Supporting Information available for

CAl_3X (X=B/Al/Ga/In/Tl) with 16 valence electrons: Can planar tetracoordinate carbon be stable?

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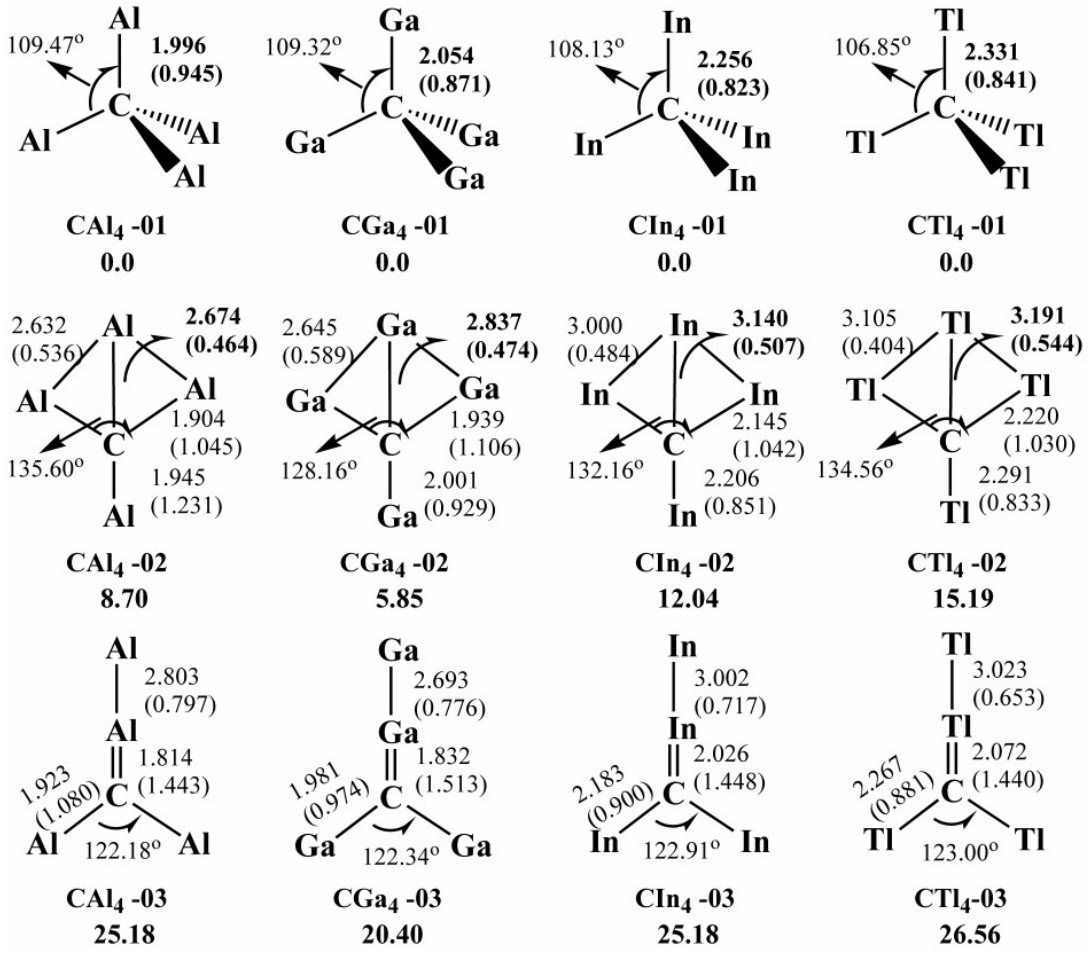
1.



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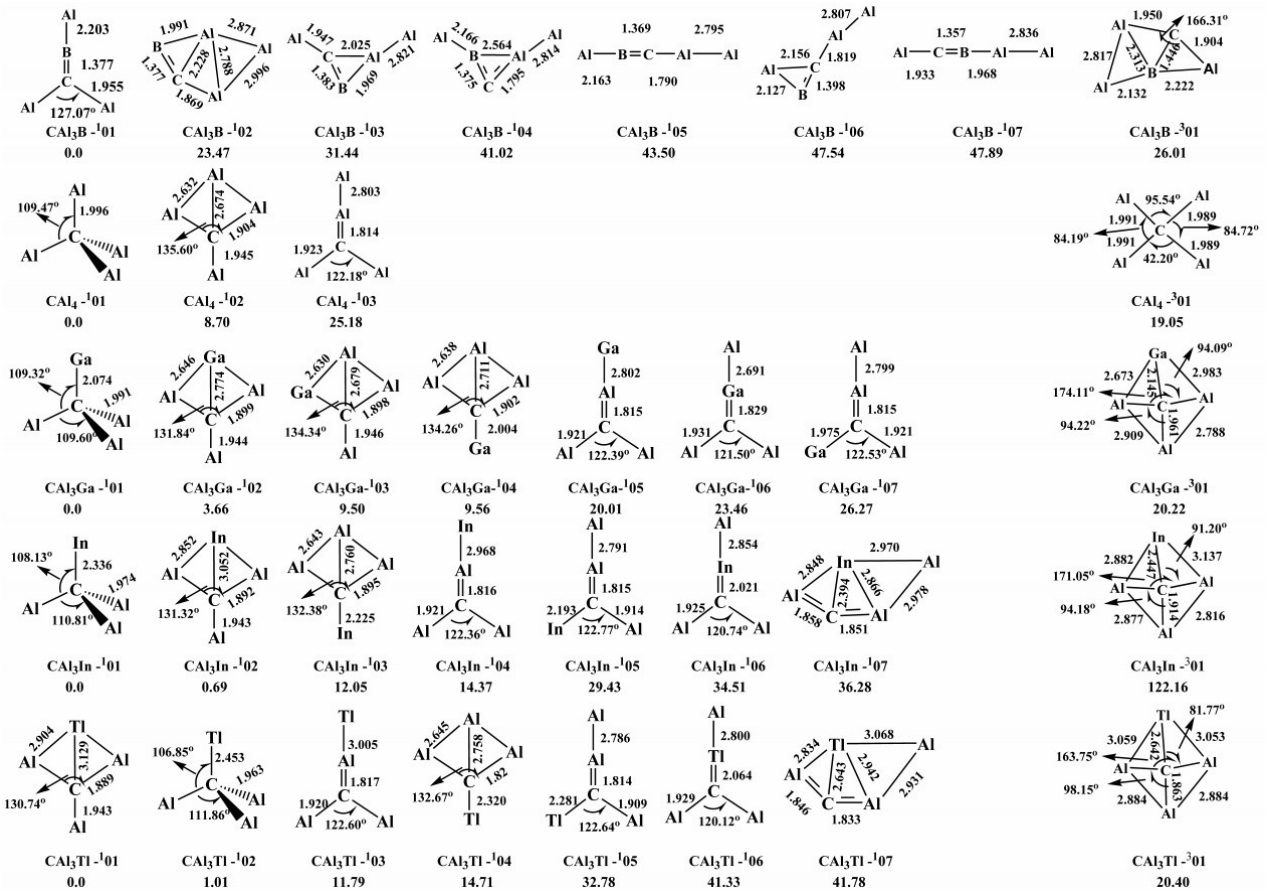

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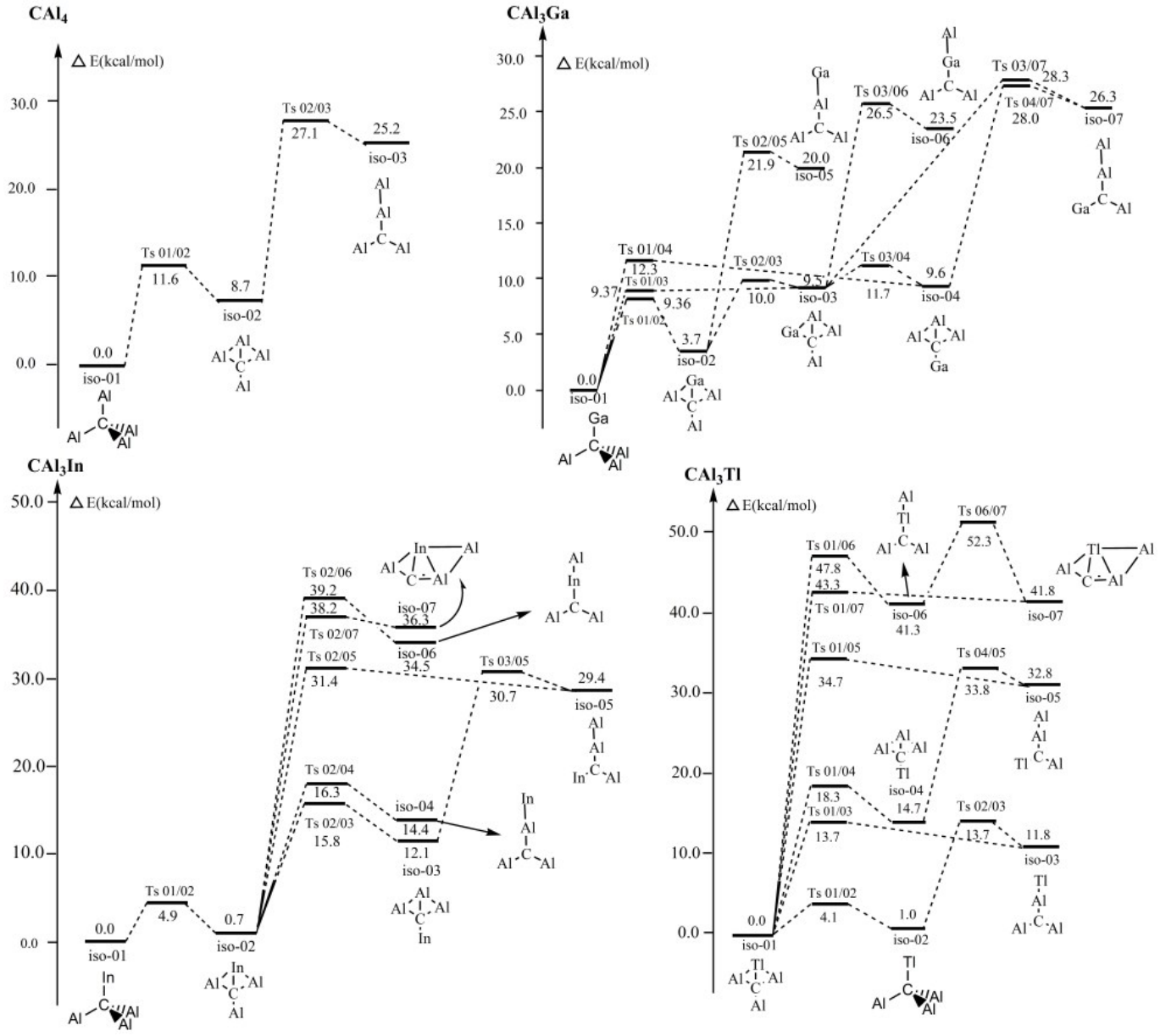

Fig. S3 Schematic pathways for the low-lying isomers of CAl_3X (X=Al/Ga/In/Tl). The energy differences were obtained at the CCSD(T)/def2-QZVP//B3LYP/def2-QZVP+ZPVE level. The energy values are in kcal/mol.

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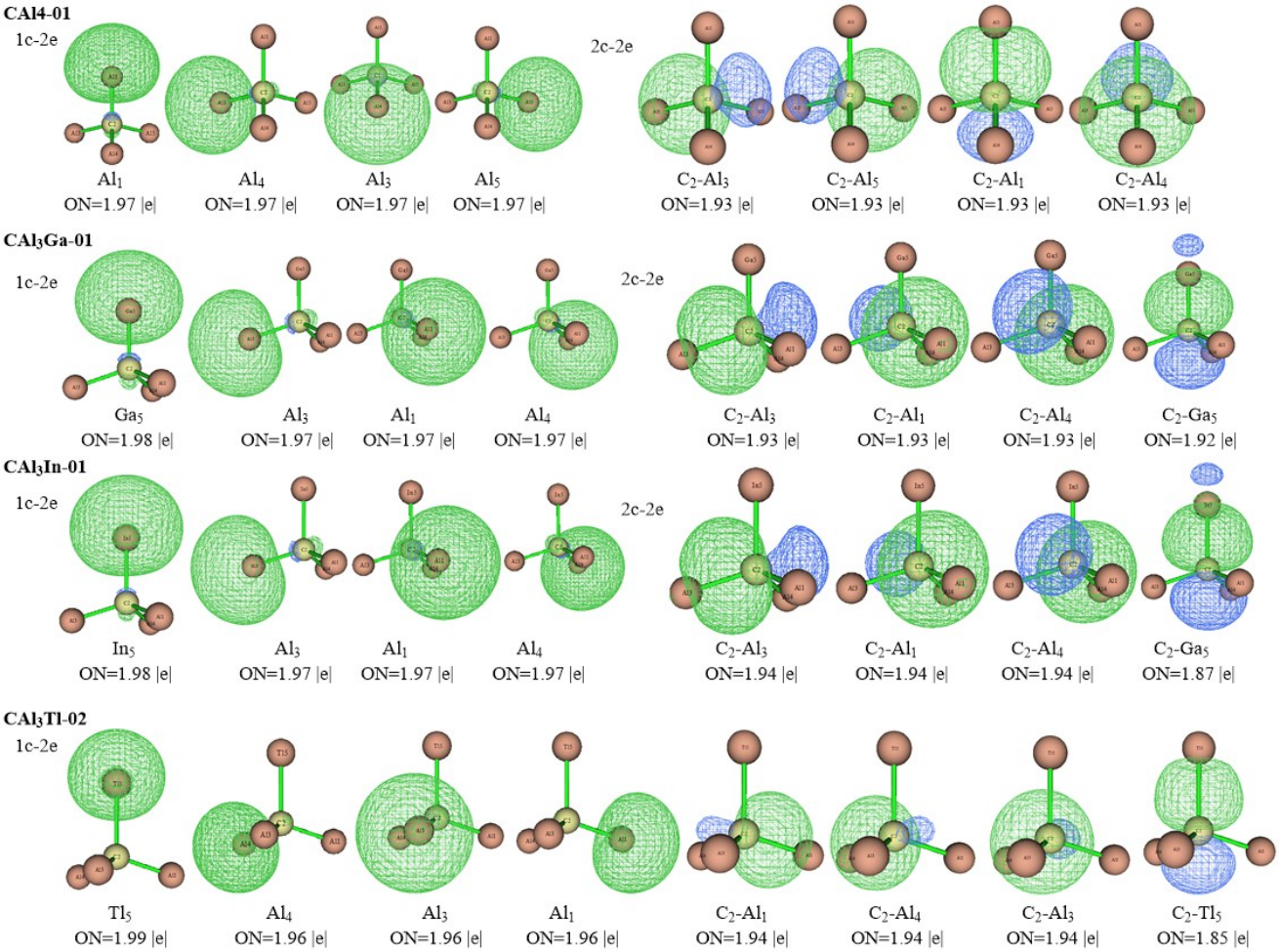

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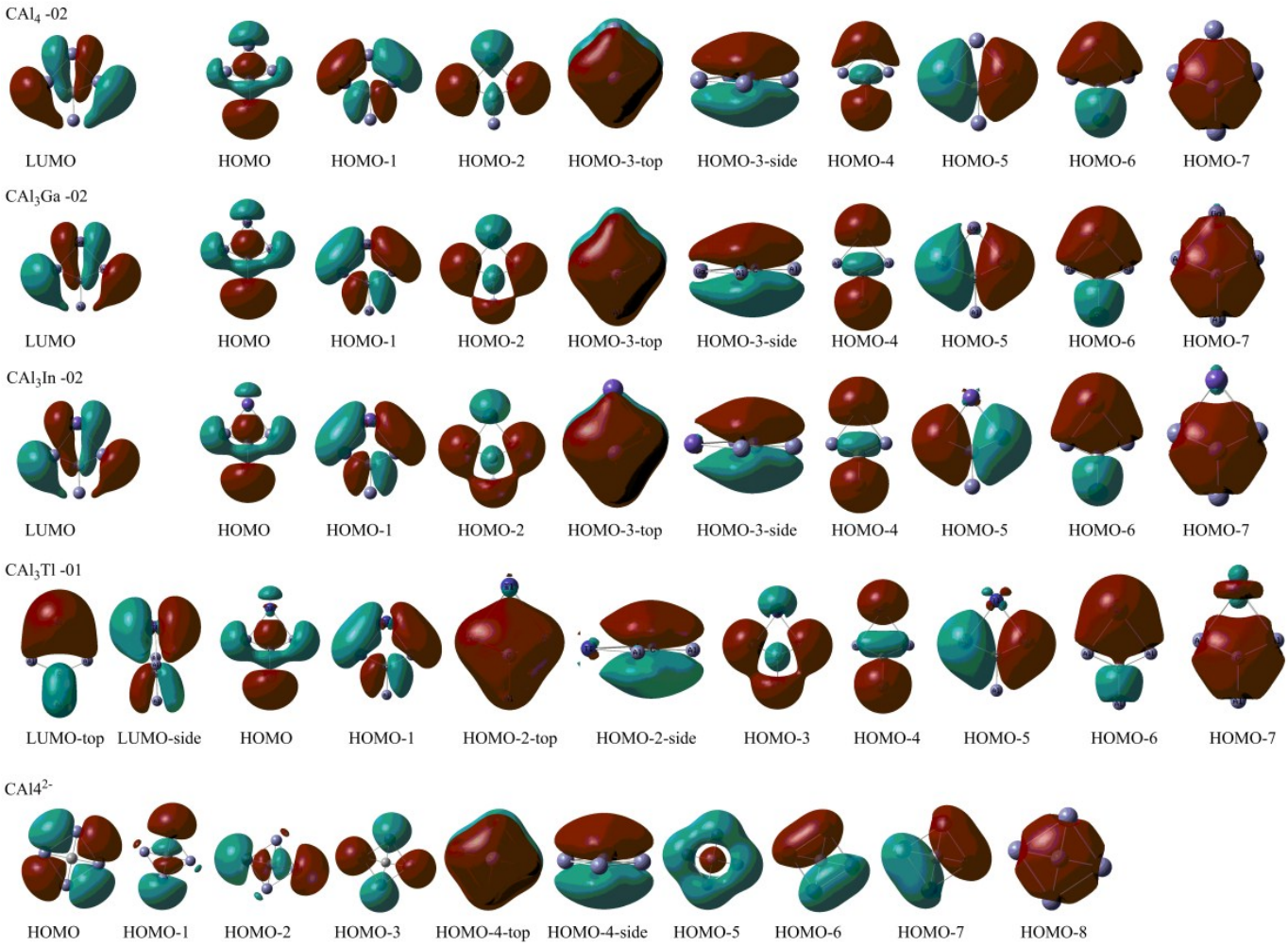
5.



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		CCSD(T)/def2-QZVP//B3LYP-def2-QZVP + ZPVE	CCSD(T)/def2-QZVP//PBE0-def2-QZVP + ZPVE	CBS-QB3/6-311g(2d,d,p)//B3LYP-6-311g(2d,d,p) + ZPVE	CCSD(T)/CBS+ZPVE
CAl_4	Isomer-01	0.0	0.0	0.0	0.0
	Isomer-02	8.70	8.64	9.51	8.61
CAl_3Ga	Isomer-01	0.0	0.0	0.0	0.0
	Isomer-02	3.66	3.55	3.28	3.57
	Isomer-03	9.50	9.54	10.89	9.40
	Isomer-04	9.56	9.55	11.44	9.47
	Isomer-05	20.01	20.12	20.54	19.97
CAl_3In	Isomer-01	0.0	0.0	---	0.0
	Isomer-02	0.69	0.98	---	0.50
	Isomer-03	12.05	11.79	---	12.06
	Isomer-04	14.37	13.49	---	14.38
CAl_3Tl	Isomer-01	0.0	0.0	---	0.0
	Isomer-02	1.01	1.08	---	1.10
	Isomer-03	11.79	12.10	---	11.92
	Isomer-04	14.71	14.90	---	14.76

7. Table S2 The influence of temperature on the free energy barrier ΔG of CAl_3X (X=Al/Ga/In) between ts01/02 and iso-02, and for CAl_3Tl between ts01/02 and iso-01 at the level of B3LYP/def2-QZVP and ZPE.

	Tem (K)	ΔG (kcal/mol)		Tem (K)	ΔG (kcal/mol)
CAl_4	100	3.34	CAl_3Ga	100	6.24
	300	4.00		300	6.73
	500	4.88		500	7.43
	800	6.43		800	8.73
	1000	7.59		1000	9.72
CAl_3In	100	5.22	CAl_3Tl	100	5.27
	300	5.73		300	5.53
	500	6.46		500	6.02
	800	7.81		800	7.01
	1000	8.84		1000	7.80

8. Table S3 Charge analysis of the ptC structures of CAl_3X (X=Al/Ga/In/Tl) at the level of B3LYP/def2-QZVP.

type / charge / system	ptC				ionization potential (IP) / ev
CAl_3X	Mulliken |e|	NPA |e|	Hirshfeld charge |e|	ADCH |e|	
X=Al	0.114	0.358	0.143	0.017	5.967
X=Ga	0.134	0.303	0.168	0.057	5.962
X=In	0.241	0.412	0.220	0.140	5.559
X=Tl	0.252	0.408	0.250	0.180	5.374
NaCl	0.686	0.903	0.575	0.764	4.952
KCl	0.767	0.920	0.623	0.784	4.008

9. Table S4 The infrared vibrational frequency values (cm^{-1}) and the infrared vibrational Intensities (km/mol) in parenthesis of CAl_3X (X=Al/Ga/In/Tl) at the level of B3LYP/def2-QZVP.

system		Infrared vibrational frequency values (Infrared vibrational Intensities)								
		1	2	3	4	5	6	7	8	9
CAl_3B	dbC	54.6(1.5)	91.1(0.2)	113.3(0.8)	214.2(5.8)	215.3(0.3)	316.7(21.8)	493.6(307.4)	723.5(462.7)	1566.5(21.0)
CAl_4	Isomer-01	92.9(0.0)	93.0(0.0)	166.5(10.1)	166.5(10.1)	166.5(10.1)	349.6(0.0)	608.4(238.2)	608.7(238.3)	608.7(238.3)
	Isomer-02	50.7(0.2)	102.1(2.3)	110.4(13.5)	210.1(1.7)	257.1(4.0)	266.7(21.2)	395.1(10.0)	734.1(475.8)	799.4(21.4)
	Isomer-03	35.3(0.5)	45.6(1.8)	115.3(3.9)	144.2(0.6)	162.5(7.4)	226.2(58.4)	416.1(85.7)	769.3(250.4)	932.2(74.3)
CAl_3Ga	Isomer-01	85.5(0.0)	85.7(0.0)	139.6(9.7)	158.4(7.3)	158.6(7.3)	314.5(1.3)	537.6(224.4)	622.1(252.6)	622.7(253.3)
	Isomer-02	45.7(0.1)	107.3(0.5)	108.7(6.2)	208.3(2.8)	212.4(15.3)	219.0(1.5)	393.5(13.3)	750.1(398.7)	813.5(30.6)
	Isomer-03	50.4(0.1)	93.1(2.6)	98.5(9.1)	203.0(1.8)	205.7(6.4)	263.7(9.9)	335.8(3.0)	700.30(351.2)	769.7(175.0)
	Isomer-04	45.1(0.0)	96.3(0.7)	97.8(7.1)	208.0(3.3)	248.5(13.8)	263.6(21.5)	350.50(30.9)	664.1(426.4)	808.9(21.9)
	Isomer-05	32.9(0.7)	43.9(1.9)	102.9(6.5)	143.92(0.8)	162.0(6.8)	184.7(29.0)	415.0(68.7)	773.3(247.0)	929.5(71.4)
	Isomer-06	38.5(0.1)	43.0(0.2)	110.2(2.4)	132.8(1.1)	167.9(5.1)	221.5(75.4)	364.4(43.7)	754.7(263.6)	856.0(157.3)
	Isomer-07	31.4(0.1)	43.4(1.1)	103.6(3.3)	129.4(0.4)	154.8(9.5)	216.4(40.9)	360.7(108.2)	716.4(266.3)	923.3(84.8)
	Isomer-01	75.4(0.1)	75.4(0.1)	124.2(12.0)	151.1(5.3)	151.4(5.3)	288.4(8.8)	475.1(179.5)	654.5(254.1)	655.5(254.4)
	Isomer-02	35.9(0.0)	91.2(6.3)	110.6(0.0)	183.2(14.3)	203.3(2.5)	203.4(2.5)	392.8(16.1)	749.0(370.1)	836.2(48.3)

	Isomer-03	39.6(0.1)	85.6(0.3)	93.2(4.1)	203.6(4.5)	242.8(31.4)	260.1(23.3)	321.3(42.8)	630.9(391.5)	824.1(19.4)
	Isomer-04	31.2(0.6)	42.1(1.7)	92.(9.2)	143.1(1.0)	161.9(5.9)	166.1(19.7)	412.5(64.9)	774.2(257.7)	927.8(104.1)
	Isomer-05	28.8(0.1)	41.5(0.8)	94.8(2.9)	120.5(0.9)	143.0(10.3)	209.7(29.3)	329.1(128.7)	692.1(268.2)	924.0(79.6)
	Isomer-06	37.0(0.0)	39.4(0.1)	106.4(1.4)	122.2(1.2)	159.8(4.7)	201.1(71.6)	337.1(16.5)	761.1(205.9)	769.6(146.5)
	Isomer-07	33.8(0.0)	73.6(23.4)	115.9(12.1)	147.5(1.6)	147.7(9.7)	214.7(25.4)	235.1(13.1)	472.5(8.0)	1010.7(22.7)
CAl_3Tl	Isomer-01	33.4(0.0)	85.2(5.0)	108.9(0.5)	171.4(11.3)	191.5(3.4)	201.1(2.7)	393.2(16.4)	753.2(333.4)	846.8(64.8)
	Isomer-02	64.5(0.1)	64.7(0.1)	109.8(11.2)	147.2(4.2)	147.2(4.2)	270.9(13.7)	448.4(141.0)	677.5(269.1)	678.3(269.7)
	Isomer-03	31.1(0.5)	42.5(1.3)	84.0(9.0)	143.3(1.4)	158.9(13.0)	162.1(5.1)	412.3(59.3)	777.1(262.2)	925.6(116.5)
	Isomer-04	39.4(0.2)	81.0(0.2)	86.8(2.5)	202.3(5.8)	234.1(50.9)	258.1(23.8)	303.4(44.8)	607.8(370.7)	835.0(19.4)
	Isomer-05	28.5(0.0)	41.2(0.7)	89.6(3.0)	112.0(1.2)	142.7(11.5)	202.7(20.3)	308.6(145.5)	675.8(276.7)	928.3(81.0)
	Isomer-06	41.9(0.0)	42.7(0.0)	102.7(1.1)	122.2(1.3)	166.5(4.2)	198.6(76.7)	319.1(8.4)	732.9(191.6)	752.9(206.8)
	Isomer-07	32.6(0.1)	68.6(1.1)	133.0(15.9)	137.6(10.9)	140.4(15.0)	181.6(16.9)	215.5(38.8)	510.9(10.9)	1039.8(32.7)

10. Table S5 The Adiabatic electron affinity (AEA) and vertical electron affinity (VEA) values of CAl_3X (X=Al/Ga/In/Tl) are calculated at the level of CCSD(T)/def2-QZVP//B3LYP/def2-QZVP + ZPVE. The values are in eV.

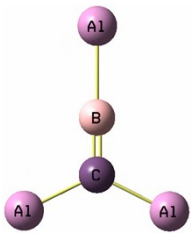
		AEA	VEA				AEA	VEA
CAl_3B	dbC	**1.50**	**1.10**			Isomer-01	**1.41**	**1.14**
						Isomer-02	**0.97**	**1.20**
	Isomer-01	**1.45**	**1.14**		CAl_3In	Isomer-03	1.47	1.31
CAl4	Isomer-02	**2.41**	**1.54**			Isomer-04	1.71	1.73
	Isomer-03	1.91	1.84			Isomer-05	1.76	1.67
						Isomer-06	1.85	1.91
	Isomer-01	**1.41**	**1.09**					
	Isomer-02	**1.30**	**1.13**			Isomer-01	**0.68**	**1.11**
	Isomer-03	2.38	1.43			Isomer-02	**1.79**	**1.12**
CAl_3Ga	Isomer-04	2.38	1.54		CAl_3Tl	Isomer-03	1.71	1.63
	Isomer-05	1.88	1.80			Isomer-04	1.33	1.23
	Isomer-06	1.83	1.76			Isomer-05	1.58	1.59
	Isomer-07	1.88	1.79			Isomer-06	1.81	1.87

11. Table S6 At the level of CCSD(T)/def2-QZVP//B3LYP/def2-QZVP, T1 diagnostic of the global structures in CAl_3X(X=B/Al/Ga/In/Tl).

		T1 Diagnostic			T1 Diagnostic			T1 Diagnostic			T1 Diagnostic
CAl3B	dbC	0.024		Isomer-01	0.021		Isomer-01	0.019		Isomer-01	0.025
				Isomer-02	0.030		Isomer-02	0.025		Isomer-02	0.019
CAl_4	Isomer-01	0.022	CAl_3Ga	Isomer-03	0.030	CAl_3In	Isomer-03	0.028	CAl_3Tl	Isomer-03	0.021
	Isomer-02	0.037		Isomer-04	0.031		Isomer-04	0.022		Isomer-04	0.028
	Isomer-03	0.029		Isomer-05	0.025		Isomer-05	0.024		Isomer-05	0.023
				Isomer-06	0.028		Isomer-06	0.028		Isomer-06	0.030
				Isomer-07	0.026		Isomer-07	0.030		Isomer-07	0.034

12.

Table S7 Cartesian coordinates of the singlet CAl_3X (X=Al/Ga/In/Tl) within 50 kcal/mol and the transition state structures at B3LYP/def2-QZVP level.

CAl_3B-^{1}01	
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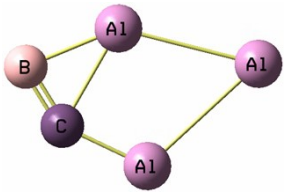
CAl_3B-^{1}02	
6 -1.821832 0.039849 0.000000 13 -0.624256 -1.395179 0.000000 5 -1.989231 1.406222 0.000000 13 2.230190 -0.485701 0.000000 13 0.000000 1.321633 0.000000	
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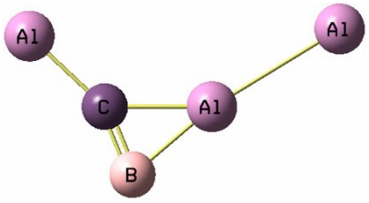
13 -1.326399 -2.556294 0.000000 6 -1.357177 -0.609392 0.000000 5 -1.952932 0.639107 0.000000 13 0.000000 0.893731 0.000000 13 2.703916 1.698010 0.000000	
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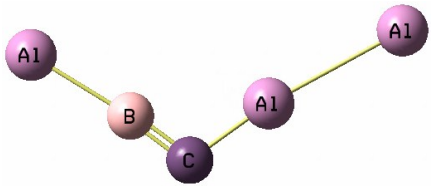
13 -1.050004 -3.337010 0.000000 5 -1.293467 -1.184527 0.000000 6 -1.571932 0.162094 0.000000 13 0.000000 1.029373 0.000000 13 2.272998 2.688412 0.000000	
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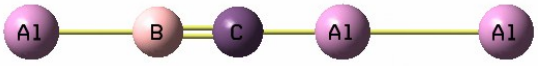
13 3.982695 -0.000852 0.000002 13 1.187655 0.001014 -0.000007 6 -0.602344 0.000741 -0.000008 5 -1.971553 0.000377 0.000042 13 -4.134056 -0.000649 -0.000007	
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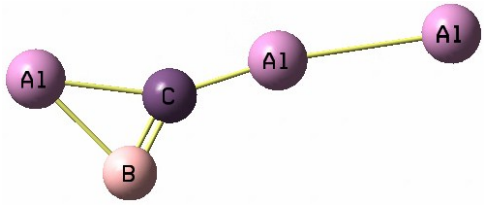
5 1.065327 -2.024145 0.000000 6 0.054036 -1.058290 0.000000 13 -0.806036 -3.035334 0.000000 13 0.000000 0.759760 0.000000 13 0.371355 3.542533 0.000000	
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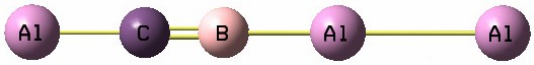
13 -0.002664 -4.061628 0.000000 13 -0.001206 -1.225418 0.000000 5 0.000000 0.742115 0.000000	

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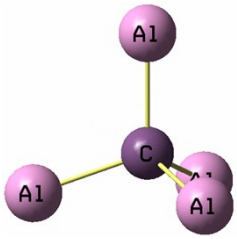
CAl_4-[1]01	
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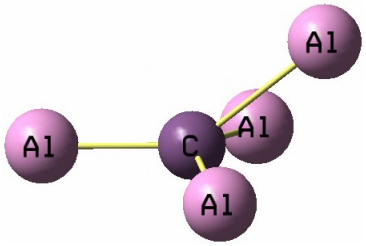
Ts 01/02	
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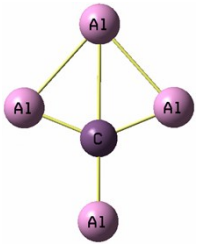
CAl_4-[1]02	
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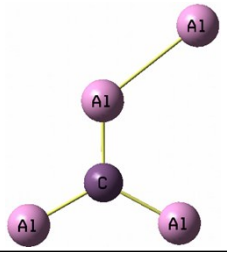
Ts 02/03	
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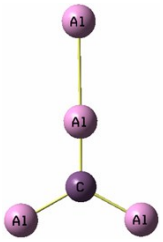
CAl_4-[1]03	
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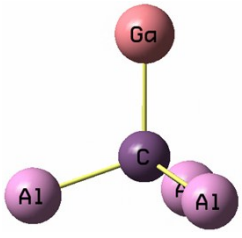
CAl_3Ga-[1]01	
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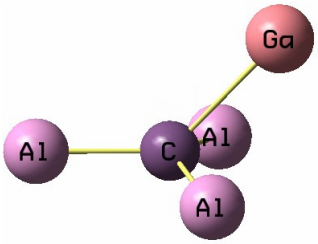
Ts 01/02	
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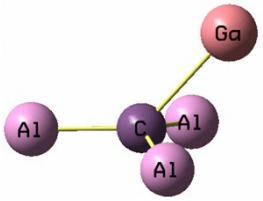
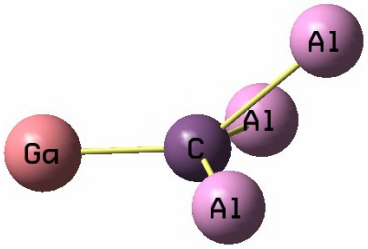
6 0.777922 0.000125 0.197640 31 -1.499662 -0.000191 -0.374273 13 0.394981 -1.784570 0.824914 13 2.427994 0.000337 -0.848579 13 0.394102 1.784631 0.824945	
Ts 01/04	
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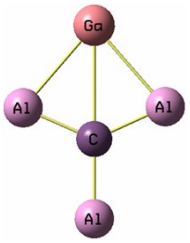
CAl_3Ga-[1]02	
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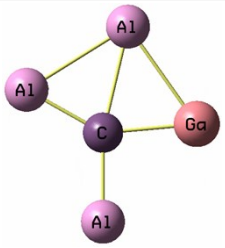
Ts 02/03	
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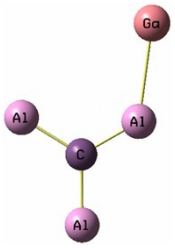
Ts 02/05	
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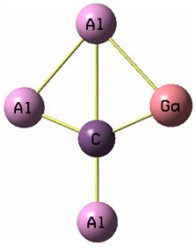
CAl_3Ga-[1]03	
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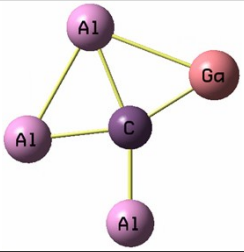
Ts 03/04	
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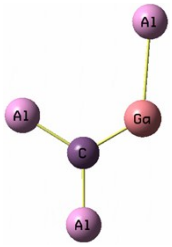
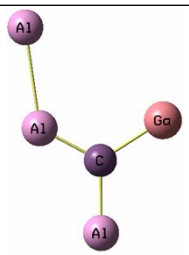
6 0.742953 -0.765611 0.000000 13 -0.440173 -2.285206 0.000000 13 -2.569802 1.399917 0.000000 13 2.667074 -0.963370 0.000000 31 0.000000 0.923427 0.000000	
Ts 03/07	
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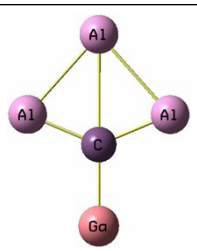
CAl_3Ga-[1]04	
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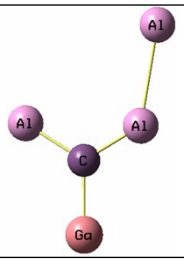
Ts 04/07	
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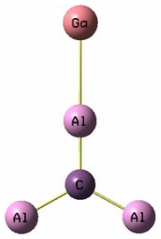
CAl_3Ga-[1]05	
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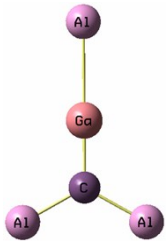
CAl_3Ga-[1]06	
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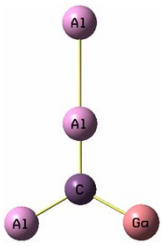
CAl_3Ga-[1]07	
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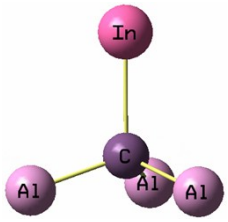
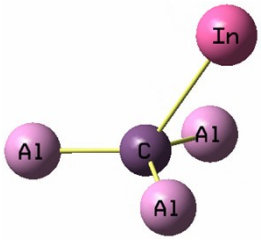
13 -1.576507 -0.938958 1.624581 6 -0.962829 -0.000402 0.000000 13 -1.576507 1.875644 0.000000 13 -1.576507 -0.938958 -1.624581 49 1.372669 0.000652 0.000000	
Ts 01/02	
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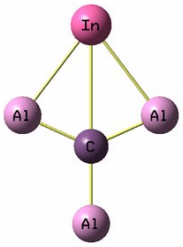
CAl_3In-^{1}02	
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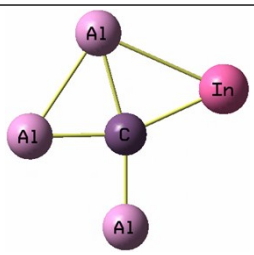
Ts 02/03	
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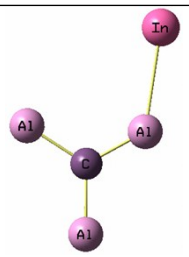
Ts 02/04	
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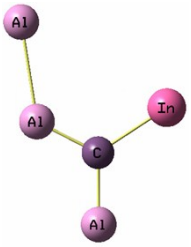
Ts 02/05	
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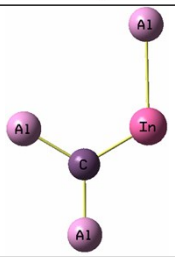
Ts 02/06	
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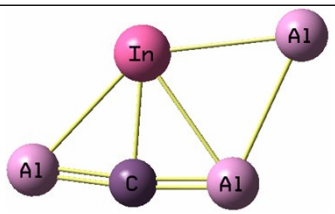
13 -2.802736 0.098095 -0.000520 6 1.133015 1.266365 0.000737 13 2.730295 0.301913 -0.000648 13 -0.556785 2.023702 0.000169 49 0.028201 -0.798090 0.000175	
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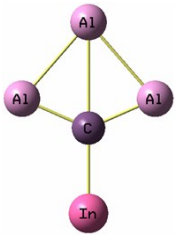
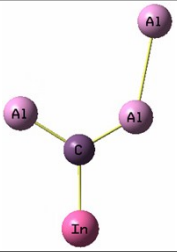
6 0.000000 0.566721 0.000000 13 1.734000 1.331077 0.000000 49 -0.000377 -1.658702 0.000000 13 0.000776 3.327105 0.000000 13 -1.733354 1.332287 0.000000	
Ts 03/05	
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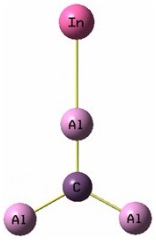
CAl_3In-^{1}04	
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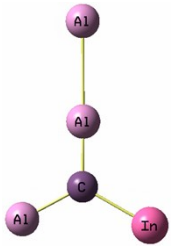
CAl_3In-^{1}05	
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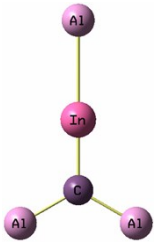
CAl_3In-^{1}06	
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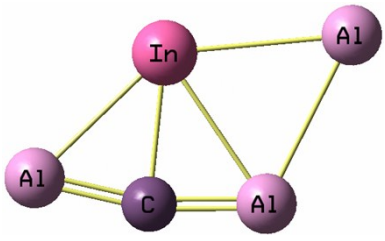
CAl_3In-^{1}07	
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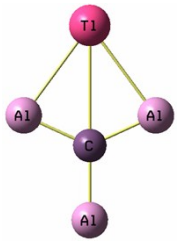
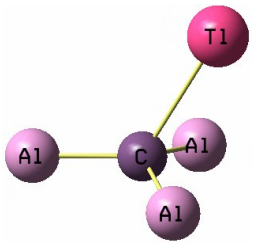
6 0.000094 -1.973476 0.000000 13 -0.000208 -3.916050 0.000000 13 1.717296 -1.186185 0.000000 13 -1.717131 -1.186224 0.000000 81 0.000000 1.155442 0.000000	
Ts 01/02	
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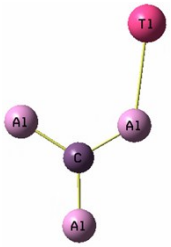
Ts 01/03	
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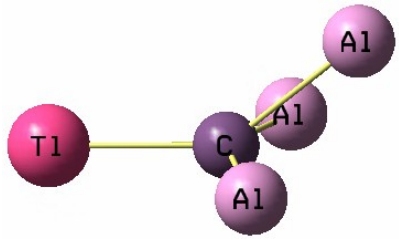
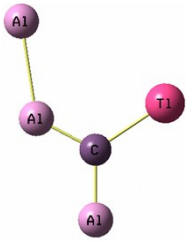
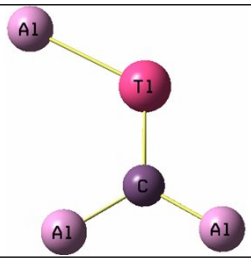
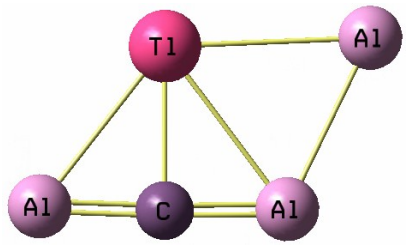
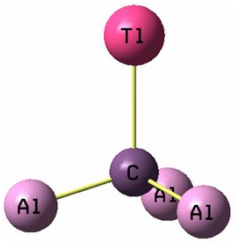
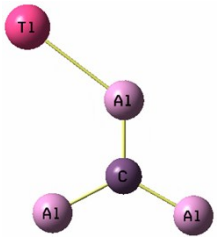
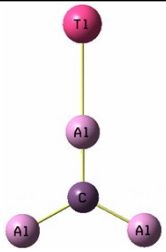
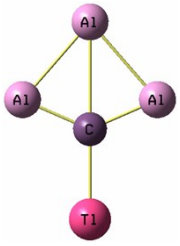
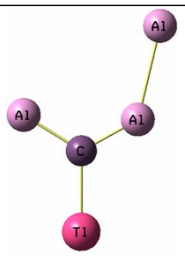
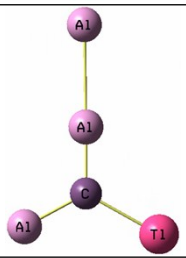
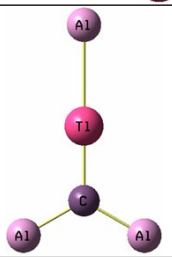
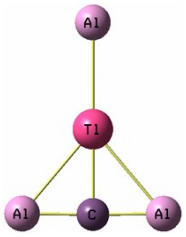
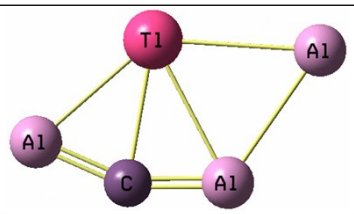
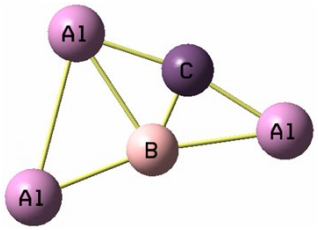
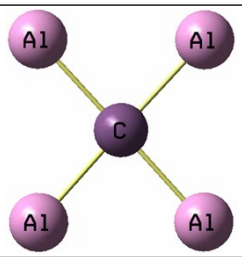
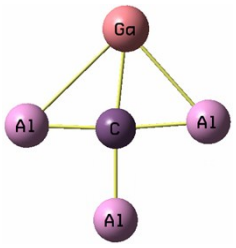
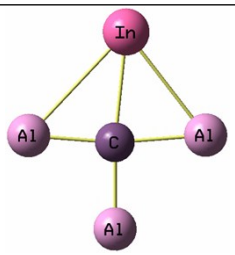
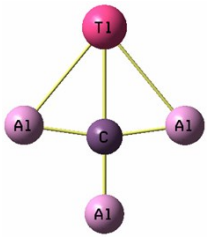
Ts 01/04	
13 -1.729889 -1.815781 0.550530 6 -1.170374 -0.000177 0.303847 13 -3.201454 0.000439 -0.803868 13 -1.728261 1.816208 0.550579 81 1.155520 -0.000126 -0.070213	
Ts 01/05	
13 -0.076807 3.088173 -0.000006 6 0.496059 1.264175 -0.000003 13 3.465684 -1.480373 -0.000004 13 2.288436 0.927316 -0.000011 81 -0.947919 -0.500513 0.000003	
Ts 01/06	
13 -3.055731 -0.712932 -0.000031 6 -1.477240 0.397382 -0.000046 13 -1.627204 2.309886 -0.000129 13 2.629134 1.202110 -0.000012 81 0.439047 -0.478668 0.000031	
Ts 01/07	
6 -1.021939 1.581993 -0.000105 13 2.834400 0.405481 0.000193 13 0.679482 2.276390 -0.000129 13 -2.723354 0.795046 0.000191 81 -0.051176 -0.675208 -0.000033	
CAl_3Tl-^{1}02	

13 1.966822 1.813200 -0.497505 6 1.400552 0.000700 -0.000664 13 1.974727 -0.475221 1.815126 13 1.969399 -1.335857 -1.320997 81 -1.052415 -0.000392 0.000591	
Ts 02/03	
6 2.741332 0.014018 -0.000139 13 4.454099 -0.864432 0.000575 13 1.215353 -0.985389 -0.000875 13 2.562497 1.918360 -0.000187 81 -1.524239 -0.012039 0.000089	
CAl_3Tl-[1]03	
13 1.698542 4.010659 0.000000 6 0.010043 3.097555 0.000000 13 -1.668947 4.028168 0.000000 13 0.000000 1.280112 0.000000 81 -0.005494 -1.725081 0.000000	
CAl_3Tl-[1]04	
6 0.000000 1.050327 0.000000 13 1.733088 1.809141 0.000000 81 -0.000234 -1.269929 0.000000 13 0.000936 3.808455 0.000000 13 -1.732566 1.810275 0.000000	
Ts 04/05	
6 0.807493 0.476145 -0.000097 13 1.308327 2.315785 -0.000375 13 4.824598 -0.635473 -0.000594 13 2.111376 -0.792451 -0.000108 81 -1.382974 -0.177766 0.000180	
CAl_3Tl-[1]05	
13 -4.763070 -1.055537 -0.003026 13 -2.242941 0.132457 0.005609 81 1.256048 -0.376121 -0.000243 13 -0.536966 2.837325 -0.001953 6 -0.613532 0.930104 0.001911	
CAl_3Tl-[1]06	
13 -1.671512 -2.592629 0.000000 6 0.000248 -1.629751 0.000000 13 1.672012 -2.592592 0.000000 81 0.000000 0.433915 0.000000 13 -0.000615 3.233790 0.000000	
Ts 06/07	

6 2.000742 0.000073 -0.000001 13 -3.137262 0.000042 -0.000004 13 1.978168 -1.892705 -0.000003 13 1.978014 1.892853 -0.000003 81 -0.279635 -0.000036 0.000002	
CAl_3Tl-^{1}07	
13 2.816411 -0.574678 0.000000 13 0.425726 -2.269603 0.000000 81 0.000000 0.641311 0.000000 6 -1.302723 -1.658367 0.000000 13 -2.640880 -0.386181 0.000000	

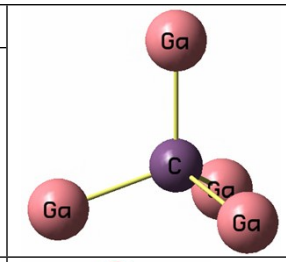
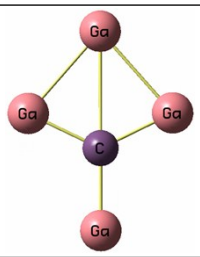
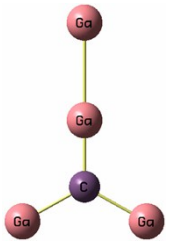
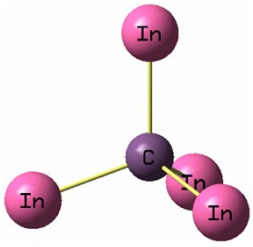
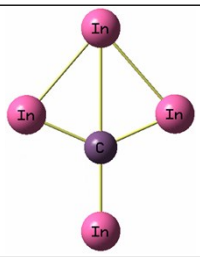
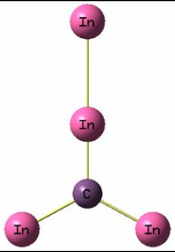
13.

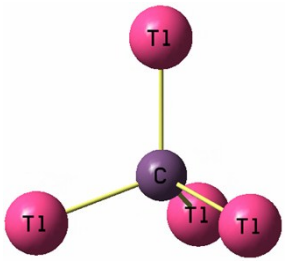
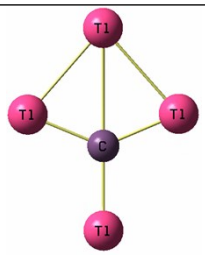
Table S8 Cartesian coordinates of the global minimum structures of the triplet CAl_3X (X=Al/Ga/In/Tl) at the B3LYP/def2-QZVP level of theory.

CAl_3B-^{3}01	
13 -2.131899 0.618265 0.000000 13 -0.505593 -1.682207 0.000000 5 0.000000 0.574678 0.000000 6 1.012740 -0.457899 0.000000 13 2.170074 1.054250 0.000000	
CAl_4-^{3}01	
6 0.000000 0.011165 0.000000 13 -0.746010 1.852608 0.000000 13 1.773880 0.908475 0.000000 13 0.734896 -1.843104 0.000000 13 -1.762766 -0.923132 0.000000	
CAl_3Ga-^{3}01	
13 1.947224 0.082297 0.000000 6 0.000000 0.578774 0.000000 13 0.343450 2.509285 0.000000 13 -1.905088 0.860692 0.000000 31 -0.161698 -1.559749 0.000000	
CAl_3In-^{3}01	
13 1.968439 0.631919 0.000000 6 0.000000 1.056391 0.000000 13 0.265900 2.951599 0.000000 13 -1.910069 1.163818 0.000000 49 -0.086031 -1.388851 0.000000	
CAl_3Tl-^{3}01	
6 0.001197 -1.563184 0.000000 81 0.000000 1.078886 0.000000 13 1.934975 -1.289796 0.000000 13 -1.933448 -1.284372 0.000000 13 -0.002080 -3.426650 0.000000	

14.

Table S9 Cartesian coordinates of low-lying isomers of CX_4 (X=Al/Ga/In/Tl) within 50 kcal/mol at the level of B3LYP/def2-QZVP. X=Al have been given in the Table S7.

CGa_4-^{1}01	
31 0.000000 1.676371 1.186200 6 0.000000 0.000000 0.000041 31 -1.676318 0.000000 -1.186204 31 0.000000 -1.676371 1.186200 31 1.676318 0.000000 -1.186204	
CGa_4 -^{1}02	
6 0.000000 0.603466 0.000000 31 1.744094 -0.244232 0.000000 31 -0.000021 2.604828 0.000000 31 -0.000013 -2.233132 0.000000 31 -1.744060 -0.244264 0.000000	
CGa_4 -^{1}03	
31 -1.735485 -2.015220 0.000000 6 0.000684 -1.060465 0.000000 31 1.735888 -2.016644 0.000000 31 0.000000 0.772011 0.000000 31 -0.000535 3.465103 0.000000	
CIn_4-^{1}01	
49 0.000000 1.841895 -1.302088 6 0.000000 0.000000 0.000369 49 1.842248 0.000000 1.302065 49 0.000000 -1.841895 -1.302088 49 -1.842248 0.000000 1.302065	
CIn_4-^{1}02	
6 0.000000 0.648431 0.000000 49 1.960983 -0.221414 0.000000 49 -0.000094 2.854731 0.000000 49 0.000062 -2.491222 0.000000 49 -1.960951 -0.221495 0.000000	
CIn_4-^{1}03	
49 -0.000289 3.822759 0.000000 49 0.000000 0.821139 0.000000 49 1.917601 -2.248193 0.000000 6 0.000160 -1.205067 0.000000 49 -1.917331 -2.248145 0.000000	
CTl_4-^{1}01	

81 0.000000 1.904036 1.345179 6 0.000000 0.000000 0.000016 81 -1.904006 0.000000 -1.345180 81 0.000000 -1.904036 1.345179 81 1.904006 0.000000 -1.345180	
CTl_4-^{1}02 81 -0.002195 2.932593 0.000000 6 0.000000 0.642045 0.000000 81 2.048337 -0.214391 0.000000 81 -2.047593 -0.216407 0.000000 81 0.001450 -2.549353 0.000000	
CTl_4-^{1}03 6 0.001564 -1.228230 0.000000 81 0.000000 0.843995 0.000000 81 -1.991083 -2.309480 0.000000 81 -0.002464 3.866787 0.000000 81 1.993431 -2.310322 0.000000