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Gas–Phase Synthesis and Reactivity of Dimethylaurate

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Supporting Information

Complete citation for reference 19: Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Supporting Information:

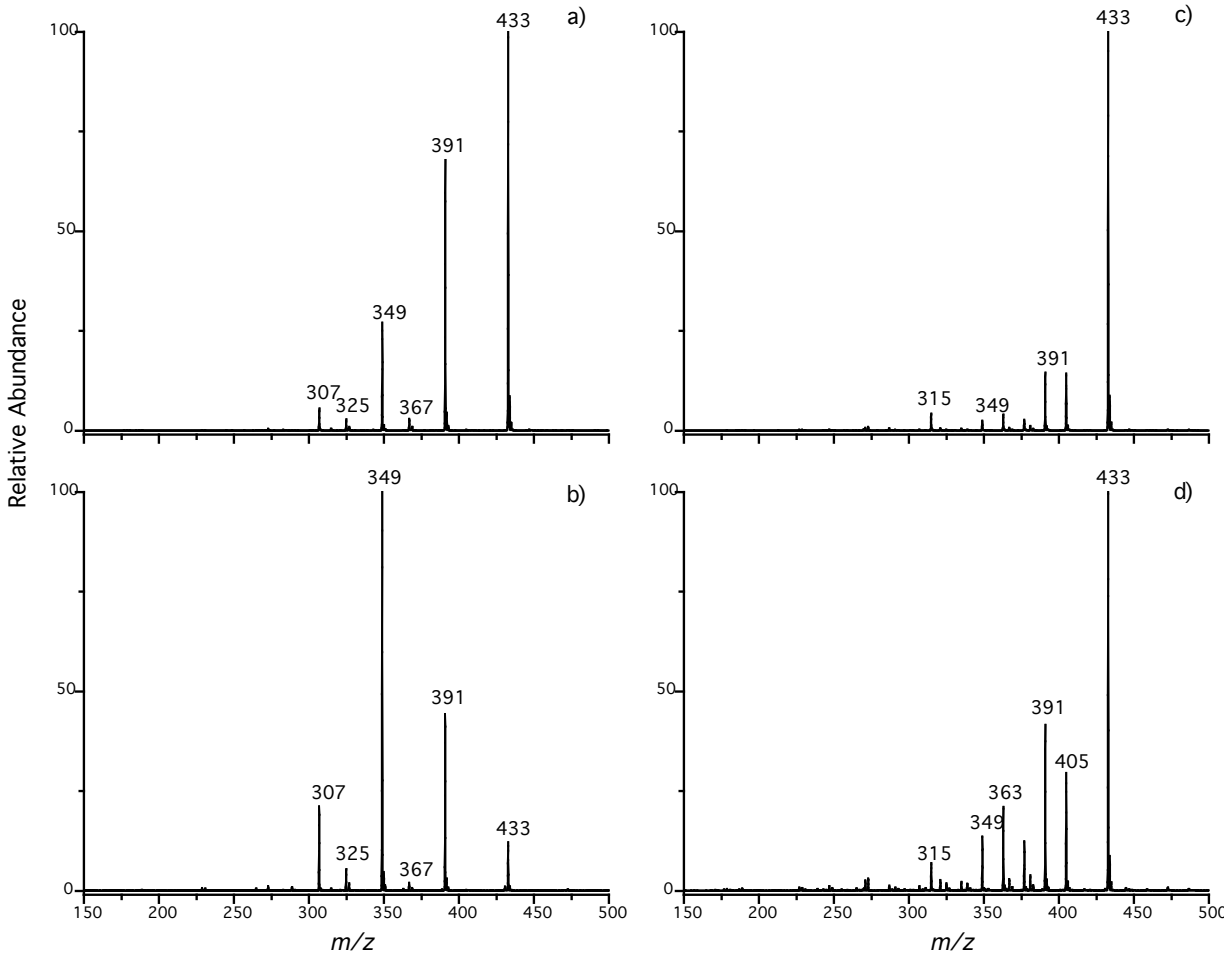


Figure S1: ESI/MS of gold(III) acetate (1mM) dissolved in water a) fresh sample; b) sample after 2 hours; and methanol:water (50:50 v/v) c) fresh sample; d) sample after 2 hours.

m/z	Assignment
307	$[CH_3CO_2Au(OH)_3]^-$
349	$[(CH_3CO_2)_2Au(OH)_2]^-$ or $[CH_3CO_2Au(OCH_3)_3]^-$
377	$[(CH_3CO_2)_2Au(OCH_3)_2]^-$
391	$[(CH_3CO_2)_3AuOH]^-$
405	$[(CH_3CO_2)_3AuOCH_3]^-$
433	$[(CH_3CO_2)_4Au]^-$

Table S1: Ions formed via ESI.

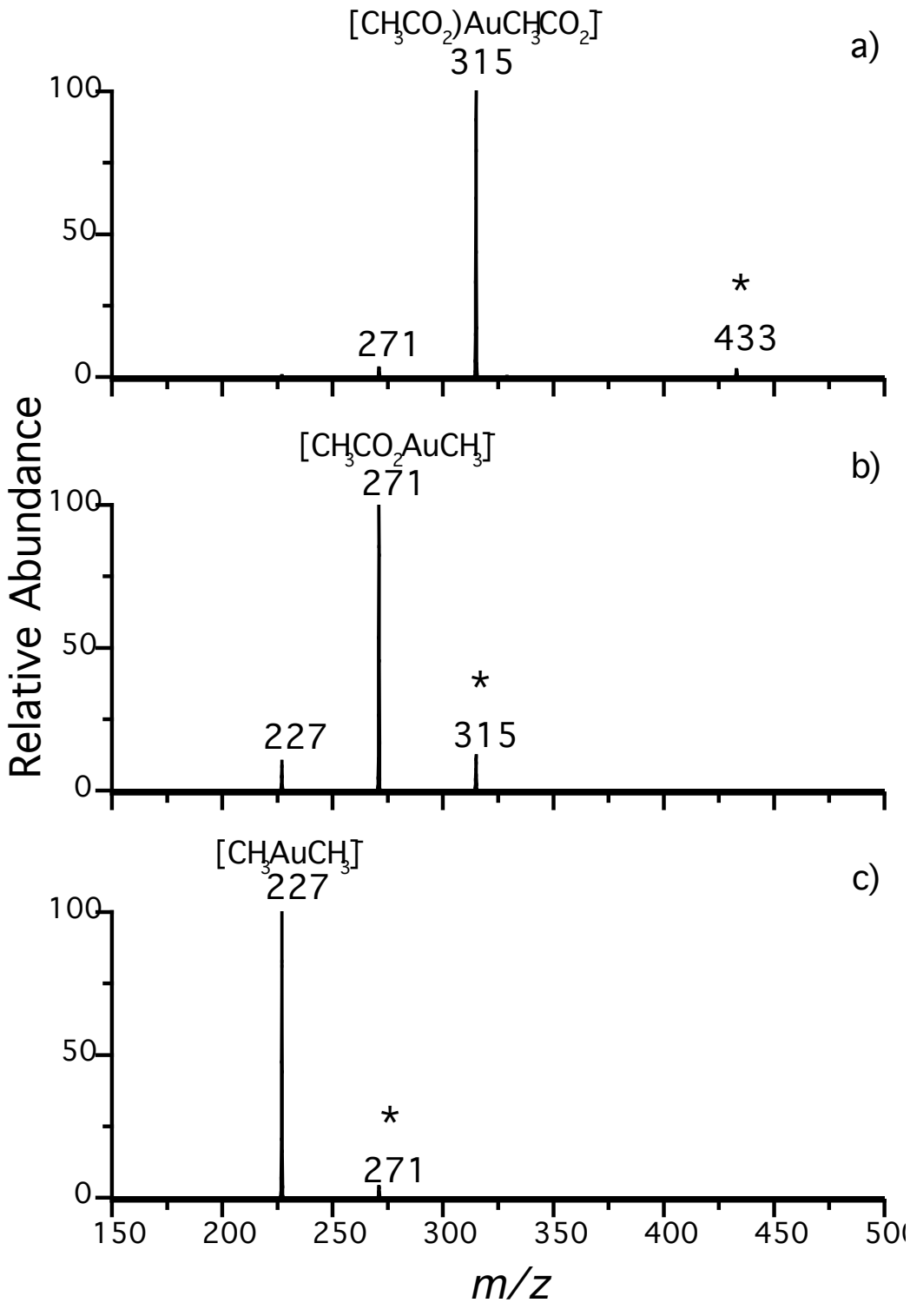
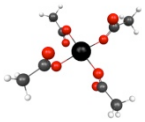


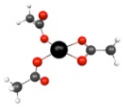
Figure S2: Mass spectra showing the formation of $[CH_3AuCH_3]^-$ via a series of collision induced dissociation experiments (CID): **(a)** MS^2 CID spectrum of $[(CH_3CO_2)_4Au]^-$, *m/z* 433; **(b)** MS^3 CID spectrum of $[CH_3CO_2AuO_2CCH_3]^-$, *m/z* 315; **(c)** MS^4 CID spectrum of $[CH_3CO_2AuCH_3]^-$, *m/z* 271. The mass selected precursor ion is marked with an * in each case.



$[(CH_3CO_2)_4Au]^-$ C_{2v}

Au	79.0	0.00027000	-0.00032900	0.00000000
C	6.0	-1.94446301	1.93390298	0.96314001
C	6.0	-1.93495703	-1.94420099	-0.96274000
C	6.0	1.93475997	1.94440103	-0.96262801
O	8.0	-1.64174104	1.62454295	2.10869908
O	8.0	-1.43754101	1.43592894	-0.14566900
O	8.0	1.43671000	1.43724799	0.14605001
O	8.0	1.62586200	1.64153802	-2.10825896
O	8.0	1.64193499	-1.62640095	2.10789108
O	8.0	1.43844700	-1.43613505	-0.14639100
O	8.0	-1.43570101	-1.43838203	0.14600800
O	8.0	-1.62656796	-1.64063895	-2.10832405
C	6.0	-2.99412990	-3.00165296	-0.65042102
H	1.0	-2.55955410	-3.80020809	-0.03879200
H	1.0	-3.81059790	-2.55445504	-0.07224800
H	1.0	-3.38387609	-3.41700792	-1.58300698
C	6.0	-3.00486898	2.99018407	0.65099603
H	1.0	-3.81621599	2.54434299	0.06460500
H	1.0	-3.40199900	3.39799404	1.58380198
H	1.0	-2.56886196	3.79415607	0.04756700
C	6.0	2.98966908	3.00605202	-0.65009302
H	1.0	2.53803205	3.82424688	-0.07770000
H	1.0	3.78617311	2.57594991	-0.03278900
H	1.0	3.40798092	3.39305997	-1.58249497
C	6.0	1.94546700	-1.93448901	0.96221799
C	6.0	3.00617504	-2.99028897	0.64952803
H	1.0	2.56886697	-3.79631090	0.04972600
H	1.0	3.81511211	-2.54538703	0.05915500
H	1.0	3.40649700	-3.39543104	1.58212197

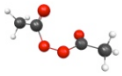
Sum of electronic and zero-point Energies = -1049.623871



$[(CH_3CO_2)_3Au]$

Au	79.0	0.21650700	-0.00405900	-0.00324000
C	6.0	-2.65466309	3.06007910	-0.44248101
H	1.0	-2.54190207	3.20748711	-1.51987398
H	1.0	-3.61198807	2.55490804	-0.26978299
H	1.0	-2.65777397	4.02008104	0.07791300
C	6.0	-2.71042705	-3.01139498	0.45929900
H	1.0	-2.59007907	-3.16372609	1.53518403
H	1.0	-3.65875912	-2.48612189	0.29724699
H	1.0	-2.73857999	-3.96985292	-0.06318600
C	6.0	4.20589304	-0.01785000	0.01827900
H	1.0	4.59609985	0.55126202	-0.82916403
H	1.0	4.53894520	0.46753499	0.94398302
H	1.0	4.58712006	-1.04186904	0.00693900
C	6.0	-1.53644204	2.19886994	0.11700100
C	6.0	2.71536708	-0.02336100	-0.00964400
C	6.0	-1.58033097	-2.17200398	-0.10951200
O	8.0	2.04231095	0.94924700	-0.50869000
O	8.0	2.03005695	-0.98944497	0.48531899
O	8.0	-0.98917103	2.38872695	1.19084299
O	8.0	-1.23894501	1.19416296	-0.71043903
O	8.0	-1.25395799	-1.17575002	0.71728301
•8.0		-1.04823101	-2.37007594	-1.18943202

•Sum of electronic and zero-point Energies = -821.053037

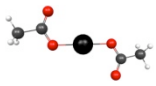


$[CH_3CO_2MeO_2CH_3]^-$

O	8.0	1.12844300	-1.17209101	-0.80468601
O	8.0	0.65623200	0.29733101	0.88501799
O	8.0	-0.65623099	-0.29735401	0.88501102
O	8.0	-1.12844205	1.17211199	-0.80466002
C	6.0	-2.81507611	-0.40178901	-0.02177500
H	1.0	-2.81130290	-1.21404600	-0.75765800
H	1.0	-3.02454710	-0.82642299	0.96284199
H	1.0	-3.58723402	0.31888899	-0.30008000
C	6.0	1.47317803	-0.28677699	-0.06953700
C	6.0	2.81507492	0.40178701	-0.02176600
H	1.0	2.81135702	1.21394897	-0.75775498
H	1.0	3.02448606	0.82655102	0.96280801
H	1.0	3.58724499	-0.31893101	-0.29993099

Sum of electronic and zero-point Energies = -456.779641

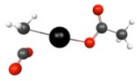
Figure S3: Calculated Cartesian coordinates and energies (Hartrees) for species relevant to the fragmentation of $[(CH_3CO_2)_4Au]^-$



$[CH_3CO_2AuO_2CCH_3]^-$

C	6.0	-2.96340895	-0.16013899	-0.00089400
C	6.0	-4.30895805	0.57811701	0.00116900
O	8.0	-1.95624304	0.66709101	-0.00067400
O	8.0	-2.92190099	-1.39311898	-0.00109700
H	1.0	-4.38517189	1.21433794	0.89126199
H	1.0	-5.13524580	-0.13804300	-0.01012900
H	1.0	-4.37785387	1.23563004	-0.87378103
C	6.0	2.96340704	0.16014700	0.00001500
C	6.0	4.30895901	-0.57810700	0.00045700
O	8.0	2.92189002	1.39312696	-0.00093600
O	8.0	1.95624804	-0.66709000	0.00088200
H	1.0	5.13526392	0.13811900	0.00272900
H	1.0	4.38257313	-1.22322595	-0.88338202
H	1.0	4.38042784	-1.22681701	0.88179499
Au	79.0	0.00000100	-0.00000200	0.00002100

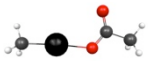
Sum of electronic and zero-point Energies = -592.784884



TS $[CH_3CO_2AuO_2CCH_3]^- \rightarrow [CH_3CO_2AuCH_3]^- + CO_2$ (-338cm^{-1})

Au	79.0	0.11505100	0.09118800	-0.01150100
O	8.0	-1.76429403	-0.78206003	-0.09157700
C	6.0	-2.81187201	-0.00865000	0.00709100
O	8.0	-2.81764197	1.21767700	0.13290900
C	6.0	-4.11904907	-0.80582303	-0.04093400
H	1.0	-4.17137003	-1.48087704	0.82168800
H	1.0	-4.97597980	-0.12741300	-0.02617000
H	1.0	-4.15061188	-1.42817199	-0.94245398
O	8.0	3.10008597	-0.85848701	-1.01708198
C	6.0	2.70456910	-0.39400399	0.05620200
O	8.0	2.74215102	-0.75137401	1.24211299
C	6.0	2.15248609	1.24751997	-0.13708200
H	1.0	1.39704704	1.77924705	0.49133399
H	1.0	3.07279611	1.64844799	0.30190399
H	1.0	2.09985304	1.56463599	-1.18026805

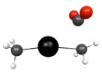
Sum of electronic and zero-point Energies = -592.718659



$[CH_3CO_2AuCH_3]^-$

Au	79.0	-0.67999297	-0.07546600	0.00002700
O	8.0	1.40479100	-0.62586600	0.00076700
C	6.0	2.38917994	0.21059801	0.00038200
O	8.0	2.33777690	1.44981205	0.00013900
C	6.0	3.76233912	-0.49057701	-0.00057800
H	1.0	3.85434508	-1.13050401	-0.88739902
H	1.0	4.57253504	0.24510300	0.00573000
H	1.0	3.85043502	-1.14235103	0.87789899
C	6.0	-2.69337392	0.31615800	-0.00051400
H	1.0	-2.88921189	1.35727000	-0.29861900
H	1.0	-3.22941399	-0.34149900	-0.70194799
H	1.0	-3.12864304	0.16514800	0.99926001

Sum of electronic and zero-point Energies = -404.197803



TS $[CH_3CO_2AuCH_3]^- \rightarrow [CH_3AuCH_3]^- + CO_2$ (-341 cm^{-1})

Au	79.0	0.50680703	0.09676400	-0.00000300
C	6.0	2.40405989	-0.72521198	0.00006000
O	8.0	-2.31946802	-0.76111501	1.15023899
C	6.0	-2.08299994	-0.43602800	0.00001300
O	8.0	-2.31934190	-0.76138502	-1.15016401
C	6.0	-1.42029297	1.44550800	-0.00010200
H	1.0	-1.05092800	1.93434095	-0.91175097
H	1.0	-2.50490189	1.60551906	-0.00034300
H	1.0	-1.05128896	1.93432105	0.91169697
H	1.0	2.55204201	-1.34820104	0.89324403
H	1.0	2.54895711	-1.35523498	-0.88868302
H	1.0	3.17428207	0.05925800	-0.00437000

Sum of electronic and zero-point Energies = -404.137166

$[CH_3AuCH_3]^-$

Au	79.0	0.00000000	0.00010900	-0.00013700
C	6.0	-2.12720299	-0.00040400	0.00052500
H	1.0	-2.53713489	-0.36932200	0.95716602
H	1.0	-2.53817892	1.01211405	-0.15818900
H	1.0	-2.53784704	-0.64466500	-0.79670697
C	6.0	2.12720299	-0.00040500	0.00052500
H	1.0	2.53817797	1.01211500	-0.15818700
H	1.0	2.53713489	-0.36932299	0.95716500
H	1.0	2.53784704	-0.64466399	-0.79670900

Sum of electronic and zero-point Energies = -215.585267

CO_2

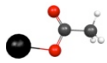
C	6.0	0.00000000	0.00000000	0.00000000
O	8.0	0.00000000	0.00000000	1.16979396
O	8.0	0.00000000	0.00000000	-1.16979396

Sum of electronic and zero-point Energies = -188.57585

$CH_3CO_2^-$

O	8.0	0.70457202	1.16242397	0.00002000
O	8.0	0.80539101	-1.11075401	0.00002000
C	6.0	0.20919301	0.00116600	-0.00009800
C	6.0	-1.35404205	-0.04939700	-0.00004100
H	1.0	-1.72823596	-1.08034205	-0.00285600
H	1.0	-1.74091601	0.47551799	0.88480002
H	1.0	-1.74146199	0.48085099	-0.88142800

Sum of electronic and zero-point Energies = -228.487580



$[CH_3CO_2Au]$

C	6.0	1.95726800	0.13221800	-0.00034900
C	6.0	3.39722300	-0.36717600	-0.00000600
O	8.0	1.08345997	-0.85304701	-0.00025200
O	8.0	1.66684496	1.32613504	-0.00006700
H	1.0	3.57797289	-0.97818601	0.89024198
H	1.0	4.07762289	0.48575699	-0.01111200
H	1.0	3.57312489	-0.99909002	-0.87629801
Au	79.0	-0.82731801	-0.01118300	0.00002300

Sum of electronic and zero-point Energies = -364.190197

$[CH_3Au]$

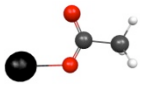
Au	79.0	0.22006799	0.00000000	0.00000000
C	6.0	-1.82346404	-0.00000100	-0.00001000
H	1.0	-2.14818501	0.99234599	-0.32082400
H	1.0	-2.14819193	-0.77404600	-0.69889098
H	1.0	-2.14820290	-0.21829100	1.01976299

Sum of electronic and zero-point Energies = -175.647426

$[CH_3Au]$.-

Au	79.0	-0.23313800	0.00000100	0.00000000
C	6.0	1.92640996	0.00000400	-0.00000100
H	1.0	2.28639007	-0.41409799	0.95212299
H	1.0	2.28643298	-0.61756700	-0.83462900
H	1.0	2.28664899	1.03154802	-0.11746100

Sum of electronic and zero-point Energies = -175.672986



$[CH_3CO_2Au]$.-

C	6.0	-2.20323205	0.14356600	-0.00029600
C	6.0	-3.59156895	-0.53700000	0.00022500
O	8.0	-1.23603296	-0.70928401	-0.00048500
O	8.0	-2.13788295	1.38260198	-0.00006700
H	1.0	-3.69090295	-1.18486297	-0.87968600
H	1.0	-4.38802624	0.21389900	-0.00469800
H	1.0	-3.69391394	-1.17566299	0.88656700
Au	79.0	0.93079698	-0.01113100	0.00003400

Sum of electronic and zero-point Energies = -364.277241

Me.

C	6.0	0.00000400	-0.00000200	-0.00001800
H	1.0	1.07251894	-0.15388601	0.00003600
H	1.0	-0.40299401	1.00575805	0.00003600
H	1.0	-0.66954798	-0.85185802	0.00003600

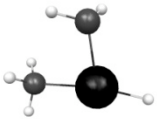
Sum of electronic and zero-point Energies = -39.811971

Me-

C	6.0	-0.00008700	-0.00000200	0.12094500
H	1.0	0.51700997	0.90736097	-0.24182799
H	1.0	0.52777100	-0.90114200	-0.24183100
H	1.0	-1.04426003	-0.00620700	-0.24201100

Sum of electronic and zero-point Energies = -39.811839

Figure S4: Calculated Cartesian coordinates and energies (Hartrees) for species relevant to the fragmentation of $[CH_3CO_2AuO_2CCH_3]^-$ and $[CH_3CO_2AuCH_3]^-$.



TS $[CH_3AuCH_3]^-$ → $[CH_3CH_2AuH]^-$ (-117 cm^{-1})

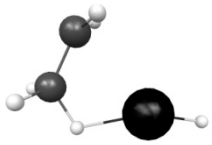
Au	79.0	-0.26557499	-0.09935900	-0.00294700
C	6.0	0.64091903	1.83990502	-0.13521200
H	1.0	1.75050604	1.76833797	-0.17594500
H	1.0	0.44400400	2.19124603	0.90722299
H	1.0	-1.94596601	0.07437000	0.05653200
C	6.0	1.76045406	-0.75286299	0.02710400
H	1.0	2.30145502	-0.43307701	0.92622900
H	1.0	1.70560300	-1.85382497	0.02617300
H	1.0	2.31660104	-0.41992000	-0.85871202

Sum of electronic and zero-point Energies = -215.493737

$[CH_3CH_2AuH]^-$

Au	79.0	0.45343000	-0.01650400	-0.00000800
C	6.0	-1.58419096	0.66687697	-0.00001000
H	1.0	-1.74387097	1.31839204	0.87817103
H	1.0	-1.74375403	1.31800699	-0.87849700
C	6.0	-2.66783190	-0.43148601	0.00016200
H	1.0	-2.57749391	-1.08487701	-0.88002503
H	1.0	-2.57767105	-1.08442104	0.88070601
H	1.0	-3.70459890	-0.03526400	-0.00004500
H	1.0	2.03857589	-0.54039800	-0.00059900

Sum of electronic and zero-point Energies = -215.578504



TS $[CH_3CH_2AuH]^-$ → $[HAuH]^-$ + C_2H_4 (-577 cm^{-1})

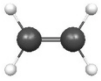
Au	79.0	-0.43505099	-0.00698700	-0.00000200
H	1.0	-1.90572298	0.57692999	-0.00004900
C	6.0	2.25933003	0.80757898	-0.00005200
C	6.0	2.10297608	-0.66780502	0.00006200
H	1.0	2.01094294	1.34616804	-0.91671300
H	1.0	2.01093197	1.34631205	0.91652101
H	1.0	1.01488495	-1.27063501	0.00010000
H	1.0	2.53205204	-1.14263701	0.89122099
H	1.0	2.53206491	-1.14277601	-0.89101601

Sum of electronic and zero-point Energies = -215.493737

$[HAuH]^-$

Au	79.0	0.00000000	0.00000000	0.00000000
H	1.0	0.00000000	0.00000000	1.68150496
H	1.0	0.00000000	0.00000000	-1.68151498

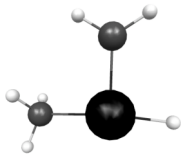
Sum of electronic and zero-point Energies = -137.012661



C_2H_4

C	6.0	-0.66759598	0.00000000	-0.00016000
C	6.0	0.66759300	0.00000000	-0.00019000
H	1.0	-1.24046302	0.92477602	0.00050000
H	1.0	-1.24046397	-0.92477602	0.00050000
H	1.0	1.24047303	-0.92476797	0.00054900
H	1.0	1.24047303	0.92476797	0.00054900

Sum of electronic and zero-point Energies = -78.540582



Triplet $CH_3Au(CH_2)H^-$

Au	79.0	-0.07623100	-0.24994500	-0.00044700
C	6.0	-1.19329202	1.59079695	0.00007500
H	1.0	-0.67845601	2.55840898	-0.03212900
H	1.0	-2.28687310	1.61546004	0.03325300
H	1.0	-1.45645905	-1.18979394	0.00140700
C	6.0	1.83981800	0.73816401	0.00210600
H	1.0	2.03737998	1.18722904	0.98865700
H	1.0	2.67039204	0.05147200	-0.22608399
H	1.0	1.85711503	1.54911900	-0.74289900

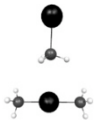
Sum of electronic and zero-point Energies= -215.457801

Figure S5: Calculated Cartesian coordinates and energies (Hartrees) relevant to $[CH_3AuCH_3]^-$ fragmentation.

CH_3I

I	53.0	-0.33378500	-0.00000100	0.00000100
C	6.0	1.85739398	0.00000000	-0.00003300
H	1.0	2.18210411	-0.89739197	-0.52322602
H	1.0	2.18202305	0.90198702	-0.51530600
H	1.0	2.18210506	-0.00456300	1.03868699

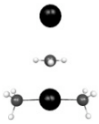
Sum of electronic and zero-point Energies = -51.291937



$[CH_3AuCH_3]$-(CH_3I) T-shaped precomplex

C	6.0	1.91112399	2.13354707	-0.00011500
H	1.0	1.38370204	2.52647710	-0.88664800
H	1.0	2.91966200	2.58131409	-0.00382000
H	1.0	1.38975298	2.52681398	0.88980103
Au	79.0	2.01373506	0.00880100	0.00001800
I	53.0	-3.49719000	-0.01608600	-0.00003700
C	6.0	2.13766599	-2.11370611	-0.00013300
C	6.0	-1.23445404	-0.00271500	0.00030800
H	1.0	1.64977598	-2.56019497	0.88337100
H	1.0	3.18775892	-2.45302296	0.00742000
H	1.0	1.66297698	-2.55903912	-0.89139599
H	1.0	-0.93483299	-0.54199201	-0.89190501
H	1.0	-0.94341999	1.04183996	-0.01924600
H	1.0	-0.93544602	-0.50770599	0.91257101

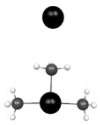
Sum of electronic and zero-point Energies = -266.888910



TS $[CH_3AuCH_3]^- + CH_3I \rightarrow [(CH_3)_3Au](I)^-$ (-248 cm^{-1})

C	6.0	-1.91930497	-2.12631893	-0.00036000
H	1.0	-1.27221203	-2.56089902	-0.77810299
H	1.0	-2.94374800	-2.48840809	-0.18717900
H	1.0	-1.59753394	-2.54285908	0.96749699
Au	79.0	-1.86643004	0.00000000	-0.00137800
I	53.0	3.32816505	0.00000000	-0.00324500
C	6.0	-1.91930199	2.12631989	-0.00035900
C	6.0	0.63937598	-0.00000100	0.03205200
H	1.0	-1.59753001	2.54285908	0.96749800
H	1.0	-2.94374490	2.48841000	-0.18717700
H	1.0	-1.27220905	2.56089902	-0.77810198
H	1.0	0.63200098	0.93480200	0.56688702
H	1.0	0.61355698	0.00000200	-1.04536498
H	1.0	0.63200098	-0.93480599	0.56688303

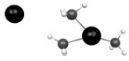
Sum of electronic and zero-point Energies = -266.883406



Post complex $[(CH_3)_3Au](I^-)$

C	6.0	1.98001301	2.12398410	-0.00239400
H	1.0	1.32644999	2.56095695	-0.76965898
H	1.0	3.00970888	2.46105409	-0.20606799
H	1.0	1.67886901	2.53546405	0.97153902
Au	79.0	1.90132499	0.00000000	-0.00261900
I	53.0	-3.44888711	-0.00000200	-0.00342400
C	6.0	1.98003101	-2.12398195	-0.00239400
C	6.0	-0.27705300	0.00000300	0.04868700
H	1.0	1.67886996	-2.53546596	0.97153300
H	1.0	3.00973392	-2.46104693	-0.20604800
H	1.0	1.32648599	-2.56095910	-0.76967299
H	1.0	-0.51584798	-0.91807199	0.57211798
H	1.0	-0.51004899	0.00008500	-1.01102197
H	1.0	-0.51584101	0.91800302	0.57225502

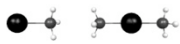
Sum of electronic and zero-point Energies = -266.885708



TS $[(CH_3)_3Au](I^-) \rightarrow CH_3CH_3 + CH_3Au + I^-$ (-307 cm^{-1})

C	6.0	4.07239199	-0.05610400	-0.45413399
H	1.0	4.65237617	-0.50262600	0.36471701
H	1.0	4.45929193	0.95795798	-0.62475699
H	1.0	4.25737190	-0.64211297	-1.36426699
Au	79.0	2.02793908	0.00368800	0.00540600
C	6.0	0.15156800	1.11306798	0.41170600
C	6.0	0.13295101	-1.05025804	0.47107601
H	1.0	-0.52465701	1.17580402	-0.43754601
H	1.0	0.81871599	1.98625600	0.46329501
H	1.0	-0.40973300	1.02246594	1.33807802
H	1.0	-0.90987003	-0.83283401	0.23547700
H	1.0	0.25772601	-1.29840004	1.52551496
H	1.0	0.49576500	-1.85009003	-0.18644500
I	53.0	-3.76312494	-0.00656600	-0.08137800

Sum of electronic and zero-point Energies = -266.870577



$[CH_3AuCH_3]$-(CH_3I) SN2 pre-complex

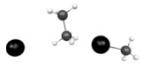
C	6.0	4.99471521	0.00014200	-0.00028300
H	1.0	5.40157223	-0.85288000	-0.56966901
H	1.0	5.40263796	-0.06628800	1.02277005
H	1.0	5.40180397	0.91944301	-0.45482600
Au	79.0	2.87326002	0.00003600	0.00008500
I	53.0	-4.83358002	-0.00008200	-0.00002400
C	6.0	0.73984098	-0.00106500	-0.00041500
C	6.0	-2.59874701	0.00114600	0.00027600
H	1.0	0.34405601	-0.08255300	1.02620804
H	1.0	0.34500799	-0.84984201	-0.58427399
H	1.0	0.34382799	0.92840397	-0.44367200
H	1.0	-2.28666711	-0.93300998	0.45672500
H	1.0	-2.28704596	0.07282300	-1.03700304
H	1.0	-2.28783798	0.86411500	0.58076698

Sum of electronic and zero-point Energies = -266.885367

TS $[CH_3AuCH_3]^- + CH_3I \rightarrow CH_3CH_3 + CH_3Au + I^-$ (-448 cm^{-1})

C	6.0	4.81577921	-0.04215200	0.00015000
H	1.0	5.22769785	0.97684401	-0.03692200
H	1.0	5.19276905	-0.59696400	-0.87138599
H	1.0	5.19399786	-0.53258902	0.90896702
Au	79.0	2.71983790	0.00195400	-0.00003000
I	53.0	-4.64594793	-0.00809300	-0.00000400
C	6.0	0.48648900	0.04021400	-0.00001100
C	6.0	-1.87853801	0.03465500	0.00012300
H	1.0	0.29558399	-0.50190902	-0.92406797
H	1.0	0.30869699	1.11380696	-0.00931300
H	1.0	0.29576200	-0.48579100	0.93335599
H	1.0	-1.90082002	0.56600600	-0.93552703
H	1.0	-1.90091002	0.57990801	0.92775202
H	1.0	-1.88706601	-1.04103899	0.00816600

Sum of electronic and zero-point Energies = -266.869912



Post complex $(CH_3CH_3)[CH_3Au](I^-)$

C	6.0	4.35233116	-0.57456303	0.06274800
H	1.0	4.94303417	0.23699801	-0.37578100
H	1.0	4.52333212	-1.49922395	-0.49889499
H	1.0	4.64587688	-0.71997899	1.10812902
Au	79.0	2.36741400	-0.09278500	-0.01933200
I	53.0	-4.15506315	-0.24219100	-0.00518500
C	6.0	-0.25063699	0.68099099	0.17828301
C	6.0	-0.52089298	2.17059398	-0.03662000
H	1.0	0.45115101	0.29401800	-0.61445898
H	1.0	0.12294800	0.47285399	1.18896306
H	1.0	-1.16032100	0.08057800	0.03830400
H	1.0	0.37117901	2.78372788	0.14309500
H	1.0	-1.31587303	2.49639702	0.64265102
H	1.0	-0.87352800	2.35863709	-1.05646300

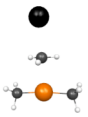
Sum of electronic and zero-point Energies = -266.938649

CH_3CH_3

C	6.0	-0.76627702	0.00000000	0.00000000
C	6.0	0.76627702	0.00000000	0.00000000
H	1.0	-1.16515994	-0.97165197	-0.31555399
H	1.0	-1.16513097	0.21253499	0.99926299
H	1.0	-1.16517496	0.75911099	-0.68367797
H	1.0	1.16517496	-0.75910997	0.68367898
H	1.0	1.16513097	-0.21253701	-0.99926299
H	1.0	1.16515994	0.97165298	0.31555200

Sum of electronic and zero-point Energies = -79.757233

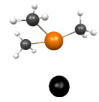
Figure S6: Calculated Cartesian coordinates and energies (Hartrees) for $[CH_3AuCH_3]^-$ reaction with CH_3I.



TS $[CH_3CuCH_3]^-$ + CH_3I → $[(CH_3)_3Cu](I)^-$ (-216 cm^{-1})

C	6.0	2.73568296	-1.96027100	0.00781800
H	1.0	2.12631011	-2.42473197	0.80096298
H	1.0	3.78235102	-2.27281189	0.17682700
H	1.0	2.41738009	-2.40524697	-0.95066601
Cu	29.0	2.62529612	0.00000200	0.00095300
I	53.0	-2.41072607	-0.00000100	0.00330400
C	6.0	2.73566389	1.96027601	0.00781800
C	6.0	0.21537800	-0.00000900	-0.04014500
H	1.0	2.41735196	2.40525007	-0.95066398
H	1.0	3.78233004	2.27283001	0.17682201
H	1.0	2.12629008	2.42473006	0.80096602
H	1.0	0.27856401	0.93447697	-0.57233697
H	1.0	0.30543101	0.00000100	1.03473794
H	1.0	0.27856100	-0.93450701	-0.57231897

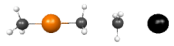
Sum of electronic and zero-point Energies= -328.443145



TS $[(CH_3)_3Cu](I^-)$ → CH_3CH_3 + CH_3CuI^- (-389 cm^{-1})

C	6.0	-1.71348298	2.12873912	-0.13130300
H	1.0	-2.79977393	2.32387590	-0.08477500
H	1.0	-1.31871605	2.65332294	-1.01627696
H	1.0	-1.25087202	2.60268402	0.74928099
Cu	29.0	-1.25903499	0.19187599	-0.15705900
C	6.0	-1.41317701	-1.75544500	-0.63310498
C	6.0	-2.62392306	-0.87030900	0.86936402
H	1.0	-0.74515402	-2.39544511	-0.05750700
H	1.0	-0.89173299	-1.37777805	-1.53088105
H	1.0	-2.32376409	-2.27223992	-0.94168401
H	1.0	-2.61614490	-1.88775504	1.26434505
H	1.0	-3.57925010	-0.64147002	0.39329100
H	1.0	-2.42140102	-0.17124000	1.69024396
I	53.0	1.67853498	-0.02672200	0.06526300

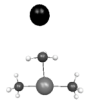
Sum of electronic and zero-point Energies= -328.439597



TS $[CH_3CuCH_3]^-$ + CH_3I → CH_3CH_3 + CH_3Cu + I^- (-406 cm^{-1})

C	6.0	-5.80970812	-0.04270500	-0.00007700
H	1.0	-6.20096111	-0.51953697	0.91435200
H	1.0	-6.19831181	-0.61162901	-0.86142999
H	1.0	-6.23859596	0.97203797	-0.05332000
Cu	29.0	-3.86458111	0.00463200	0.00004400
I	53.0	3.32069397	-0.00803900	-0.00000600
C	6.0	-1.83204901	0.04334800	-0.00005600
C	6.0	0.61508399	0.03439900	0.00005900
H	1.0	-1.62472796	-0.48484999	-0.93148899
H	1.0	-1.62484205	-0.49625400	0.92483199
H	1.0	-1.63693404	1.11634696	0.00645200
H	1.0	0.57579201	-1.04044700	-0.00543900
H	1.0	0.59238100	0.56820703	0.93407899
H	1.0	0.59231001	0.57760501	-0.92853200

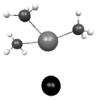
Sum of electronic and zero-point Energies= -328.431602



TS $[CH_3AgCH_3]^-$ + CH_3I → $[(CH_3)_3Ag](I)^-$ (143cm^{-1})

C	6.0	-2.39977288	-2.14434099	-0.00341900
H	1.0	-1.73186600	-2.57898402	-0.76081401
H	1.0	-3.42581201	-2.48217702	-0.22272100
H	1.0	-2.11220193	-2.55396891	0.97643900
Ag	47.0	-2.33371210	0.00000000	-0.00280200
I	53.0	2.87694001	0.00000000	-0.00314600
C	6.0	-2.39977002	2.14434195	-0.00341900
C	6.0	0.03738900	-0.00000100	0.04081600
H	1.0	-2.11220002	2.55396891	0.97643900
H	1.0	-3.42580891	2.48217893	-0.22272100
H	1.0	-1.73186302	2.57898402	-0.76081401
H	1.0	0.11167400	0.93460500	0.57269198
H	1.0	0.09598600	0.00000600	-1.03664696
H	1.0	0.11167400	-0.93461502	0.57267898

Sum of electronic and zero-point Energies= -278.084215



TS $[(CH_3)_3Ag](I^-)$ → CH_3CH_3 + CH_3AgI^- (-472 cm^{-1})

C	6.0	-1.56784594	2.31952095	-0.05083000
H	1.0	-2.64840293	2.51289201	-0.15234099
H	1.0	-1.04503000	2.84966612	-0.85938698
H	1.0	-1.23065400	2.75433803	0.90190899
Ag	47.0	-1.08966303	0.19703899	-0.08110800
C	6.0	-1.23741603	-2.05565095	-0.32992199
C	6.0	-2.91931295	-0.99147201	0.49380299
H	1.0	-0.79885602	-2.52615690	0.54958200
H	1.0	-0.46435300	-1.85400903	-1.08080494
H	1.0	-2.02682996	-2.66184592	-0.77228200
H	1.0	-3.01705003	-1.91742694	1.05999994
H	1.0	-3.59304500	-0.97655898	-0.36288199
H	1.0	-3.12631512	-0.14672500	1.15700400
I	53.0	1.95306003	-0.05527200	0.05081100

Sum of electronic and zero-point Energies= -278.071524

TS $[CH_3AgCH_3]^-$ + CH_3I → CH_3CH_3 + CH_3Ag + I^- (-408 cm^{-1})

H	1.0	-5.94291019	-0.53569698	0.90837699
H	1.0	-5.94154882	-0.60127801	-0.87009501
H	1.0	-5.97997189	0.97143799	-0.03762800
Ag	47.0	-3.42119002	0.00401600	-0.00005100
I	53.0	3.97373199	-0.00847800	-0.00000400
C	6.0	-1.17623496	0.04266700	0.00001000
C	6.0	1.28026700	0.03416600	0.00011100
H	1.0	-0.97377700	-0.49944299	-0.92191702
H	1.0	-0.97397202	-0.48183700	0.93211001
H	1.0	-0.98544002	1.11429095	-0.01013900
H	1.0	1.23277295	-1.04049599	0.00835600
H	1.0	1.24978495	0.57979500	0.92724001
H	1.0	1.24965501	0.56553698	-0.93524897

Sum of electronic and zero-point Energies= -278.078978

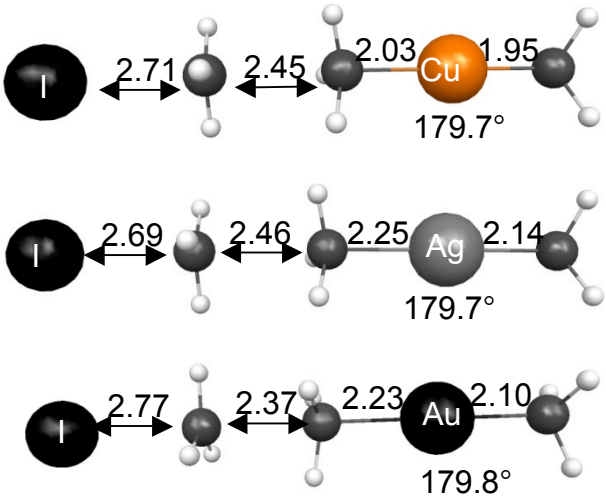


Figure S7: Calculated Cartesian coordinates and energies (Hartrees) for key transition state geometries of $[CH_3CuCH_3]^-$ $[CH_3AgCH_3]^-$ reaction with CH_3I; bond length comparison of S_N2 linear geometry for M = Cu, Ag, Au.

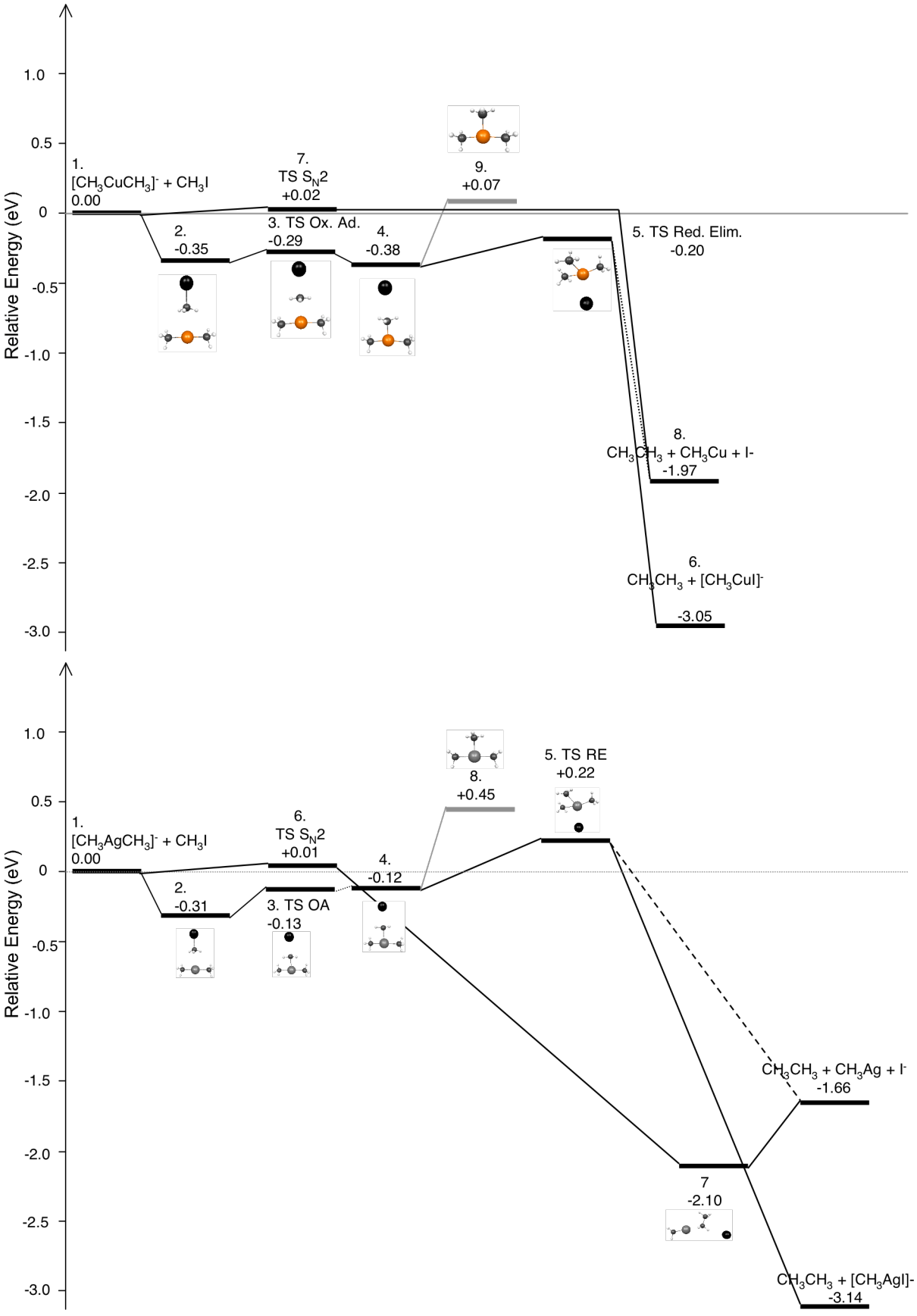
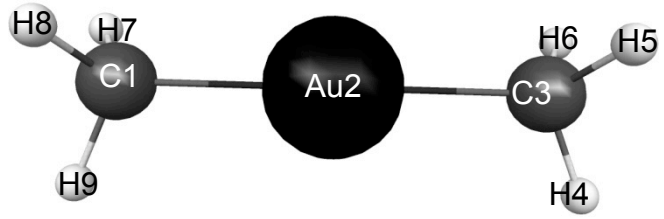


Figure S8: Comparison of $CH_3MCH_3^-$ (M= Cu and Ag) reaction with CH_3I at B3LYP.

Crystal Structure Comparison:

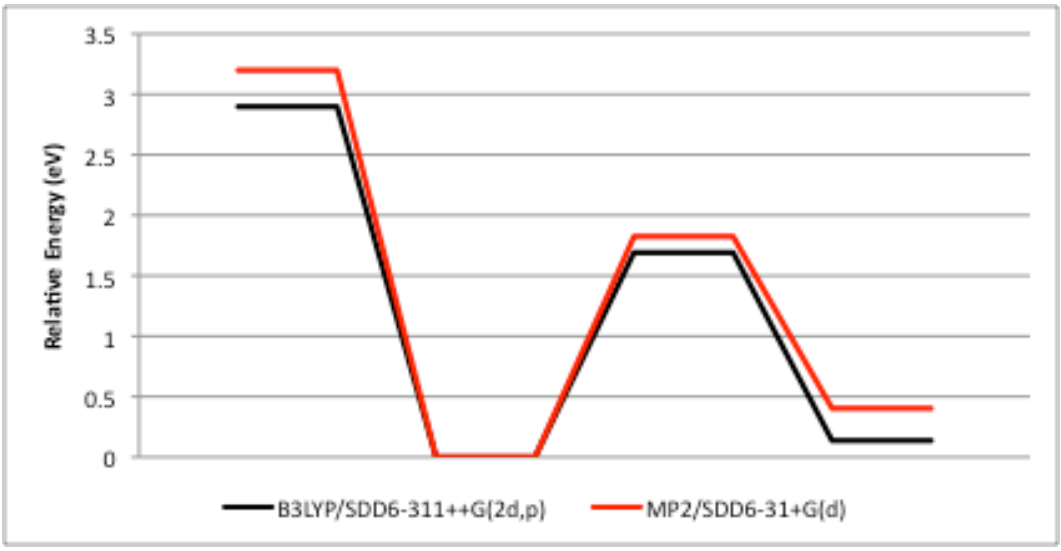


Bond length (Å)/angle (deg)	DFT value: B3LYP/SDD6-31+G(d)	Experimental value [1]	Previous theory [2,3]
C1- Au2, C3-Au2	2.13, 2.13	2.087(5), 2.076(6), 2.084(5), 2.053(5)	2.150[2], 2.109 [2], 2.13 [3]
C2-Au2-C3	179.5	178.2(2), 178.2(2)	180.0 [3]

1. Zhu, D; Lindeman, S. V.; Kochi, J. K., Organometallics, 1999, 18, 2241-2248
2. Tossell, J. A.,. *Chem. Phys. Lett.* **1998,** 286, (1-2), 73-78.
3. Nakanishi, W.; Yamanaka, M.; Nakamura, E.,. *J. Am. Chem. Soc.* **2005,** 127, (5), 1446-1453.

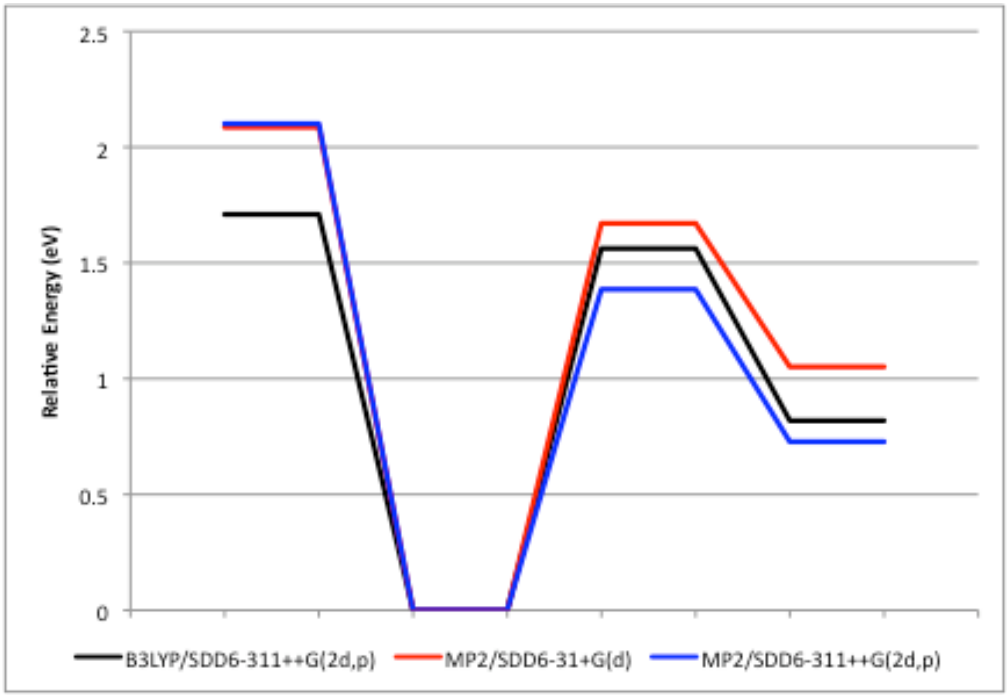
Figure S9: Comparison of experimental and computed bond lengths and geometries.

(a)



$[CH_3CO_2AuO_2CCH_3]^-$	B3LYP/SDD6-31+G(d)	B3LYP/SDD6-311+G(2d,p)	MP2/SDD6-31+G(d)
Acetate loss	2.91	2.90	3.20
Decarboxylation	1.80	1.69	1.82

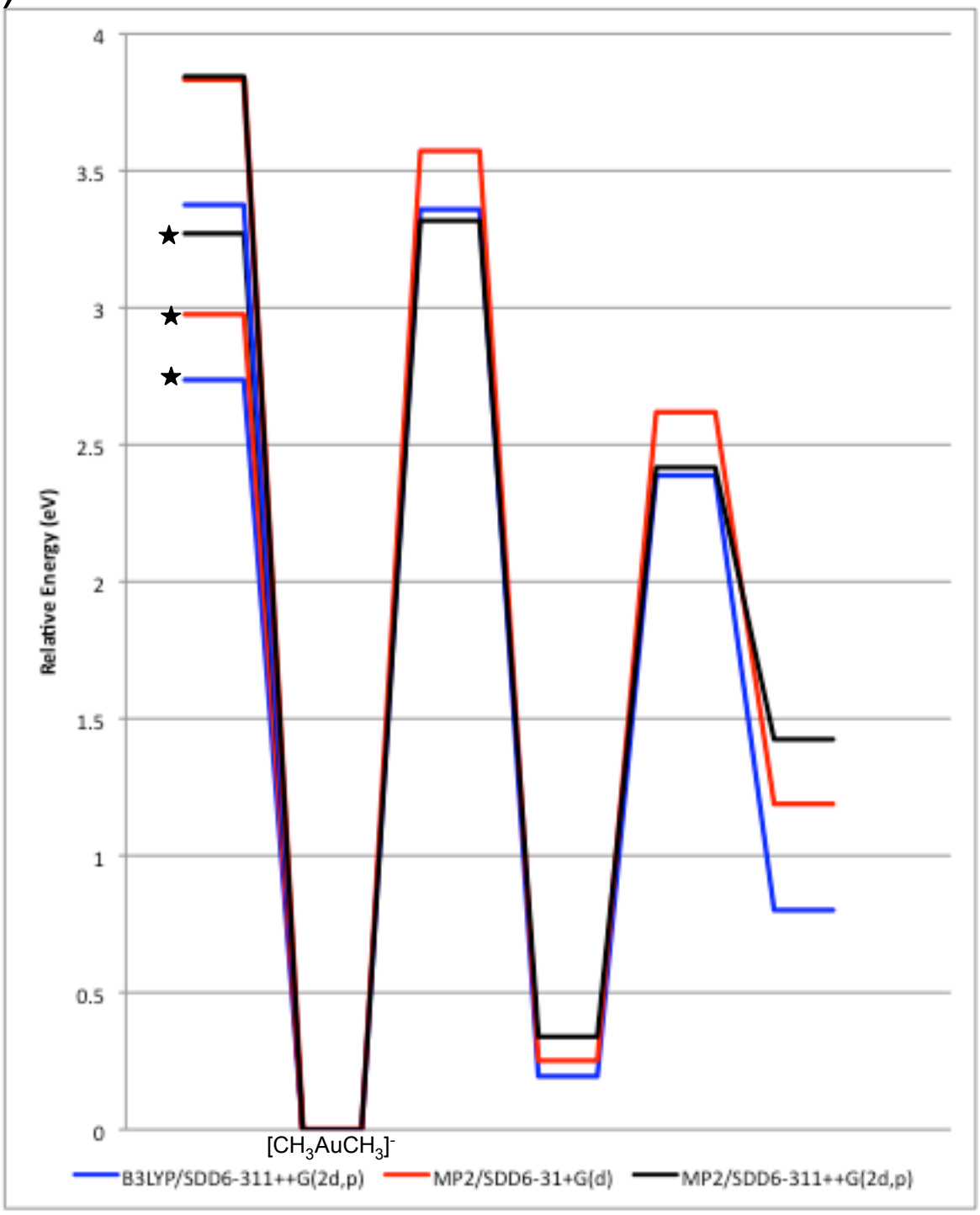
(b)



$[CH_3AuO_2CCH_3]^-$	B3LYP/SDD6-31+G(d)	B3LYP/SDD6-311+G(2d,p)	MP2/SDD6-31+G(d)	MP2/SDD6-311+G(2d,p)
Acetate loss	1.72	1.71	2.09	2.10
Decarboxylation	1.65	1.56	1.67	1.39
CH_3 Heterolysis	5.33	5.25	5.60	5.56
CH_3 Homolysis	2.95	2.74	2.98	3.27

Figure S10: Comparison of computational methods and basis sets for fragmentation of; a) $[CH_3CO_2AuO_2CCH_3]^-$; b) $[CH_3AuO_2CCH_3]^-$ and c) $[CH_3AuCH_3]^-$.Table a), b) and c) contains key energies (eV).

(c)



$[CH_3AuCH_3]^-$	B3LYP/SDD6-31+G(d)	B3LYP/SDD6-311+G(2d,p)	MP2/SDD6-31+G(d)	MP2/SDD6-311+G(2d,p)
CH_3 Heterolysis	3.42	3.38	3.83	3.84
★ CH_3 Homolysis	2.73	2.74	2.98	3.27
Rearrangement	3.43	3.36	3.57	3.32
beta hydride	2.49	2.39	2.62	2.42

Figure S10: Comparison of computational methods and basis sets for fragmentation of; a) $[CH_3CO_2AuO_2CCH_3]^-$; b) $[CH_3AuO_2CCH_3]^-$ and c) $[CH_3AuCH_3]^-$.Table a), b) and c) contains key energies (eV).

Table S11: Intensity comparison at different q values and reaction times: trapped $[CH_3CO_2AuCH_3]^-$ versus its CID fragments

MS parameter	*q= 0.25*						*q= 0.35*					
Reaction time	*30 ms*			*100 ms*			*30 ms*			*100 ms*		
	NCE[a]	*Sum Intensity*[b]	*R*[c]	*NCE*[a]	*Sum Intensity*[b]	*R*[c]	*NCE*[a]	*Sum Intensity*[b]	*R*[c]	*NCE*[a]	*Sum Intensity*[b]	*R*[c]
$CH_3Au(CH_3CO_2)^-$	0	3102716										
CID of $CH_3Au(CH_3CO_2)^-$	18	3194757	1.03	15	3241014	1.04	18	2911279	0.94	15	3242356	1.04

a: normalised collision energy, which is the relative CID energy used (the ion-trap software).

b: The sum of the integration of the intensities for all peaks present in the mass spectrum

c: ratio between the Sum of the intensities upon CID and the intensity upon trapping.