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Supporting Information

α.β-unsaturated and saturated derivatives of Be. Mg and Ca. Are they carbon or metal acids in the gas phase?

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Table S1. Total energies (E. hartrees), thermal corrections to the enthalpy (H_{corr}. hartrees) and entropies (S. cal mol^{-1} K^{-1})

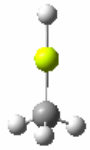
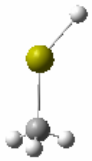
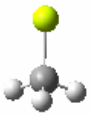
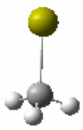
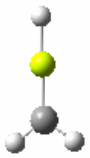
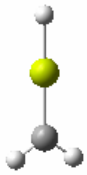
	CCSD(T)/6-311+G(3df.2p) //B3LYP/6-311+G(d.p)	B3LYP/6-311+G(3df.2p) //B3LYP/6-311+G(d.p)		
Systems	E	E	H_{corr}	S
BeH_2	-15.8453171	-15.9234791	0.016659	41.786
BeH^-	-15.2125759	-15.2838818	0.007033	41.037
MgH_2	-200.8036408	-201.2655622	0.013285	46.383
MgH^-	-200.2198097	-200.6791736	0.00579	45.085
CaH_2	-678.1921393	-678.7497159	0.01074	53.315
CaH^-	-677.6282219	-678.1809725	0.00579	47.007
$BeH\text{-}CH_3$	-55.1028937 (-55.102898)[a] (-55.1028771)[b]	-55.2744614	0.047039 (0.038271)[a] (0.047123)[b]	54.928 (53.62)[a] (57.31)[b]
$Be\text{-}CH_3^-$	-54.4742041 (-54.4742231)[a] (-54.4741985)[b]	-54.6390689	0.037881 (0.038271)[a] (0.037998)[b]	55.794 (53.620)[a] (55.870)[b]
$BeH\text{-}CH_2^-$	-54.4742669 (-54.4743341)[a] (-54.4743065)[b]	-54.646612	0.033297 (0.033238)[a] (0.032956)[b]	56.282 (56.62)[a] (56.827)[b]
$BeH\text{-}CH_2\text{-}CH_3$	-94.3308929	-94.5933815	0.077349	65.837
$BeH\text{-}CH_2\text{-}CH_2^-$	-93.7169309	-93.9795749	0.061678	63.631
$Be\text{-}CH_2\text{-}CH_3$	-93.7031226	-93.9582578	0.068147	64.337
$BeH\text{-}CH\text{-}CH_2$	-93.702621	-93.9659369	0.063010	65.293
$BeH\text{-}CH{=}CH_2$	-93.1070402	-93.362106	0.05434	62.837
$BeH\text{-}CH{=}CH^-/E$	-92.5057533	-92.7601242	0.039944	60.051
$Be\text{-}CH{=}CH_2$	-92.3486792	-92.7273323	0.045288	61.401
$BeH\text{-}CH{=}CH^-/Z$	-92.4814351	-92.7347151	0.039853	60.306
$BeH\text{-}C{=}CH_2$	-92.4820895	-92.7394595	0.040036	62.070
$BeH\text{-}C{\equiv}CH$	-91.8861473	-92.1306647	0.031645	56.957
$BeH\text{-}C{\equiv}C^-$	-91.2891196	-91.5339488	0.019681	56.767
$Be\text{-}C{\equiv}CH$	-91.2627842	-91.4985779	0.022898	56.031
$MgH\text{-}CH_3$	-240.0503793 (-240.0519179)[a]	-240.6057534	0.044211 (0.044477)[a]	59.691 (59.78)[a]
$Mg\text{-}CH_3^-$	-239.469225 (-239.469252)[a]	-240.021223	0.036695 (0.037033)[a]	58.331 (58.23)[a]
$MgH\text{-}CH_2^-$	-239.4060022 (-239.4062847)[a]	-239.9596763	0.030332 (0.030418)[a]	63.433 (61.784)[a]
$MgH\text{-}CH_2\text{-}CH_3$	-279.277493	-279.9239716	0.074453	70.655

$Mg\text{-}CH_2\text{-}CH_3^-$	-278.6976758	-279.3404122	0.066825	69.232
$MgH\text{-}CH\text{-}CH_3$	-278.6332667	-279.2776957	0.060121	71.618
$MgH\text{-}CH_2\text{-}CH_2$	-278.6505535	-279.2951586	0.058695	68.305
$MgH\text{-}CH{=}CH_2$	-278.0551815	-278.693414	0.051350	67.754
$Mg\text{-}CH{=}CH_2^-$	-277.4783398	-278.1130085	0.043927	66.548
$MgH\text{-}C{=}CH_2$	-277.4189551	-278.0542849	0.037099	67.654
MgH-CH=CH/Z	-277.4160448	-278.0524775	0.036793	67.931
MgH-CH=CH/E	-277.4393518	-278.0747957	0.036792	64.594
MgH-C≡CH	-276.8408281	-277.4670942	0.028908	61.923
$Mg\text{-}C{\equiv}CH^-$	-276.2694286	-276.8927049	0.021946	61.362
$MgH\text{-}C{\equiv}C^-$	-276.2279351	-276.8536455	0.016937	62.155
$CaH\text{-}CH_3$	-717.4354527 (-717.4369626)[a]	-718.0866763	0.042011 (0.042294)[a]	73.054 (70.25)[a]
$Ca\text{-}CH_3^-$	-716.8781207 (-716.8781349)[a]	-717.5224489	0.036320 (0.036577)[a]	61.005 (60.873)[a]
$CaH\text{-}CH_2^-$	-716.7928623 (-716.7954891)[a]	-717.4389136	0.028517 (0.028951)[a]	67.917 (66.217)[a]
$CaH\text{-}CH_2\text{-}CH_3$	-756.6623433	-757.4050445	0.072354	78.737
$Ca\text{-}CH_2\text{-}CH_3^-$	-756.1062672	-756.8409352	0.066449	72.319
$CaH\text{-}CH\text{-}CH_3$	-756.0257282	-756.7590343	0.058317	77.347
$CaH\text{-}CH_2\text{-}CH_2$	-756.046666	-756.7895284	0.056665	72.603
$CaH\text{-}CH{=}CH_2$	-755.4496145	-756.1832569	0.049032	72.783
$Ca\text{-}CH{=}CH_2^-$	-754.8890065	-755.6152304	0.043873	69.28
$CaH\text{-}C{=}CH_2^-$	-754.8190664	-755.5415246	0.035660	73.640
CaH-CH=CH/Z	-754.8160825	-755.548358	0.036005	70.318
CaH-CH=CH/E	-754.8400011	-755.5743421	0.035419	68.226
CaH-C≡CH	-754.2386059	-754.9593076	0.026732	70.431
$Ca\text{-}C{\equiv}CH^-$	-753.6838357	-754.3974799	0.021889	63.809
CaH-C≡C	-753.6452338	-754.3633931	0.014926	67.794

[a] Values calculated at CCSD(T)/6-311+(3df.2p)//CCSD/6-311+G(d.p) level of theory
[b] Values calculated at CCSD(T)/6-311+(3df.2p)//CCSD(T)/6-311+G(d.p) level of theory

Table S2. B3LYP/6-311+G(d,p) optimized geometries. Bond lengths are in Å and bond angles are in degrees.

Methyl derivatives

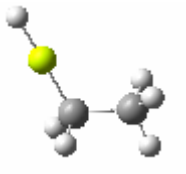
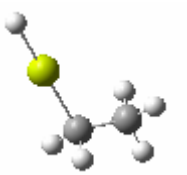
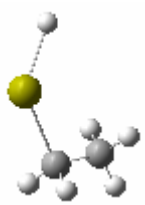
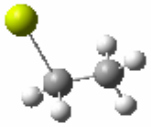
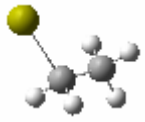
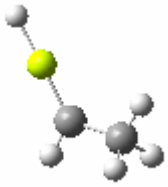
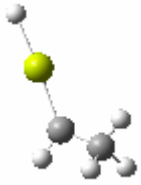
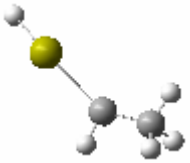
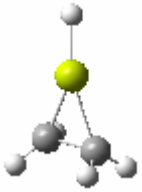
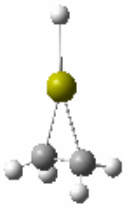
$BeH-CH_3$	$MgH-CH_3$	$CaH-CH_3$
		
$Be-CH_3^-$	$Mg-CH_3^-$	$Ca-CH_3^-$
		
$BeH-CH_2^-$	$MgH-CH_2^-$	$CaH-CH_2^-$
		

Be derivative	Neutral	Deprotonated	
		Be	C
R(Be-C)	1.673	1.724	1.586
R(Be-H_6)	1.331		1.368
τ(H_6-Be-C)	180.00		

Mg derivative	Neutral	Deprotonated	
		Mg	C
R(Mg-H_6)	1.711		1.760
R(Mg-C)	2.099	2.214	1.997
α(H_6-Mg-C)	180.00		

Ca derivative	Neutral	Deprotonated	
		Ca	C
R(Ca-H_6)	2.034		2.152
R(Ca-C)	2.407	2.440	2.305
α(H_6-Ca-C)	135.182		141.23

Ethyl Derivatives

$BeH-CH_2-CH_3$	$MgH-CH_2-CH_3$	$CaH-CH_2-CH_3$
		
$Be-CH_2-CH_3$	$Mg-CH_2-CH_3$	$Ca-CH_2-CH_3$
		
$BeH-CH-CH_3$	$MgH-CH-CH_3$	$CaH-CH-CH_3$
		
$BeH-CH_2-CH_2$	$MgH-CH_2-CH_2$	$CaH-CH_2-CH_2$
		

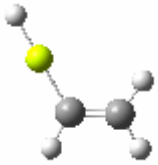
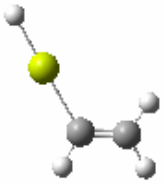
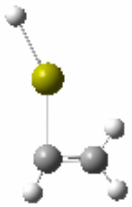
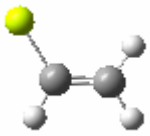
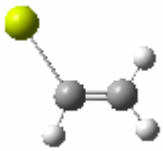
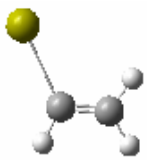
Be derivative	Neutral	Deprotonated		
		Be	C_1	C_4(cyclic)
$R(Be-H_9)$	1.330		1.369	1.387
$R(Be-C_1)$	1.680	1.737	1.588	1.719
$R(Be-C_4)$				1.719
$R(C_1-C_4)$	1.5487	1.542	1.522	1.564
$\alpha_1(H_9-Be-C_1)$	179.603		178.814	152.957

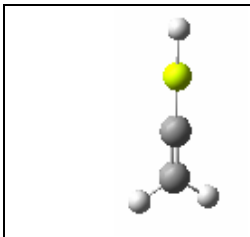
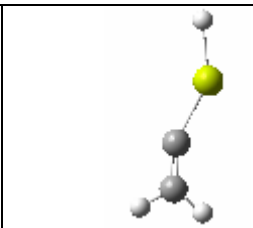
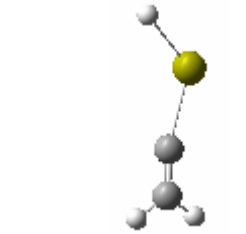
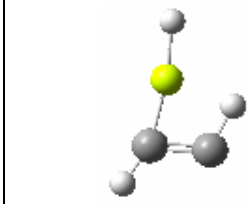
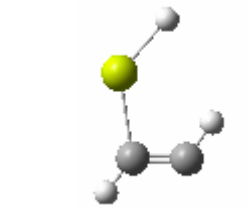
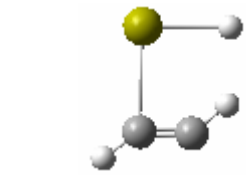
α_2(Be-C_1-C_4)	116.783	117.351	131.798	62.950
α_3(C_1-Be-C_4)				54.122
τ(H_9-Be-C_1-C_4)	180.00		-179.353	179.440

Mg derivative	Neutral	Deprotonated		
		Mg	C_1	C_4(cyclic)
R(Mg-H_9)	1.711		1.759	1.766
R(Mg-C_1)	2.116	2.235	2.005	2.127
R(Mg-C_4)				2.127
R(C_1-C_4)	1.544	1.539	1.521	1.570
α_1(H_9-Mg-C_1)	179.942		176.628	158.324
α_2(Mg-C_1-C_4)	116.777	117.076	133.467	68.345
α_3(C_1-Mg-C_4)				43.303
τ(H_9-Mg-C_1-C_4)	-179.179		-117.300	179.528

Ca derivative	Neutral	Deprotonated		
		Ca	C_1	C_4(cyclic)
R(Ca-H_9)	2.030		2.138	2.196
R(Ca-C_1)	2.415	2.455	2.327	2.371
R(Ca-C_4)				2.371
R(C_1-C_4)	1.545	1.541	1.518	1.579
α_1(H_9-Ca-C_1)	130.053		129.370	160.446
α_2(Ca-C_1-C_4)	110.609	121.357	142.218	70.556
α_3(C_1-Ca-C_4)				38.897
τ(H_9-Ca-C_1-C_4)	0.051		125.004	-177.608

Vinyl Derivatives

BeH-CH=CH_2	MgH-CH=CH_2	CaH-CH=CH_2
		
Be-CH=CH_2	Mg-CH=CH_2	Ca-CH=CH_2
		
BeH-C=CH_2	MgH-C=CH_2	CaH-C=CH_2

		
BeH-CH=CH_Z	MgH-CH=CH_Z	CaH-CH=CH_Z
		
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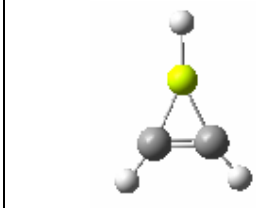
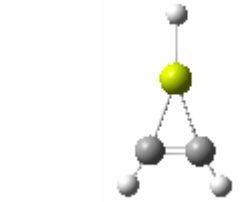
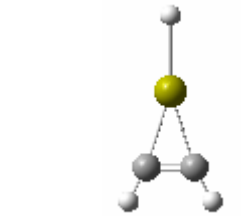
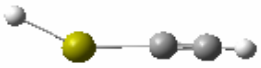
		

Be derivative	Neutral	Deprotonated			
		Be	C_4	$C_{1\_H2\ Cyclic}$	C_{1_H3}
R(Be-H_7)	1.328		1.362	1.385	1.367
R(Be-C_4)	1.667	1.740	1.565	1.664	1.598
R(Be-C_1)				1.664	
R(C_4-C_1)	1.345	1.344	1.327	1.359	1.367
α_1(H_7-Be-C_4)	178.955		179.951	155.912	171.018
α_2(Be-C_4-C_1)	122.805	124.238	179.957	65.906	80.602
α_3(C_4-Be-C_1)				48.188	
τ(H_7-Be-C_4-C_1)	0.00		0.00	180.00	180.00

Mg derivative	Neutral	Deprotonated			
		Mg	C_4	$C_{1\_H2\ Cyclic}$	C_{1_H3}
R(Mg-H_7)	1.703		1.761	1.763	1.772
R(Mg-C_4)	2.088	2.237	2.023	2.066	2.131
R(Mg-C_1)				2.065	
R(C_4-C_1)	1.343	1.346	1.330	1.371	1.312
α_1(H_7-Mg-C_4)	179.095		147.328	160.547	131.398
α_2(Mg-C_4-C_1)	123.702	123.273	155.685	70.590	98.254
α_3(C_4-Mg-C_1)				38.754	
τ(H_7-Mg-C_4-C_1)	0.00		180.00	180.00	0.00

Ca derivative	Neutral	Deprotonated			
		Ca	C_4	$C_{1\_H2\ Cyclic}$	C_{1_H3}
R(Ca-H_7)	2.037		2.156	2.194	2.096
R(Ca-C_4)	2.339	2.456	2.259	2.306	2.609
R(Ca-C_1)				2.306	
R(C_4-C_1)	1.345	1.349	1.333	1.378	1.259
α_1(H_7-Ca-C_4)	153.090		161.931	162.605	90.380
α_2(Ca-C_4-C_1)	90.125	119.577	179.983	72.617	90.913
α_3(C_4-Ca-C_1)				34.776	
τ(H_7-Ca-C_4-C_1)	180.00		180.00	180.00	0.00

Ethynyl derivatives

BeH-C≡CH	MgH-C≡CH	CaH-C≡CH
		
Be-C≡CH	Mg-C≡CH	Ca-C≡CH
		
BeH-C≡C	MgH-C≡C	CaH-C≡C
		

Be derivative	Neutral	Deprotonated	
		Be	C
R(Be-H_5)	1.322		1.352
R(Be-C_3)	1.63220	1.729	1.581
R(C_3-C_1)	1.215	1.221	1.261
α_1(H_5-Be-C_3)	180.00		180.00
α_2(Be-C_3-C_1)	180.00	180.00	180.00
τ(H_5-Be-C_3-C_1)			

Mg derivative	Neutral	Deprotonated	
		Mg	C
$R(Mg\text{-}H_5)$	1.690		1.741
$R(Mg\text{-}C_3)$	2.033	2.237	1.975
$R(C_3\text{-}C_1)$	1.218	1.228	1.261
$\alpha_1(H_5\text{-}Mg\text{-}C_3)$	180.00		180.00
$\alpha_2(Mg\text{-}C_3\text{-}C_1)$	180.00	180.00	180.00
$\tau(H_5\text{-}Mg\text{-}C_3\text{-}C_1)$			

Ca derivative	Neutral	Deprotonated	
		Ca	C(cyclic)
$R(Ca\text{-}H_5)$	2.030		2.154
$R(Ca\text{-}C_3)$	2.352	2.438	2.347
$R(Ca\text{-}C_1)$			2.346
$R(C_3\text{-}C_1)$	1.224	1.229	1.263
$\alpha_1(H_5\text{-}Ca\text{-}C_3)$	150.782		164.393
$\alpha_2(Ca\text{-}C_3\text{-}C_1)$	175.946	180.00	74.362
$\alpha_3(C_3\text{-}Ca\text{-}C_1)$			31.232
$\tau(H_5\text{-}Ca\text{-}C_3\text{-}C_1)$	-179.207		-179.882