Version: May 22, 2009

Supplementary Material for "A second metal centre enhances the reactivity of an organomagnesate: comparison of the gas phase reactions of water with $[RCCMgCl_2]^-$ and $[RCCMg_2Cl_4]^-$ (R = H & Ph)." by Khairallah, Thum and O'Hair

***Complete citation for reference 9*:** 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.

Part (A) DFT Energies of all species relevant to the decarboxylation and competing reaction which are used to calculate thermochemistry for species shown in figure 4.

Species	B3LYP/6-31+G* (Hartrees)	ZPE Scaled	B3LYP/6-31+G* + ZPE scaled [(a)]
$HC{\equiv}CCO_2MgCl_2^-$ (monomer), 20	-1386.122778	0.034136	**-1386.088641**
Decarboxylation Channel (eq. 3a)			
Reactant Complex, **21**	-1386.109141	0.033435	-1386.075705
Transition State (Freq=-297.0 cm^{-1})	-1386.070764	0.031260	**-1386.039503**
Product Complex, **22**	-1386.082484	0.031471	-1386.051012
$HC{\equiv}CMgCl_2^-$, **4**	-1197.487521	0.019492	-1197.468029
CO_2	-188.5903925	0.011342	-188.5790499
Sum of Products			**-1386.047079**
Carboxylate loss (eq. 3b)			
$HC{\equiv}CCO_2^-$	-265.3738357	0.028813	-265.3450227
$MgCl_2$	-1120.634816	0.002541	-1120.632275
Sum of Products			**-1385.977298**
Cl^- loss (eq. 3c)			
$HC{\equiv}CCO_2MgCl$	-925.7532234	0.033710	-925.7195133
Cl^-	-460.2747259	0	-460.2747259
Sum of Products			**-1385.994239**
[(Cl)Mg(μ-Cl_3)Mg(μ-O_2CCCH)]$^-$ (Dimer, 23)	-2506.849051	0.03853	-2506.810525
Decarboxylation channel (eq. 4a)			
Reactant Complex, **26**	-2506.819343	0.03755	-2506.781789
Transition State (Freq=-273.7 cm^{-1})	-2506.779581	0.03532	-2506.74426
Product Complex, **28**	-2506.790045	0.03557	-2506.754479
$HC{\equiv}CMg_2Cl_4^-$, **14**	-2318.202984	0.02378	-2318.179204
CO_2	-188.5903925	0.011343	-188.5790499
Sum of Products			-2506.758254
[(Cl)Mg(η^2-$HCCCO_2$)(μ-Cl_2)Mg(Cl)]$^-$ (Dimer, 24)	-2506.829207	0.03786	-2506.791344
Decarboxylation channel (eq. 4a)			
Reactant Complex (linear), **25**	-2506.819071	0.0374	-2506.78167
Transition State (Freq=-320.9 cm^{-1})	-2506.775724	0.035063	-2506.740661
Product Complex, **27**	-2506.795867	0.035344	-2506.760523
$HC{\equiv}CMg_2Cl_4^-$, **13**	-2318.202623	0.02354	-2318.179079
CO_2	-188.5903925	0.011343	-188.5790499
Sum of Products			-2506.758129
Carboxylate loss (eq. 4b)			
$HC{\equiv}CCO_2^-$	-265.3738357	0.028813	-265.3450227
Mg_2Cl_4	-2241.32715	0.00623	-2241.320917
Sum of Products			-2506.665939
Cl^- loss (eq. 4c)			
$HC{\equiv}CCO2Mg_2Cl_3$	-2046.447591	0.03751	-2046.410086
Cl^-	-460.2747259	0	-460.2747259
Sum of Products			-2506.684812

$MgCl_3^-$ loss (eq. 4d)			
$HC{\equiv}CCO_2MgCl$	-925.7532234	0.03371	-925.7195133
$MgCl_3^-$	-1581.013221	0.0034	-1581.009825
Sum of Products			**-2506.729338**
$MgCl_2$ loss (eq. 4e)			
$HC{\equiv}CCO_2MgCl_2^-$	-1386.122778	0.034137	-1386.088641
$MgCl_2$	-1120.634816	0.00254	-1120.632275
Sum of Products			**-2506.720916**

(a) ZPE's are corrected by 0.9806 from A.P. Scott, L. Radom, *J. Phys. Chem.*, **1996**, *100*, 16502

Part (B) DFT Energies of all species relevant to the hydrolysis reaction which are used to calculate thermochemistry for species shown in figure 6.

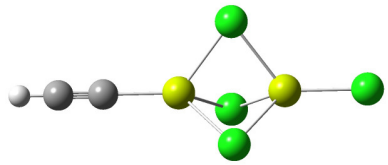
(a) ZPE's are corrected by 0.9806 from A.P. Scott, L. Radom, *J. Phys. Chem.*, **1996**, *100*, 16502

Species	B3LYP/6-31+G*	ZPE [(a)]	B3LYP/6-31+G* ZPE [(a)]
Monomer (eq. 7), 4	-1197.487521	0.019492367	-1197.468029
$[(HCCMg(Cl)_2(H_2O)]^-$ Pre complex, **29**	-1273.932758	0.044001483	-1273.888757
$[(HCCCO_2)Mg(Cl)_2]^-$ TS**,**	-1273.916348	0.039077891	-1273.87727
$[(HO)Mg(Cl)_2(HCCH)]^-$ Post complex, **30**	-1273.942219	0.042405066	-1273.899813
$[(HO)Mg(Cl)_2]^-$, **31**	-1196.593932	0.01443149	-1196.579501
H_2O	-76.4225724	0.020686738	-76.40188566
HCCH	-77.3331033	0.026239875	-77.30686342
Dimer Isomer 14 (eq. 8)			
Precomplex, **35**	-2394.646741	0.046952109	-2394.599789
TS (Freq = -660.5 cm^{-1})	-2394.645831	0.043274859	-2394.602556
Postcomplex, **36**	-2394.652312	0.046029364	-2394.606283
$HOMg_2Cl_4^-$, **37**	-2317.332519	0.019450201	-2317.313069
HCCH	-77.3331033	0.026239875	-77.30686342
Sum of Products			-2394.619933
Dimer Isomer 13 (eq. 8)			
Precomplex, **32**	-2394.654161	0.048048419	-2394.60613
TS (Freq = -861.0 cm^{-1})	-2394.621082	0.042658061	-2394.578424
Postcomplex, **33**	-2394.654399	0.045847953	-2394.60855
$HOMg_2Cl_4^-$, **34**	-2317.308459	0.017603731	-2317.290854
HCCH	-77.3331033	0.026239875	-77.30686342
Sum of Products			-2394.598227

Part (C) Cartesian Coordinates of DFT optimized structures. Note zero point correction energies are unscaled.

Isomers of the binuclear organometallate of formula $HCCMg_2Cl_4^-$

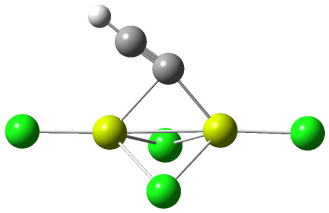
Isomer 13 (illustrated in Figure 3b)



Mg	1.372209	-0.000001	-0.000072
Cl	-0.065458	-1.257957	-1.540222
Cl	-0.065150	1.962608	-0.319573
Mg	-1.536419	-0.000191	-0.000020
Cl	-0.065370	-0.704920	1.858844
Cl	3.639961	0.000135	0.000556
C	-3.608916	0.000193	0.000430
C	-4.836343	0.000453	0.000715
H	-5.905631	0.000691	0.000967

E= -2318.2026234 Hartrees
Zero point correction = 0.024010

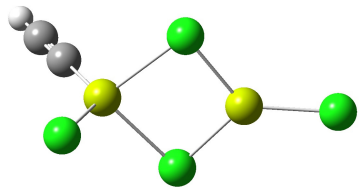
Isomer 14 (illustrated in Figure 3c)



Mg	1.502512	-0.000716	0.164909
C	0.077131	-0.008127	1.816576
Cl	0.093647	-1.722331	-0.962940
Mg	-1.373212	0.000106	-0.025235
Cl	0.093655	1.730772	-0.947636
Cl	3.777038	-0.000805	0.192307
Cl	-3.649797	0.000529	-0.100421
C	-0.931285	-0.011387	2.525945
H	-1.773903	-0.014426	3.186521

E= -2318.2029842 Hartrees
Zero point correction = 0.024251

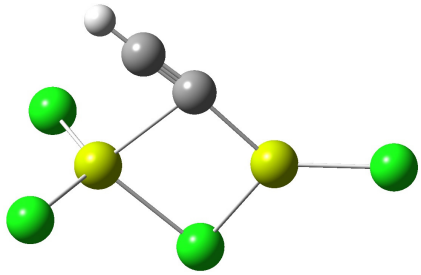
Isomer 15 (illustrated in Figure 3d)



Mg	-1.787428	0.058668	0.000008
Cl	-0.286420	0.053131	1.764784
Cl	-0.286393	0.053125	-1.764756
Mg	1.601416	-0.008306	-0.000015
Cl	2.472732	-2.132684	0.000002
Cl	-4.035904	0.099150	-0.000022
C	2.602748	1.824179	-0.000007
C	3.200908	2.897213	-0.000003
H	3.721967	3.831033	0.000001

E= -2318.1880659 Hartrees
Zero point correction= 0.023582

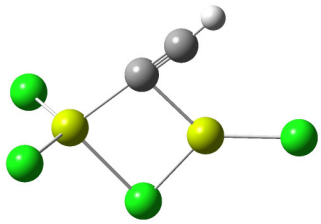
Isomer 16a (illustrated in Figure 3e)



Mg	-1.924572	-0.000613	0.140019
Cl	-0.494532	-0.000748	-1.714389
C	-0.444868	-0.001537	1.634714
Mg	1.404625	0.000239	-0.028802
Cl	2.469921	2.035841	-0.070666
Cl	-4.180216	-0.000237	0.164887
Cl	2.474338	-2.033015	-0.071917
C	0.502680	-0.002402	2.417175
H	1.310794	-0.003182	3.119515

E= -2318.191851 Hartrees
Zero point correction= 0.024000

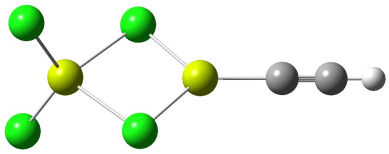
Isomer 16b (illustrated in Figure 3f)



Mg	-1.768930	-0.000095	-0.033137
Cl	-0.273586	-0.000265	-1.794060
C	-0.221073	-0.000122	1.560723
Mg	1.502469	0.000031	0.129344
Cl	2.547438	2.050199	0.109353
Cl	-4.028041	-0.000006	-0.054591
Cl	2.548160	-2.049759	0.109482
C	-1.171920	-0.000188	2.348972
H	-1.942000	-0.000234	3.094239

E= -2318.1883784 Hartrees
Zero point correction= 0.023939

Isomer 17 (illustrated in Figure 3g)

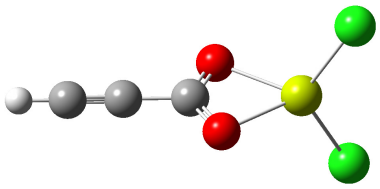


Mg	1.965985	-0.000173	0.000012
Cl	0.430136	-0.000375	1.755763
Cl	0.430099	-0.000374	-1.755733
Mg	-1.421369	0.000075	-0.000016
Cl	-2.444072	2.048723	-0.000001
C	4.023593	-0.000064	-0.000024
Cl	-2.445429	-2.047883	-0.000002
C	5.250180	-0.000008	-0.000037
H	6.319490	0.000047	-0.000046

E= -2318.1902558 Hartrees
Zero point correction= 0.023715

Species associated with the potential energy surfaces for decarboxylation (eqs 3a and 4a) and competing reactions (these species are associated with Figure 4):

Monomer, 20

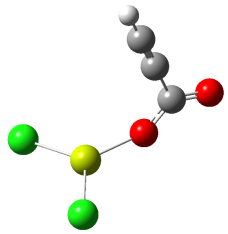


$[HCCCO_2MgCl_2]^-$

C	-3.071924	-0.000086	0.000005
C	-1.609153	-0.000082	0.000002
O	-0.996960	-0.000075	-1.110216
O	-0.996956	-0.000072	1.110218
Mg	0.817027	-0.000009	-0.000002
Cl	1.919724	2.024350	-0.000006
Cl	1.920028	-2.024191	-0.000001
C	-4.282204	-0.000061	0.000010
H	-5.349103	-0.000041	0.000016

E= -1386.122778 Hartrees
Zero point correction = 0.034812

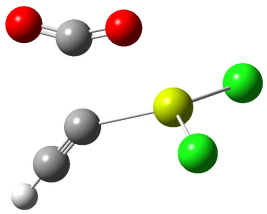
Precomplex for decarboxylation, 21



C	2.405491	0.001067	0.853935
Mg	-0.918735	-0.000173	-0.214050
Cl	-1.952702	-2.009474	0.119257
Cl	-1.950779	2.010760	0.115129
C	2.633617	0.004081	2.044864
H	2.829889	0.006789	3.093512
O	0.871302	-0.002375	-0.904674
C	2.125627	-0.001888	-0.600301
O	3.074409	-0.003392	-1.382882

E= -1386.109141 Hartrees
Zero point correction = 0.034097

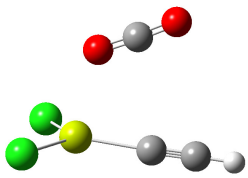
$[HCCCO_2MgCl_2]^-$ TS for decarboxylation (TS21-22).



C	1.310329	-0.001284	1.183416
Mg	-0.598638	0.000051	0.057353
Cl	-1.697349	-2.025400	-0.022505
Cl	-1.695078	2.026814	-0.020768
C	1.811817	-0.002629	2.305931
H	2.241890	-0.003768	3.285231
O	0.897971	-0.000147	-1.495135
C	1.947745	0.000093	-0.897823
O	3.126239	0.000401	-0.853237

E= -1386.070764 Hartrees
Zero point correction = 0.031879
Freq=-297.0029 cm^{-1}

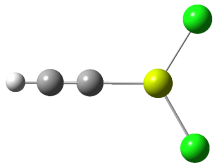
Postcomplex for decarboxylation, 22



C	0.879232	0.003538	1.732152
Mg	-0.747557	0.000940	0.378755
Cl	-1.747611	-2.004018	-0.204339
Cl	-1.744513	2.005024	-0.212573
C	1.853858	0.005912	2.482681
H	2.687514	0.011318	3.152825
O	1.089054	-0.005933	-1.391563
C	2.235759	-0.005137	-1.152809
O	3.390469	-0.002266	-0.981253

E= -1386.082484 Hartrees
Zero point correction = 0.032094

Separated products
$HCCMgCl_2$, 4 (illustrated in Figure 3a)



C	0.000000	2.152360	0.000000
Mg	0.000000	0.052158	0.000000
Cl	-1.986091	-1.125930	0.000000
Cl	1.986091	-1.125930	0.000000
C	0.000000	3.381735	0.000000
H	0.000000	4.451156	0.000000

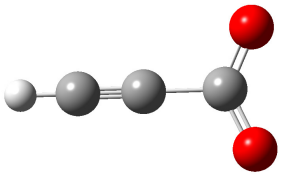
E= -1197.487521 Hartrees
Zero point correction = 0.019878

CO_2

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.169233
O	0.000000	0.000000	-1.169233

E= -188.5903925 Hartrees
Zero point correction = 0.011567

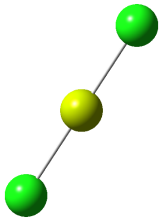
$HCCCO_2^-$



C	-0.914783	0.000000	-0.000014
C	0.595824	0.000000	-0.000005
O	1.119401	1.141028	0.000004
O	1.119401	-1.141027	0.000004
C	-2.132877	0.000000	0.000003
H	-3.199396	0.000000	0.000028

E= -265.3738357 Hartrees
Zero point correction = 0.029383

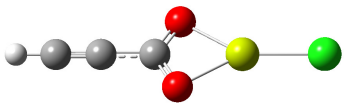
$MgCl_2$



Mg	0.000000	0.000000	0.000000
Cl	0.000000	0.000000	2.195492
Cl	0.000000	0.000000	-2.195492

E= -1120.634816 Hartrees
Zero point correction = 0.002591

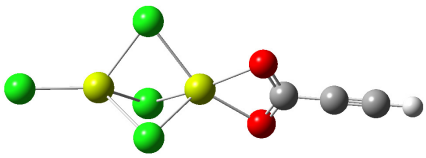
$HCCCO_2MgCl$



C	-2.806979	0.000000	0.000026
C	-1.366568	0.000000	0.000000
O	-0.722669	-1.105873	-0.000056
O	-0.722669	1.105873	-0.000056
Mg	0.977592	0.000000	-0.000006
Cl	3.179358	0.000000	0.000026
C	-4.015355	0.000000	0.000050
H	-5.084074	0.000000	0.000072

E= -925.7532234 Hartrees
Zero point correction = 0.034377

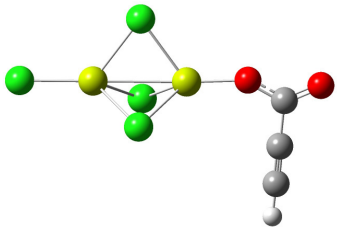
Binuclear carboxylate precursor 24 to formation of 13



Mg	-2.165146	-0.001087	0.020940
Cl	-0.779170	-1.538077	-1.281014
Cl	-0.613804	-0.237853	1.924918
Mg	0.753282	0.022874	-0.094561
Cl	-0.811849	1.838459	-0.821689
Cl	-4.429164	-0.054509	0.179122
O	2.563840	1.103311	-0.025081
O	2.548340	-1.108414	-0.047331
C	3.177307	-0.008520	-0.003313
C	4.633662	-0.018244	0.073213
C	5.841624	-0.026932	0.137543
H	6.907158	-0.034786	0.195361

E= -2506.8292074 Hartrees
Zero point correction = 0.038612

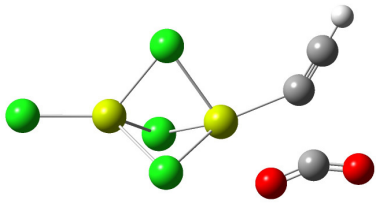
Precomplex, 25



Mg	-2.17918000	-0.09680600	-0.00050500
Cl	-0.57937100	-0.71048900	1.77045200
Cl	-1.11298900	2.12210000	-0.09937200
Mg	0.65262700	0.44152600	0.00181400
Cl	-0.53879400	-0.88363800	-1.66651100
Cl	-4.39850100	-0.52499100	-0.00648700
O	4.72850300	1.13450200	-0.01724200
O	2.49282500	0.87218700	0.01548500
C	3.71700800	0.44060600	-0.00118700
C	3.85145100	-1.02889400	0.00140700
C	3.96500100	-2.23536200	0.00389000
H	4.05138400	-3.29893500	0.00628800

E= -2506.819071
Zero-point correction= 0.038141

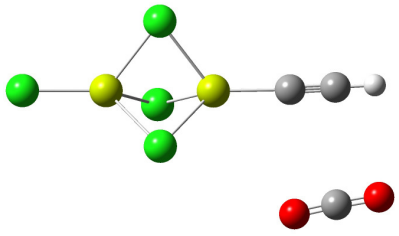
Transition State (TS25-27):



Mg	2.03358800	0.00021600	-0.00002400
Cl	0.54807800	-0.90159700	1.74298800
Cl	0.54856500	-0.90702400	-1.74043800
Mg	-0.89678500	0.07337900	-0.00028600
Cl	0.71451100	2.03072700	-0.00346600
Cl	4.29703500	-0.17211100	0.00069200
O	-4.61174000	-0.92490800	-0.00012000
O	-2.36733400	-1.49809600	0.00060200
C	-3.43079100	-0.91538000	0.00018500
C	-2.85027700	1.10347700	-0.00018000
C	-3.36203200	2.22025900	0.00045100
H	-3.78963400	3.20084300	0.00093400

E=-2506.7757237
Zero point correction = 0.035757
Freq: - 320.9484 cm^{-1}

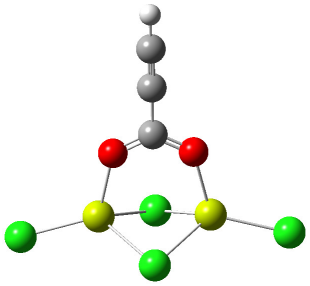
Post complex, 27



Mg	2.27978800	-0.22054900	-0.00349300
Cl	0.59983600	-0.65812300	1.73540800
Cl	0.58000200	-0.68786300	-1.71116100
Mg	-0.46023100	0.74745900	0.00742100
Cl	1.59079700	2.13333000	-0.01671300
Cl	4.41526600	-0.98173000	-0.00846200
O	-5.71935300	-0.57566500	-0.01779000
O	-3.73271400	-1.80874300	0.01696700
C	-4.70994500	-1.17002900	-0.00043300
C	-2.40055100	1.48760700	-0.00053300
C	-3.53297000	1.96205900	-0.00228000
H	-4.51767800	2.37908100	-0.00530100

E= -2506.7958669
Zero-point correction= 0.036043

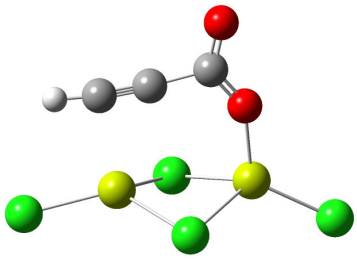
Binuclear carboxylate precursor 23 to formation of 14



Mg	1.569560	-0.503355	0.000076
Mg	-1.569342	-0.503730	-0.000207
Cl	0.000062	-1.202028	1.739823
Cl	0.000314	-1.202858	-1.739640
Cl	3.762209	-1.101294	0.000243
Cl	-3.761908	-1.102034	0.000250
O	1.130359	1.460764	-0.000379
O	-1.131001	1.460565	-0.000661
C	-0.000368	2.026645	-0.000414
C	-0.000420	3.489132	-0.000057
C	-0.000603	4.698897	0.000149
H	-0.000656	5.765987	0.000321

E= -2506.849051 Hartrees
Zero point correction = 0.039288

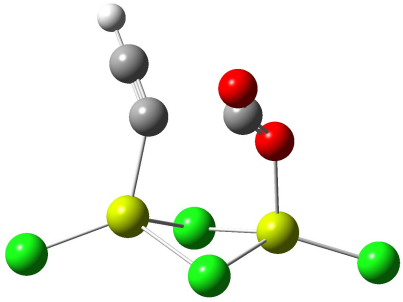
Precomplex, **26**



Mg	-1.65982500	-0.32536700	0.00012900
Mg	1.55618500	-0.53295600	0.00006300
Cl	-0.00113000	-0.95399000	-1.74570800
Cl	-0.00099900	-0.95451000	1.74582800
Cl	-3.69411300	-1.32981300	-0.00036700
Cl	3.75267400	-1.12542600	-0.00018900
O	-1.41193000	1.60409400	0.00064300
O	-0.75486500	3.76502000	-0.00030300
C	-0.55570300	2.55290500	0.00033700
C	0.88583900	2.15007000	0.00090200
C	2.08153500	1.91402400	-0.00065100
H	3.14866800	1.82854100	-0.00114000

E =-2506.8193425 Hartrees
Zero-point correction= 0.038296

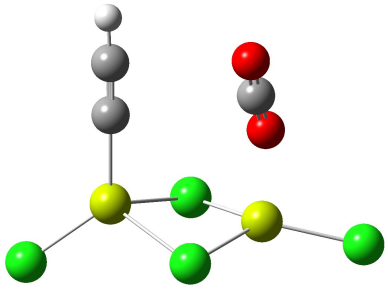
Transition State (TS26-28):



Mg	1.62779800	-0.43684200	-0.06785500
Mg	-1.58018400	-0.37866100	0.03461600
Cl	0.12806700	-0.67445000	1.80581900
Cl	0.02948500	-1.32190500	-1.60749400
Cl	3.84369600	-0.91019500	-0.08647600
Cl	-3.61531100	-1.36397700	0.33193100
O	1.28728400	1.61246200	-0.23991200
O	0.22422400	3.33209600	0.88102800
C	0.48502200	2.38729400	0.22858900
C	-1.40102500	1.71540400	-0.56157300
C	-1.89812800	2.50208500	-1.37080700
H	-2.33957600	3.19984300	-2.05158900

E= -2506.7795812 Hartrees
Zero-point correction= 0.036020
Freq.= - 273.3599 cm^{-1}

Post Complex, 28



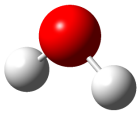
Mg	1.33921600	-0.91229800	-0.03333800
Mg	-1.84078200	0.01286300	-0.02391600
Cl	-0.13589700	-0.60429800	1.77688400
Cl	-0.30711500	-1.14656100	-1.69129700
Cl	3.43233400	-1.77742000	0.01793400
Cl	-3.85372200	-1.04691800	0.24398900
O	1.76324900	1.25247200	-0.29365400
O	1.81146500	3.48801000	0.37383700
C	1.73802900	2.37616000	0.04498300
C	-1.51338400	2.07258200	-0.34832300
C	-1.33592000	3.27234800	-0.55274700
H	-1.21644900	4.32115400	-0.72555100

E =-2506.7900453 Hartrees
Zero-point correction= 0.036270

Species associated with the potential energy surfaces for hydrolysis (eqs 7 and 8). These species are associated with Figure 6:

$HCCMgCl_2$: see above

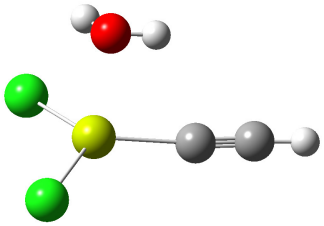
H_2O



O	0.000000	0.000000	0.117300
H	0.000000	0.771244	-0.469201
H	0.000000	-0.771244	-0.469201

E= -76.4225724 Hartrees
Zero-point correction= 0.021096

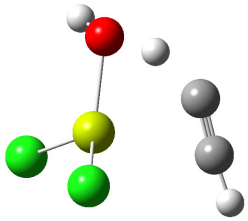
Precomplex, 29



C	1.864991	-0.929541	-0.460496
Mg	-0.095923	-0.151515	-0.088615
Cl	-0.359431	2.174000	-0.549426
Cl	-1.969532	-1.509061	-0.052858
C	3.023519	-1.329245	-0.579894
H	4.019518	-1.689413	-0.729901
O	0.654041	0.508639	1.873938
H	0.590830	1.451329	1.614661
H	1.569707	0.235900	1.668270

E= -1273.9327581 Hartrees
Zero-point correction= 0.044872

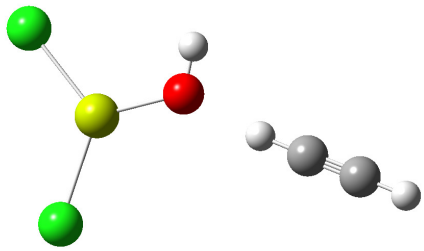
$[HCCMgCl_2]^-$ + H_2O TS (TS29-30)



C	-0.192836	2.350257	-0.290679
Mg	0.033876	-0.077946	0.182109
Cl	-1.848745	-1.314359	-0.401806
Cl	2.160221	-0.956512	-0.005131
C	0.139645	2.104643	-1.451464
H	0.431978	1.975066	-2.472744
O	-0.492220	1.013382	1.822997
H	-1.416712	0.838233	2.062478
H	-0.459951	1.890404	1.011772

E= -1273.9163478 Hartrees
Zero-point correction= 0.039851
Frequency = -890.0539 cm^{-1}

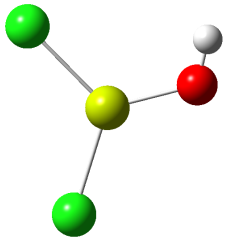
Post complex, 30



C	-3.829029	-0.391662	-0.000017
Mg	0.766007	-0.050504	0.000062
Cl	2.657944	-1.385344	-0.000104
Cl	0.928774	2.242249	-0.000007
C	-5.034808	-0.262933	-0.000150
H	-6.094391	-0.138570	-0.000273
O	-0.911570	-0.933929	0.000257
H	-0.856071	-1.900092	0.000249
H	-2.740244	-0.523676	0.000104

E = -1273.9422185 Hartrees
Zero-point correction= 0.043244

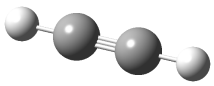
$HOMgCl_2^-$, 31



Mg	-0.009233	0.413395	-0.000041
Cl	1.940745	-0.855625	0.000004
Cl	-2.048930	-0.672254	0.000018
O	0.118406	2.291459	-0.000056
H	1.002695	2.681534	0.000562

E= -1196.5939322 Hartrees
Zero-point correction= 0.014717

HCCH

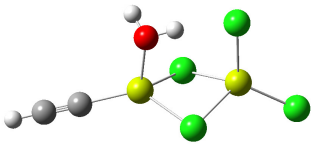


C	0.000000	0.000000	0.603800
H	0.000000	0.000000	1.671375
C	0.000000	0.000000	-0.603799
H	0.000000	0.000000	-1.671381

E = -77.3331033 Hartrees
Zero-point correction= 0.026759

Hydrolysis of Binuclear isomer 13

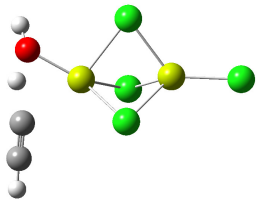
Precomplex, 32



Mg	1.501515	-0.140815	-0.016654
Cl	-0.238715	-0.662251	-1.700033
Cl	1.515378	2.232706	-0.029413
Mg	-1.795171	-0.127639	0.086607
Cl	3.435420	-1.350243	-0.049331
C	-3.820978	-0.598974	-0.002436
C	-5.017326	-0.867310	-0.072187
H	-6.056630	-1.113986	-0.123712
O	-1.544749	1.936885	0.058168
C	-0.573618	2.176189	0.068830
C	-1.927612	2.396955	-0.705104

E = -2394.654161 Hartrees
Zero-point correction= 0.048999

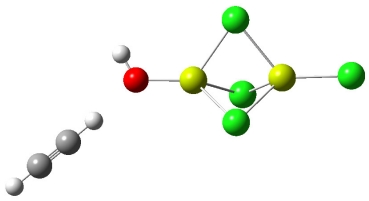
Transition State (TS32-33):



Mg	1.730615	0.086354	0.053238
C	-1.211593	2.234865	-0.014306
Mg	-1.517898	-0.112720	-0.007379
Cl	-3.573553	-1.122998	-0.018918
Cl	0.146890	-0.618010	-1.707592
C	-2.441221	2.222956	-0.051703
H	-3.511277	2.241802	-0.078980
Cl	0.104238	-0.580125	1.753849
Cl	3.905829	-0.606372	-0.031481
H	0.188862	2.206930	0.019560
O	1.369528	2.034277	0.067956
H	1.812595	2.614116	-0.568067

E = -2394.6210824 Hartrees
Zero-point correction= 0.043502
Frequency = -861.0417 cm^{-1}

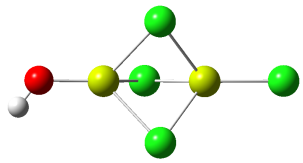
Post Complex, 33



Mg	1.792840	0.237413	0.011808
C	-1.293045	2.313269	-0.029862
Mg	-1.478610	-0.263835	-0.000633
Cl	-3.593664	-1.130677	0.007253
Cl	0.124253	-0.548275	-1.727102
C	-2.493105	2.115219	-0.034856
H	-3.550333	1.957080	-0.038845
Cl	0.113135	-0.496957	1.746812
Cl	3.846594	-0.790289	-0.002944
H	-0.187151	2.443217	-0.025798
O	1.514949	2.126566	0.006585
H	2.228609	2.758681	-0.142149

E =-2394.6523124 Hartrees
Zero-point correction= 0.046940

$HOMg_2Cl_4^-$ Isomer 34 related to 13

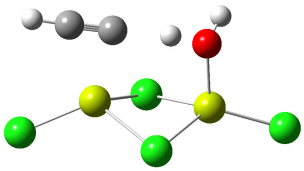


Mg	1.797980	0.025513	0.010567
Cl	0.308625	1.991473	-0.104093
Cl	0.308969	-0.906302	1.773284
Mg	-1.117560	-0.006359	0.000970
Cl	0.320873	-1.083432	-1.665608
O	3.654459	0.065959	0.021207
Cl	-3.387902	-0.007671	-0.008076
H	4.239681	-0.656687	-0.231742

E= =-2317.3084587 Hartrees
Zero-point correction= 0.017952

Hydrolysis of Binuclear isomer 14

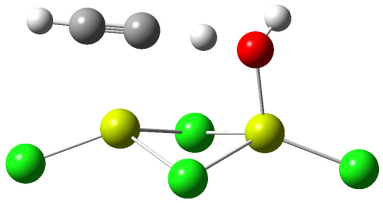
Precomplex, 35



Mg	1.713153	0.010454	0.062611
C	-1.299046	2.217092	0.012388
Mg	-1.538310	-0.045306	-0.008059
Cl	-3.529780	-1.181696	-0.039610
Cl	0.158270	-0.592439	-1.713471
C	-2.531443	2.288479	-0.024654
H	-3.598331	2.380501	-0.051429
Cl	0.105904	-0.608904	1.753638
Cl	3.921769	-0.547590	-0.041054
H	0.353420	2.178021	0.060123
O	1.397215	2.012304	0.088850
H	1.797240	2.548527	-0.612070

E= -2394.646741 Hartrees
Zero-point correction= 0.047881

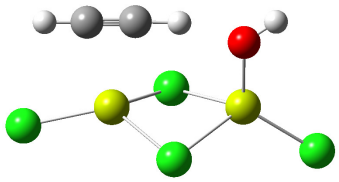
Transition State (TS35-36):



Mg	1.730615	0.086354	0.053238
C	-1.211593	2.234865	-0.014306
Mg	-1.517898	-0.112720	-0.007379
Cl	-3.573553	-1.122998	-0.018918
Cl	0.146890	-0.618010	-1.707592
C	-2.441221	2.222956	-0.051703
H	-3.511277	2.241802	-0.078980
Cl	0.104238	-0.580125	1.753849
Cl	3.905829	-0.606372	-0.031481
H	0.188862	2.206930	0.019560
O	1.369528	2.034277	0.067956
H	1.812595	2.614116	-0.568067

E= -2394.645831 Hartrees
Zero-point correction= 0.044131
Frequency = -660.4691 cm^{-1}

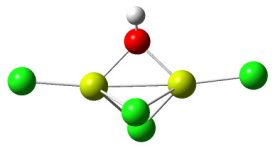
Post complex, 36



Mg	-1.911221	-0.181643	0.000204
Cl	-0.391261	-0.370422	1.917256
Cl	-0.957690	2.030862	-0.489450
Mg	0.914481	0.486094	0.005412
Cl	-0.178195	-1.202277	-1.411780
Cl	-4.116812	-0.702366	-0.013181
C	5.388589	-0.411342	-0.002308
C	6.492700	-0.910629	-0.003649
H	7.461298	-1.357979	-0.005043
O	2.724128	0.978607	-0.004770
H	2.968637	1.912733	-0.035097
H	4.397477	0.046256	-0.001703

E= -2394.652312 Hartrees
Zero-point correction= 0.04694

$HOMg_2Cl_4^-$ Isomer 37 related to 14



Mg	-1.389292	0.028108	0.170086
Cl	-0.000149	1.775050	-0.894983
Mg	1.389289	0.027982	0.170018
Cl	0.000132	-1.692171	-0.989879
Cl	-3.654676	-0.052690	0.381843
Cl	3.654678	-0.052522	0.381853
O	0.000030	0.039008	1.584365
H	0.000038	-0.605470	2.303661

E= -2317.3325193 Hartrees
Zero-point correction= 0.019835

Fig. S1:

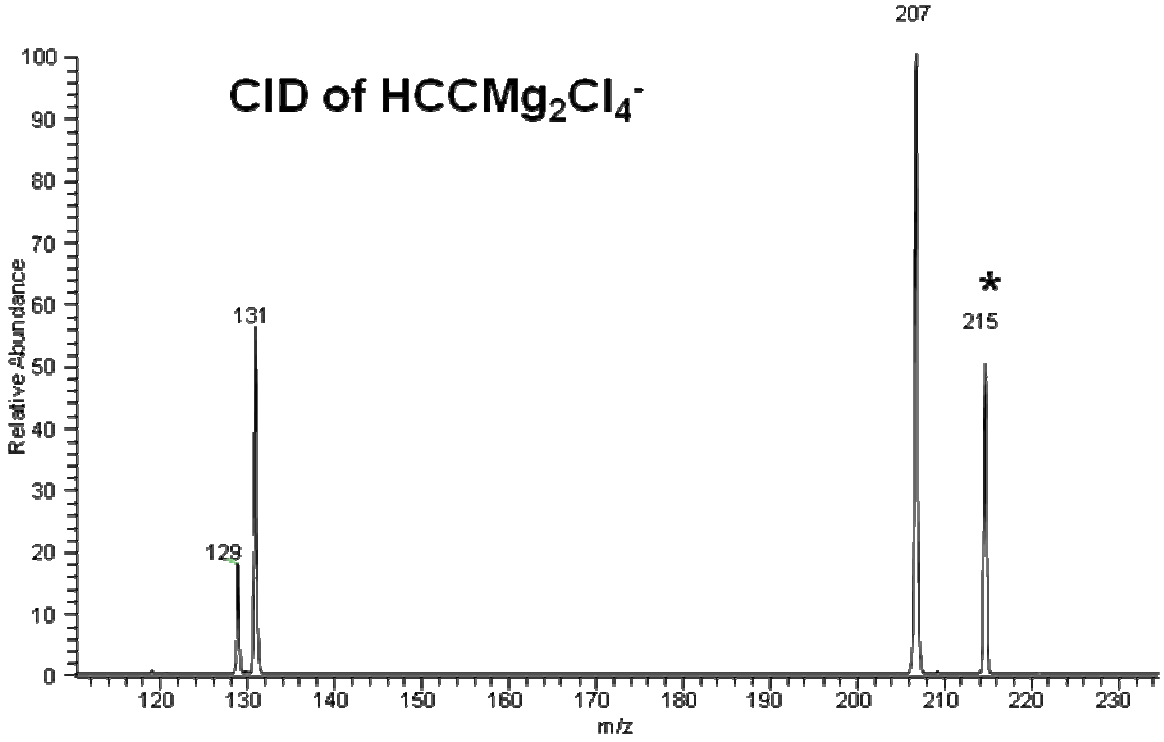


Fig. S1: CID spectrum of $[HCCMg_2Cl_4]^-$ (*m/z* 215) to produce $MgCl_3^-$ (*m/z* 129/131). The peak at *m/z* 207 corresponds to the reaction of *m/z* 215 with background water. The asterisk represents the mass selected ion.

Fig. S2:

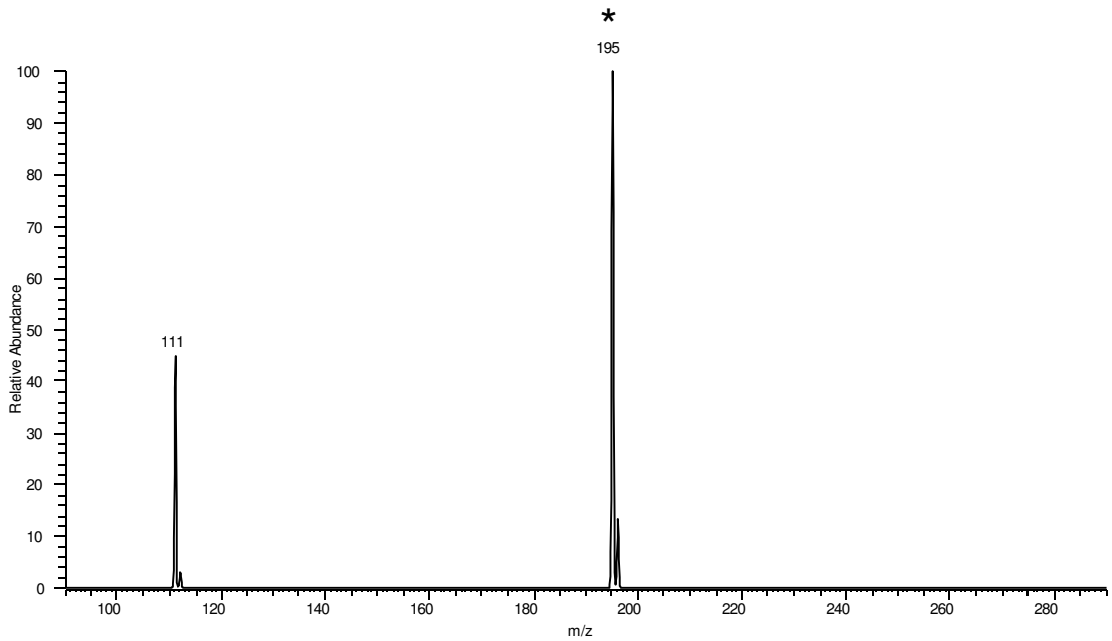


Fig. S2: Ion-molecule reaction spectrum of $[PhCCMgCl_2]^-$ (*m/z* 195) to generate $[OHMgCl_2]^-$ (*m/z* 111).reaction time = 300 ms. The asterisk represents the mass selected ion.

Fig. S3:

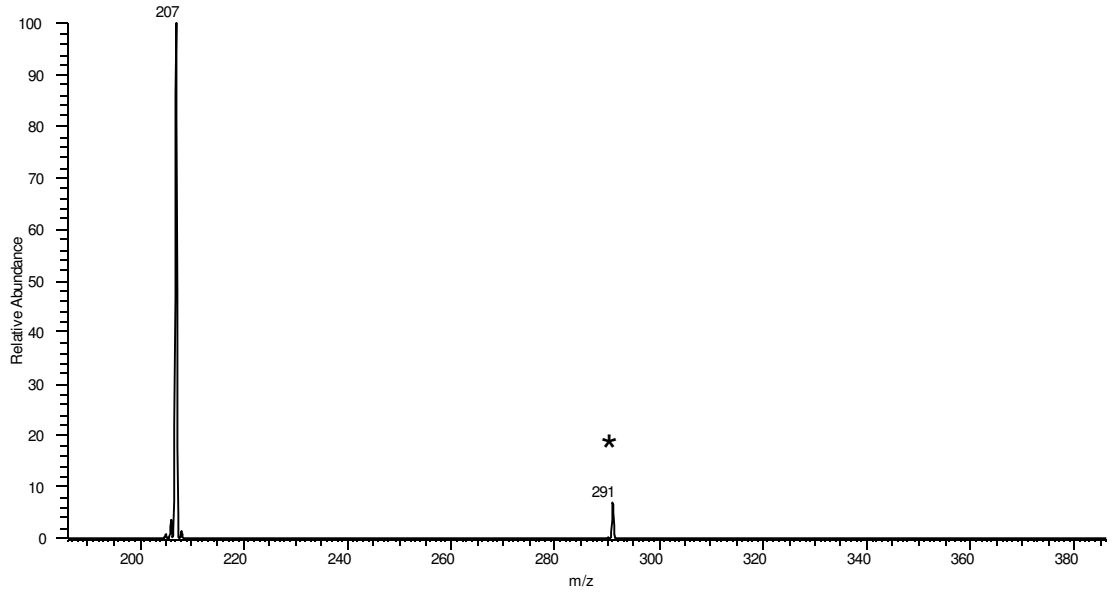


Fig. S3: Ion-molecule reaction spectrum of $[PhCCMg_2Cl_4]^-$ (*m/z* 291) to generate $[OHMg_2Cl_4]^-$ (*m/z* 207). Reaction time = 300 ms. The asterisk represents the mass selected ion.

Fig. S4:

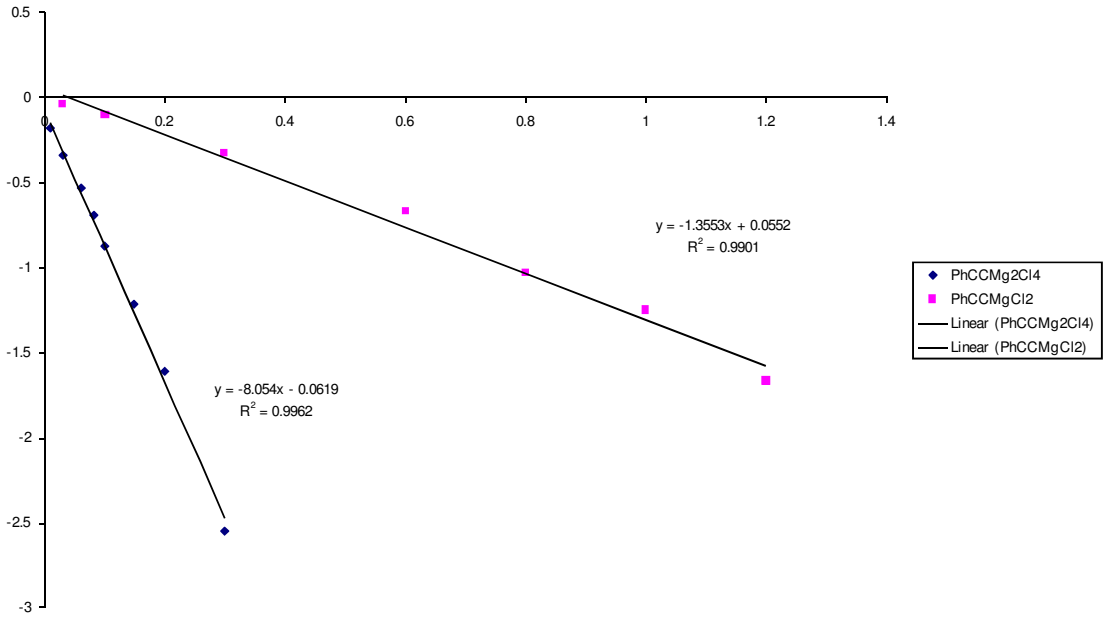


Fig. S4: The relative reaction rates of $[PhCCMg_2Cl_4]^-$ and $[PhCCMg_2Cl_4]^-$ with water. The x-axis represents the reaction delay whereas the y-axis represents the Ln of the relative ion counts.