0.249547	-0.894580
H	-3.021478	1.298224	0.000174
C	-0.243600	-0.404605	-0.000075
O	-0.640607	-1.557643	-0.000405
C	1.193246	0.035751	0.000061
C	2.125368	-0.934163	0.000323
C	1.511311	1.509843	-0.000246
H	1.078497	2.009427	0.881394
H	1.080111	2.008704	-0.883105
H	2.598976	1.673367	0.000643
H	3.192292	-0.698155	0.000441
H	1.824413	-1.983870	0.000409

3b



E_{gas} = -306.553067

G_{gas} = -306.491861

E_{DMSO} = -306.558672

$E_{BP86\text{-}D3}$ = -306.560420

G_{tot} = -306.501799

C	-2.312572	-0.087515	-0.000118
O	-1.018790	-0.735980	-0.000009
H	-2.427864	0.542449	-0.894781
H	-2.428090	0.542414	0.894550
H	-3.046273	-0.902091	-0.000229
C	0.046612	0.121393	0.000099
O	-0.063550	1.335723	0.000125
C	1.320808	-0.647646	0.000158
C	2.501578	-0.013409	-0.000172
H	1.240387	-1.737565	0.000382
H	3.447131	-0.559628	-0.000243
H	2.534875	1.079536	-0.000410

S4. References

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2. Bell, C. A.; Bernhardt, P. V.; Monteiro, M. J., A Rapid Electrochemical Method for Determining Rate Coefficients for Copper-Catalyzed Polymerizations. *J. Am. Chem. Soc.* **2011,** *133*, 11944–11947.

3. Bard, A. J.; Faulkner, L. R., *Electrochemical Methods: Fundamentals and Applications*. 2 ed.; John Wiley & Sons, Inc.: New York, 2001.