Supporting Information available for

A sixteen-valence-electron carbon-group_13 family with global penta-atomic planar tetracoordinate carbon: ionic strategy

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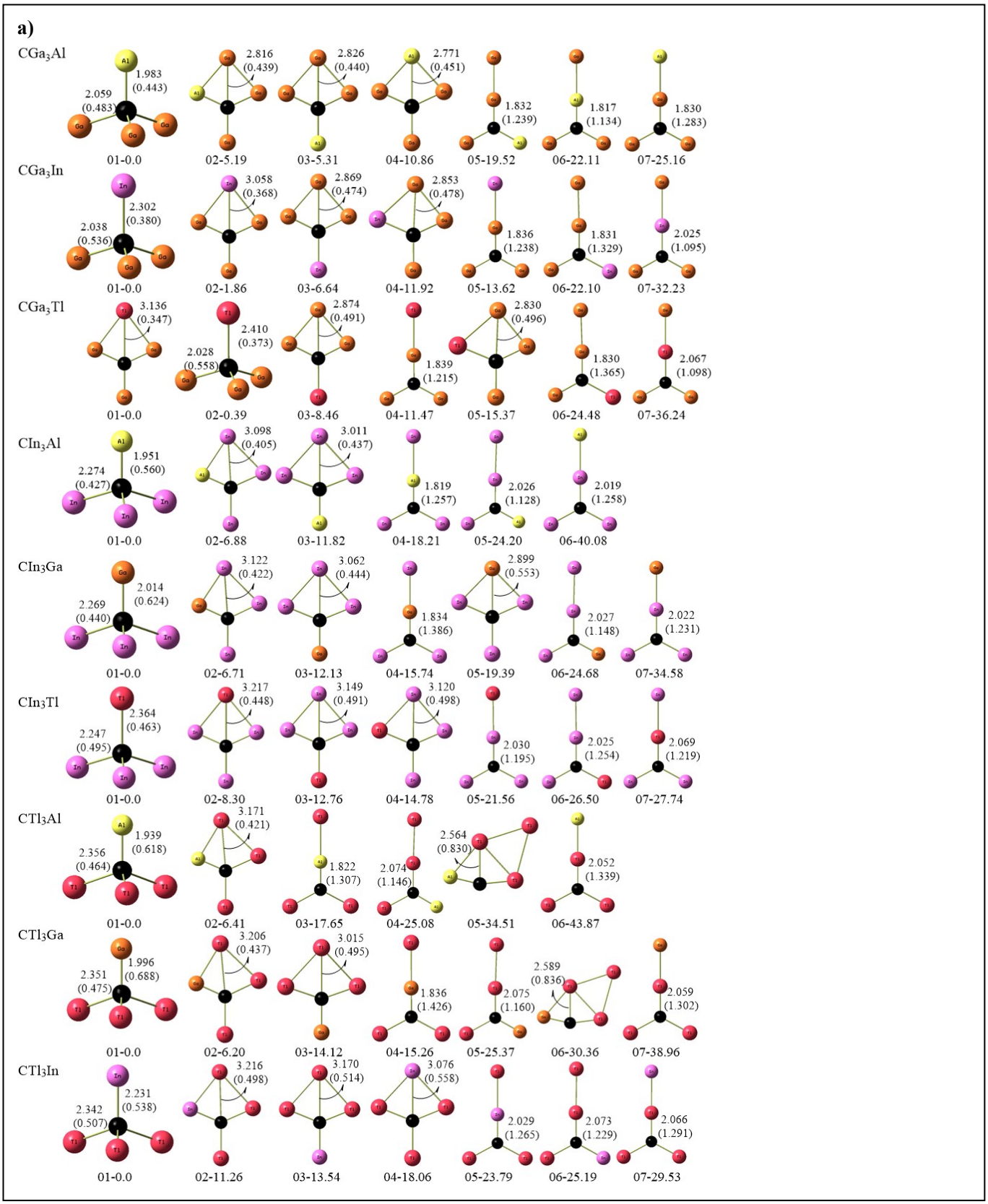
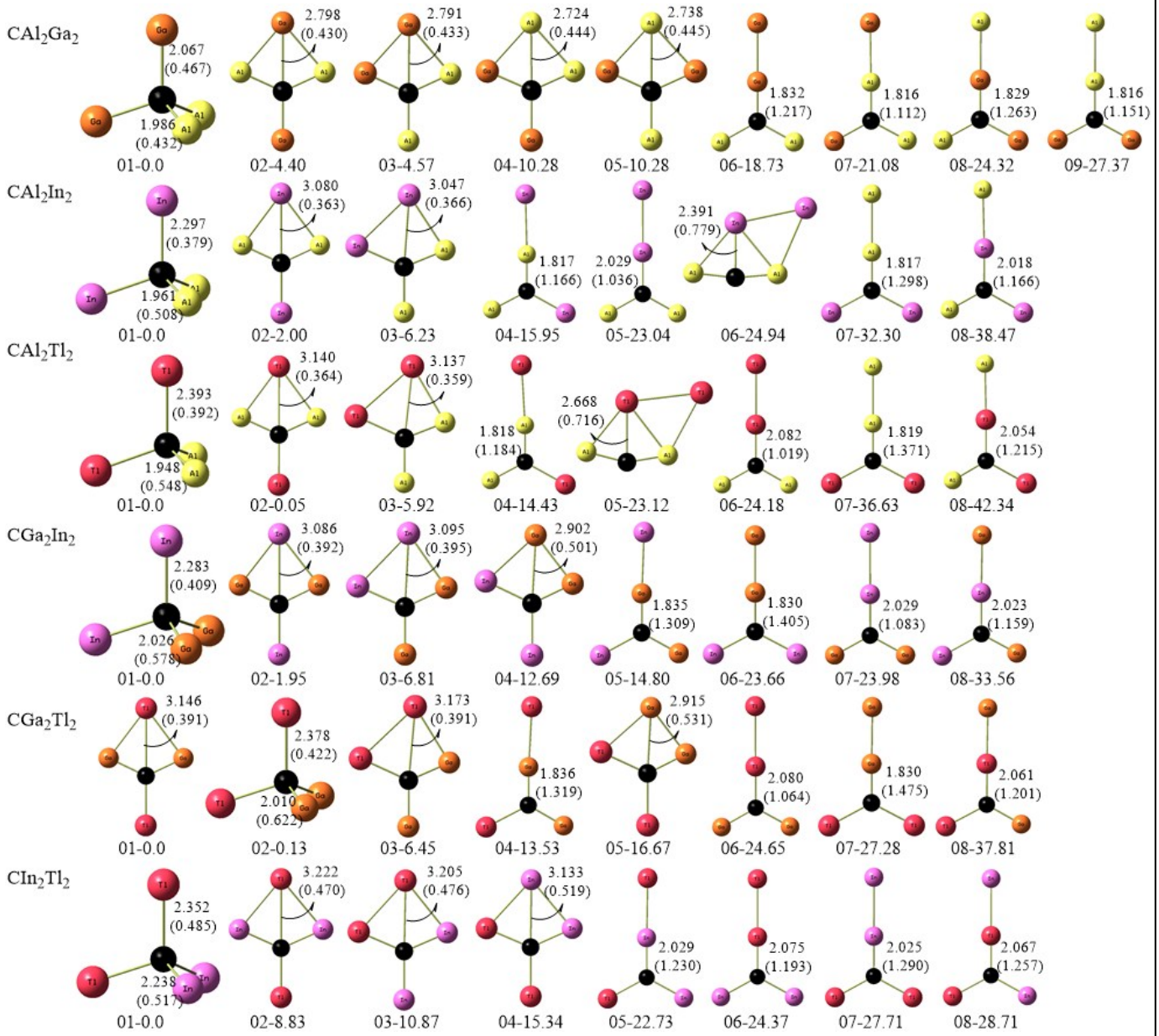
1. Table S1 Relative energies of the first three low-lying isomers of the 8 global minimum and one isoenergetic ptC structures computed via three methods. All the energies were corrected by zero-point energies (in kcal/mol).

		CCSD(T)/def2-QZVP//B3LYP-def2-QZVP + ZPVE	CCSD(T)/def2-QZVP//PBE0-def2-QZVP + ZPVE	CCSD(T)/CBS+ZPVE
CGa_3Tl	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.39	0.39	0.47
	Isomer-03	8.46	8.53	8.55
CGa_2Tl_2	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.13	0.004	0.16
	Isomer-03	6.45	6.24	6.37
CAl_2Tl_2	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.05	0.28	-0.004
	Isomer-03	5.92	5.72	5.79
CAl_2GaTl	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.19	0.05	0.20
	Isomer-03	0.91	0.81	1.01
CAl_2InTl	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.79	0.63	0.86
	Isomer-03	3.98	4.00	3.96
$CAlGa_2Tl$	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.16	0.05	0.18
	Isomer-03	0.62	0.58	0.72
$CAlGaTl_2$	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.02	-0.16	0.06
	Isomer-03	6.06	5.77	5.98
CGa_2InTl	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.83	0.75	0.90
	Isomer-03	3.67	3.72	3.64
CAlGaInTl	Isomer-01	0.0	0.0	0.0
	Isomer-02	0.78	0.67	0.85
	Isomer-03	3.82	3.88	3.79

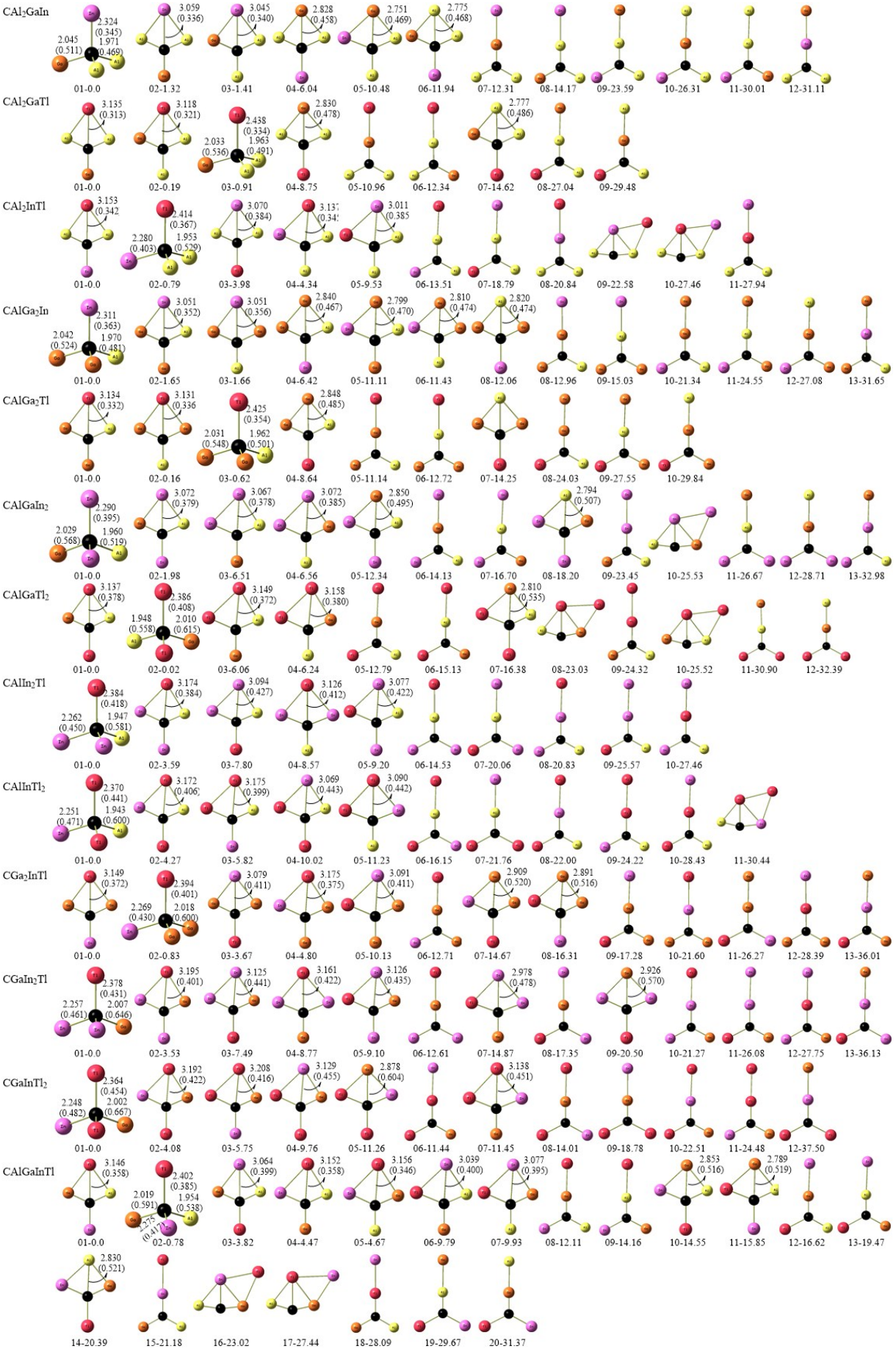
2. Fig. S1 Key geometrical parameters of low-lying isomers (around 30 kcal/mol) of the singlet **a)** ternary CX_3Y, **b)** ternary CX_2Y_2, **c)** quaternary CX_2YZ and quinary CXYZK (X, Y, Z, K=Al/Ga/In/Tl) at the level of CCSD(T)/def2-QZVP//B3LYP/def2-QZVP + ZPVE. The Wiberg bond indexes are in parentheses, and bond lengths are in Å, and the relative energy values are in kcal/mol.



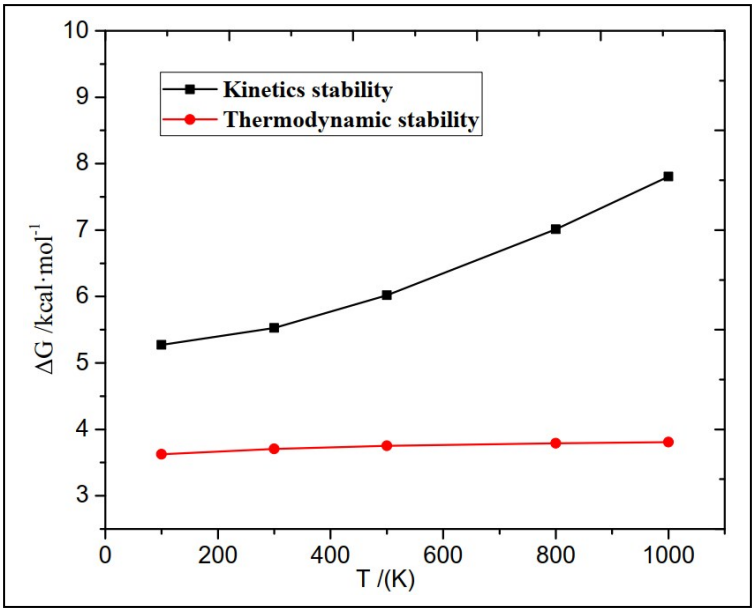
b)


CAl2Ga2
2.067 (0.467)
1.986 (0.432)
01-0.0
2.798 (0.430)
02-4.40
2.791 (0.433)
03-4.57
2.724 (0.444)
04-10.28
2.738 (0.445)
05-10.28
1.832 (1.217)
06-18.73
1.816 (1.112)
07-21.08
1.829 (1.263)
08-24.32
1.816 (1.151)
09-27.37
CAl2In2
2.297 (0.379)
1.961 (0.508)
01-0.0
3.080 (0.363)
02-2.00
3.047 (0.366)
03-6.23
1.817 (1.166)
04-15.95
2.029 (1.036)
05-23.04
2.391 (0.779)
06-24.94
1.817 (1.298)
07-32.30
2.018 (1.166)
08-38.47
CAl2Tl2
2.393 (0.392)
1.948 (0.548)
01-0.0
3.140 (0.364)
02-0.05
3.137 (0.359)
03-5.92
1.818 (1.184)
04-14.43
2.668 (0.716)
05-23.12
2.082 (1.019)
06-24.18
1.819 (1.371)
07-36.63
2.054 (1.215)
08-42.34
CGa2In2
2.283 (0.409)
2.026 (0.578)
01-0.0
3.086 (0.392)
02-1.95
3.095 (0.395)
03-6.81
2.902 (0.501)
04-12.69
1.835 (1.309)
05-14.80
1.830 (1.405)
06-23.66
2.029 (1.083)
07-23.98
2.023 (1.159)
08-33.56
CGa2Tl2
3.146 (0.391)
01-0.0
2.378 (0.422)
2.010 (0.622)
02-0.13
3.173 (0.391)
03-6.45
1.836 (1.319)
04-13.53
2.915 (0.531)
05-16.67
2.080 (1.064)
06-24.65
1.830 (1.475)
07-27.28
2.061 (1.201)
08-37.81
CIn2Tl2
2.352 (0.485)
2.238 (0.517)
01-0.0
3.222 (0.470)
02-8.83
3.205 (0.476)
03-10.87
3.133 (0.519)
04-15.34
2.029 (1.230)
05-22.73
2.075 (1.193)
06-24.37
2.025 (1.290)
07-27.71
2.067 (1.257)
08-28.71

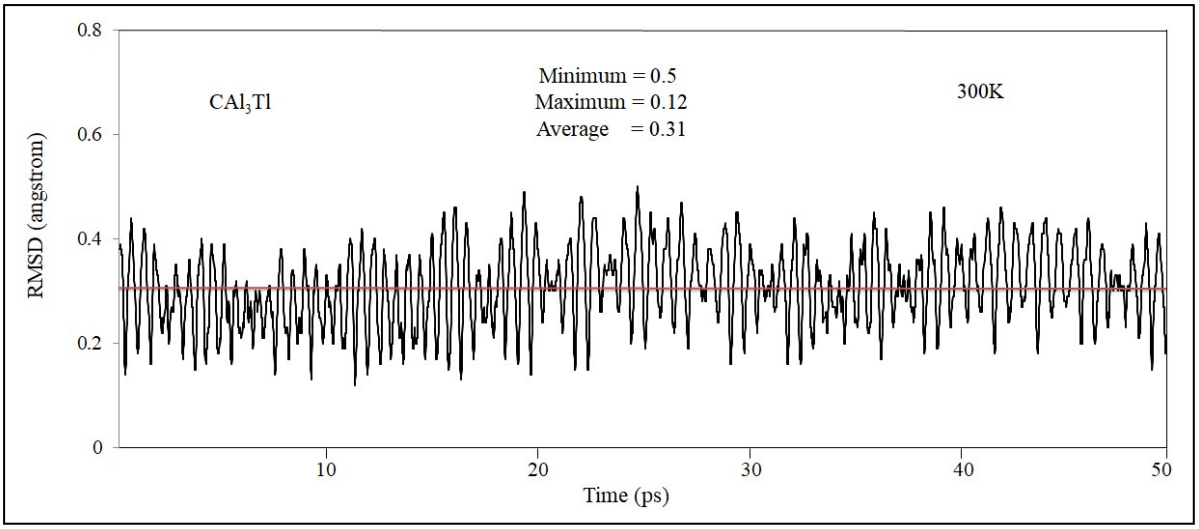
c)


CAl2GaIn
01-0.0
02-1.32
03-1.41
04-6.04
05-10.48
06-11.94
07-12.31
08-14.17
09-23.59
10-26.31
11-30.01
12-31.11
CAl2GaTl
01-0.0
02-0.19
03-0.91
04-8.75
05-10.96
06-12.34
07-14.62
08-27.04
09-29.48
CAl2InTl
01-0.0
02-0.79
03-3.98
04-4.34
05-9.53
06-13.51
07-18.79
08-20.84
09-22.58
10-27.46
11-27.94
CAlGa2In
01-0.0
02-1.65
03-1.66
04-6.42
05-11.11
06-11.43
08-12.06
08-12.96
09-15.03
10-21.34
11-24.55
12-27.08
13-31.65
CAlGa2Tl
01-0.0
02-0.16
03-0.62
04-8.64
05-11.14
06-12.72
07-14.25
08-24.03
09-27.55
10-29.84
CAlGaIn2
01-0.0
02-1.98
03-6.51
04-6.56
05-12.34
06-14.13
07-16.70
08-18.20
09-23.45
10-25.53
11-26.67
12-28.71
13-32.98
CAlGaTl2
01-0.0
02-0.02
03-6.06
04-6.24
05-12.79
06-15.13
07-16.38
08-23.03
09-24.32
10-25.52
11-30.90
12-32.39
CAlIn2Tl
01-0.0
02-3.59
03-7.80
04-8.57
05-9.20
06-14.53
07-20.06
08-20.83
09-25.57
10-27.46
CAlInTl2
01-0.0
02-4.27
03-5.82
04-10.02
05-11.23
06-16.15
07-21.76
08-22.00
09-24.22
10-28.43
11-30.44
CGa2InTl
01-0.0
02-0.83
03-3.67
04-4.80
05-10.13
06-12.71
07-14.67
08-16.31
09-17.28
10-21.60
11-26.27
12-28.39
13-36.01
CGaIn2Tl
01-0.0
02-3.53
03-7.49
04-8.77
05-9.10
06-12.61
07-14.87
08-17.35
09-20.50
10-21.27
11-26.08
12-27.75
13-36.13
CGaInTl2
01-0.0
02-4.08
03-5.75
04-9.76
05-11.26
06-11.44
07-11.45
08-14.01
09-18.78
10-22.51
11-24.48
12-37.50
CAlGaInTl
01-0.0
02-0.78
03-3.82
04-4.47
05-4.67
06-9.79
07-9.93
08-12.11
09-14.16
10-14.55
11-15.85
12-16.62
13-19.47
14-20.39
15-21.18
16-23.02
17-27.44
18-28.09
19-29.67
20-31.37

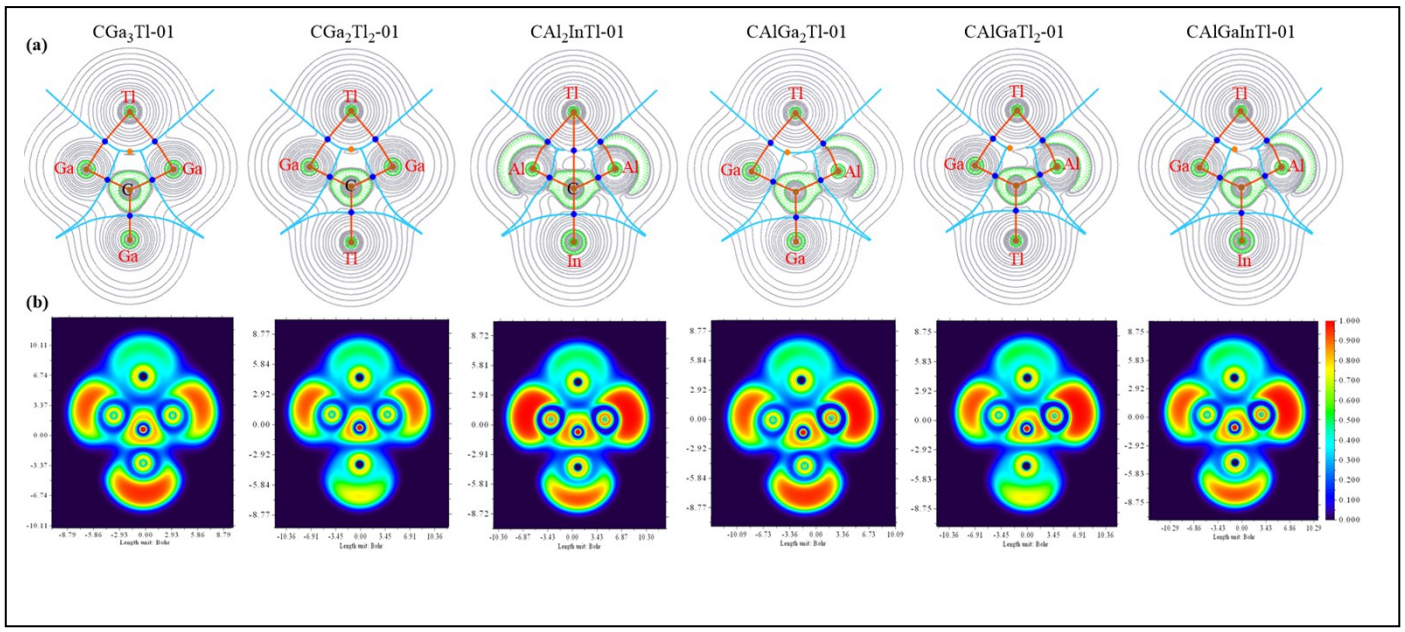
3. Fig. S2 Effects of temperature on the relative energies and the barriers between thC and ptC (GM) in CAl_3Tl system at the level of B3LYP/def2-QZVP +ZPVE.



4. Fig. S3 Born-Oppenheimer molecular dynamics (BOMD) simulations on GM ptC of CAl_3Tl at 300 K at B3LYP/def2-TZVP level.



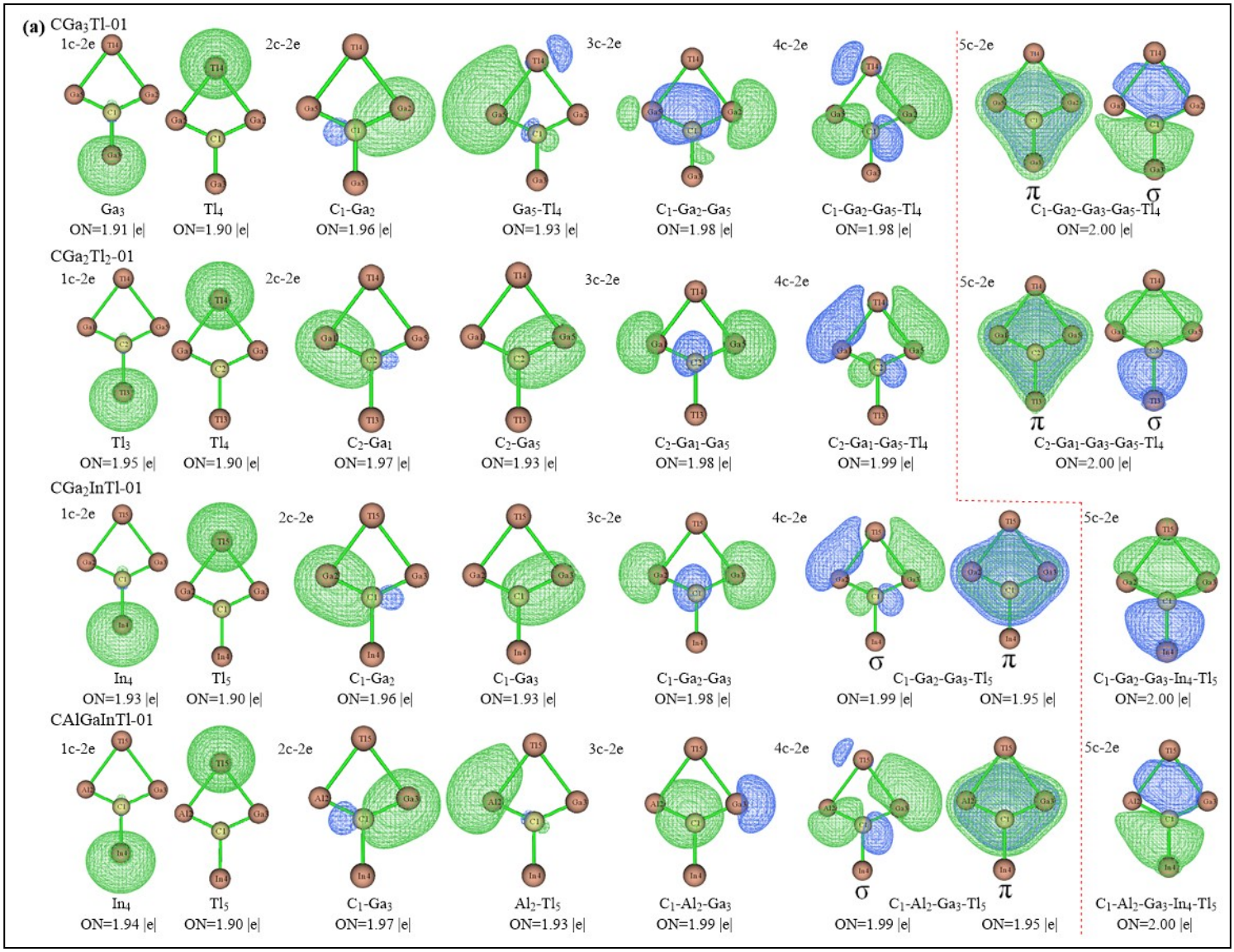
5. Fig. S4 (a) and **(b)** Contour plots of Laplacian distribution $\nabla^2\rho(\mathbf{r})$ and the ELF contour map of **CGa_3Tl-01**, **CGa_2Tl_2-01**, **CAl_2InTl-01**, **$CAlGa_2Tl$-01**, **$CAlGaTl_2$-01** and **CAlGaInTl-01**.

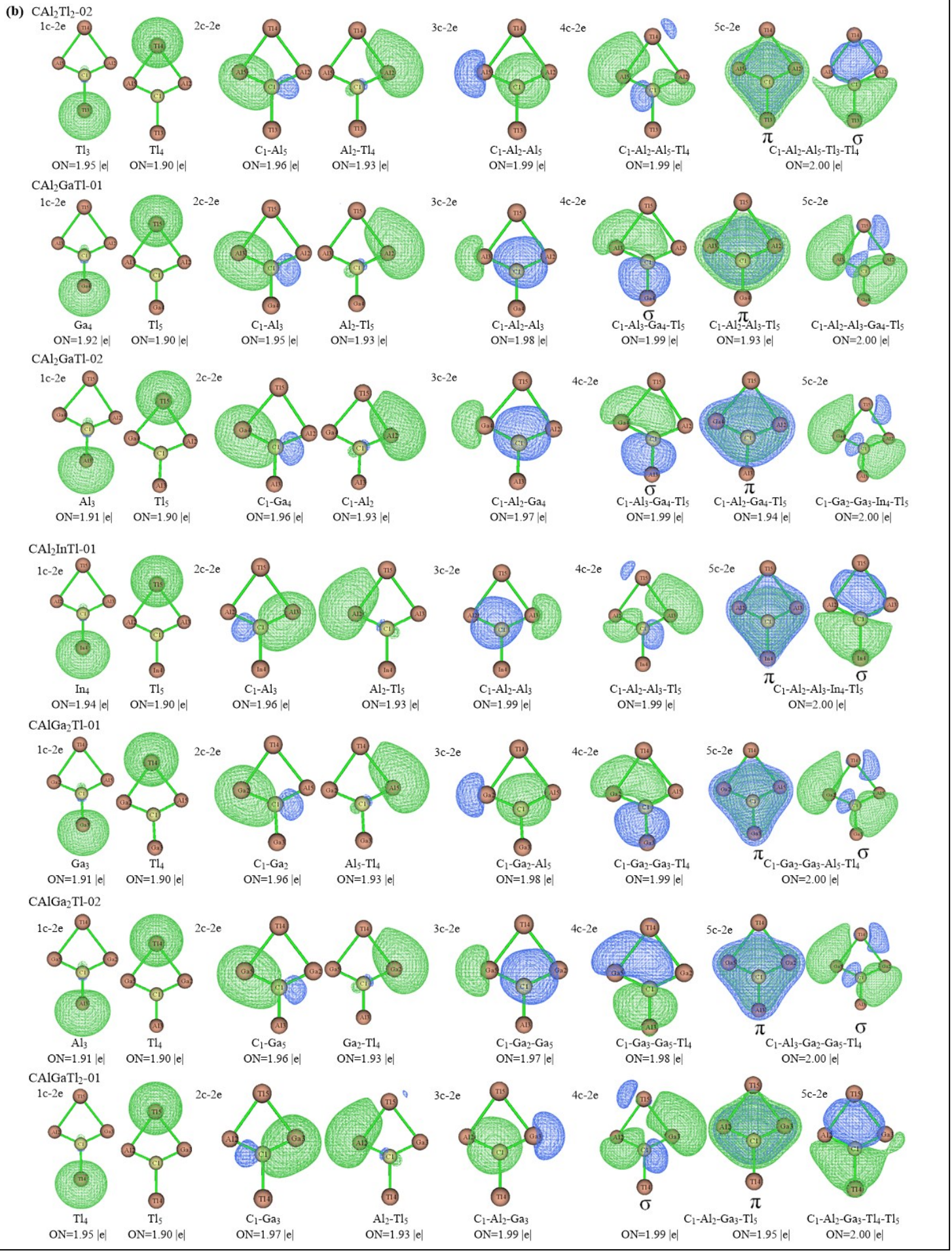


6. Table S2 Topological properties of the global minima and local minima ptCs of $CX_aY_bZ_cK_d$ (X, Y, Z, K=Al/Ga/In/Tl; $0 \leq a, b, c, d \leq 4$, a+b+c+d=4) systems ring critical point (all units are atomic units) at the B3LYP/def2-QZVP level (Density of all electrons $\rho(\mathbf{r})$, Eigenvalues of Hessian λ_1, λ_2, λ_3, Laplacian of electron density $\nabla^2\rho(\mathbf{r})$).

The distant Tl atom / system	$\rho(\mathbf{r})$	λ_1	λ_2	λ_3	$\nabla^2\rho(\mathbf{r})$	Curvature of electron density
CGa_3Tl	0.0241	0.00004	0.0576	-0.0142	0.0434	-0.0142
CAl_2Tl_2	0.0250	-0.0004	0.0578	-0.0145	0.0428	-0.0145
CGa_2Tl_2	0.0240	0.0559	0.0008	-0.0139	0.0428	-0.0139
CAl_2GaTl	0.0249	0.0593	-0.0008	-0.0148	0.0436	-0.0148
CAl_2InTl	0.0246	0.0571	-0.0002	-0.0144	0.0425	-0.0144
$CAlGa_2Tl$	0.0240	0.0087	0.0491	-00143	0.0435	-0.0143
$CAlGaTl_2$	0.0242	0.0521	0.0054	-0.0141	0.0434	-0.0141
CGa_2InTl	0.0239	0.0560	0.0008	-0.0139	0.0429	-0.0139
CAlGaInTl	0.0240	0.0520	0.0053	-0.0141	0.0432	-0.0141

7. Fig. S5 AdNDP analysis of global minima and local minima ptCs of $CX_aY_bZ_cK_d$ (X, Y, Z, K=Al/Ga/In/Tl; $0 \le a, b, c, d \le 4$, a+b+c+d=4) at the level of B3LYP/def2-TZVP. Occupation numbers (ON) in |e|.




(b) CAl2Tl2-02
1c-2e
2c-2e
3c-2e
4c-2e
5c-2e
Tl3 ON=1.95 |e|
Tl4 ON=1.90 |e|
C1-Al5
Al2-Tl4
C1-Al2-Al5 ON=1.99 |e|
C1-Al2-Al5-Tl4 ON=1.99 |e|
π
σ
C1-Al2-Al5-Tl3-Tl4 ON=2.00 |e|
CAl2GaTl-01
Ga4 ON=1.92 |e|
Tl5 ON=1.90 |e|
C1-Al3
Al2-Tl5
C1-Al2-Al3 ON=1.98 |e|
C1-Al3-Ga4-Tl5 ON=1.99 |e|
C1-Al2-Al3-Tl5 ON=1.93 |e|
C1-Al2-Al3-Ga4-Tl5 ON=2.00 |e|
CAl2GaTl-02
Al3 ON=1.91 |e|
Tl5 ON=1.90 |e|
C1-Ga4
C1-Al2
C1-Al2-Ga4 ON=1.97 |e|
C1-Al3-Ga4-Tl5 ON=1.99 |e|
C1-Al2-Ga4-Tl5 ON=1.94 |e|
C1-Ga2-Ga3-In4-Tl5 ON=2.00 |e|
CAl2InTl-01
In4 ON=1.94 |e|
Tl5 ON=1.90 |e|
C1-Al3
Al2-Tl5
C1-Al2-Al3 ON=1.99 |e|
C1-Al2-Al3-Tl5 ON=1.99 |e|
C1-Al2-Al3-In4-Tl5 ON=2.00 |e|
CAlGa2Tl-01
Ga3 ON=1.91 |e|
Tl4 ON=1.90 |e|
C1-Ga2
Al5-Tl4
C1-Ga2-Al5 ON=1.98 |e|
C1-Ga2-Ga3-Tl4 ON=1.99 |e|
C1-Ga2-Ga3-Al5-Tl4 ON=2.00 |e|
CAlGa2Tl-02
Al3 ON=1.91 |e|
Tl4 ON=1.90 |e|
C1-Ga5
Ga2-Tl4
C1-Ga2-Ga5 ON=1.97 |e|
C1-Ga3-Ga5-Tl4 ON=1.98 |e|
C1-Al3-Ga2-Ga5-Tl4 ON=2.00 |e|
CAlGaTl2-01
Tl4 ON=1.95 |e|
Tl5 ON=1.90 |e|
C1-Ga3
Al2-Tl5
C1-Al2-Ga3 ON=1.99 |e|
C1-Al2-Ga3-Tl5 ON=1.95 |e|
C1-Al2-Ga3-Tl4-Tl5 ON=2.00 |e|

8. Fig. S6 Molecular orbitals of the 8 global minima and one isoenergetic ptCs of $CX_aY_bZ_cK_d$ (X, Y, Z, K=Al/Ga/In/Tl; $0 \leq a, b, c, d \leq 4$, a+b+c+d=4) calculated at the level of B3LYP/def2-QZVP.

9. Table S3 NPA charge (q, |e|) of low-lying ptC and thC isomers in [A][B] (A=CX_2Y/CXYZ, B=Al/Ga/In/Tl) at the B3LYP/def2-QZVP level.

	ptC		q(B)	q(C)		thC		q(B)	q(C)
1	CAl_4	Ⅰ	0.358	-2.703		CAl_4	Ⅰ	0.783	-3.132
2	CAl_3Ga		0.303	-2.677		CAl_3Ga		0.744	-3.064
3	CAl_3In		0.412	-2.713		CAl_3In		0.805	-3.067
4	CAl_3Tl		0.408	-2.717		CAl_3Tl		0.806	-3.030
5	CAl_2Ga_2	Ⅱ	0.287	-2.595		CAl_2Ga_2	Ⅱ	0.735	-2.991
6	CAl_2GaIn		0.394	-2.632		CAl_2GaIn		0.797	-2.982
7	CAl_2GaTl		0.393	-2.638		CAl_2GaTl		0.798	-2.941
8	CAl_2In_2	Ⅲ	0.376	-2.632		CAl_2In_2	Ⅲ	0.780	-2.999
9	CAl_2InTl		0.373	-2.638		CAl_2InTl		0.781	-2.960
10	CAl_2Tl_2		0.357	-2.586		CAl_2Tl_2		0.769	-2.929
11	$CAlGa_3$	Ⅳ	0.316	-2.507		$CAlGa_3$	Ⅳ	0.721	-2.915
12	$CAlGa_2In$		0.422	-2.545		$CAlGa_2In$		0.786	-2.914
13	$CAlGa_2Tl$		0.418	-2.552		$CAlGa_2Tl$		0.787	-2.872
14	$CAlGaIn_2$	Ⅴ	0.405	-2.540		$CAlGaIn_2$	Ⅴ	0.770	-2.930
15	CAlGaInTl		0.403	-2.547		CAlGaInTl		0.771	-2.890
16	$CAlGaTl_2$		0.387	-2.493		$CAlGaTl_2$		0.757	-2.849
17	$CAlIn_3$	Ⅵ	0.366	-2.564		$CAlIn_3$	Ⅵ	0.754	-2.956
18	$CAlIn_2Tl$		0.366	-2.570		$CAlIn_2Tl$		0.754	-2.918
19	$CAlInTl_2$		0.351	-2.519		$CAlInTl_2$		0.740	-2.878
20	$CAlTl_3$		0.356	-2.463		$CAlTl_3$		0.727	-2.838
21	CGa_4	Ⅶ	0.348	-2.418		CGa_4	Ⅶ	0.711	-2.843
22	CGa_3In		0.450	-2.455		CGa_3In		0.776	-2.847
23	CGa_3Tl		0.448	-2.461		CGa_3Tl		0.777	-2.804
24	CGa_2In_2	Ⅷ	0.434	-2.444		CGa_2In_2	Ⅷ	0.761	-2.860
25	CGa_2InTl		0.433	-2.455		CGa_2InTl		0.761	-2.819
26	CGa_2Tl_2		0.417	-2.400		CGa_2Tl_2		0.748	-2.777
27	$CGaIn_3$	Ⅸ	0.398	-2.460		$CGaIn_3$	Ⅸ	0.746	-2.885
28	$CGaIn_2Tl$		0.399	-2.469		$CGaIn_2Tl$		0.745	-2.845
29	$CGaInTl_2$		0.383	-2.415		$CGaInTl_2$		0.732	-2.805
30	$CGaTl_3$		0.390	-2.359		$CGaTl_3$		0.718	-2.764
31	CIn_4		0.357	-2.508		CIn_4		0.731	-2.923
32	CIn_3Tl		0.361	-2.514		CIn_3Tl		0.730	-2.875
33	CIn_2Tl_2		0.345	-2.460		CIn_2Tl_2		0.717	-2.839
34	$CInTl_3$		0.356	-2.407		$CInTl_3$		0.704	-2.801
35	CTl_4		0.372	-2.359		CTl_4		0.689	-2.756

10. Table S4 Infrared vibrational frequency values (cm^{-1}) and the infrared vibrational intensities (km/mol) in parenthesis for the lowest energy ptC and thC of $CX_aY_bZ_cK_d$ (X, Y, Z, K=Al/Ga/In/Tl; $0 \leq a, b, c, d \leq 4$, a+b+c+d=4) at the level of B3LYP/def2-QZVP.

system		1	2	3	4	5	6	7	8	9
CGa_3Tl	Isomer-01	24.5 (0.2)	71.1 (2.4)	73.1 (0.2)	110.7 (2.0)	125.3 (2.9)	182.1 (4.9)	232.8 (7.3)	646.1 (347.0)	725.0 (115.4)
	Isomer-02	50.5 (0.02)	51.1 (0.02)	82.3 (3.1)	97.7 (1.6)	98.2 (1.7)	189.8 (0.4)	427.7 (221.6)	563.3 (269.6)	563.6 (269.7)
CAl_2Tl_2	Isomer-01	42.2 (0.003)	66.2 (0.00)	100.2 (8.5)	105.8 (5.1)	114.1 (0.9)	231.0 (3.7)	368.4 (196.1)	574.5 (238.2)	711.8 (259.7)
	Isomer-02	25.2 (1.2)	54.5 (0.8)	77.5 (0.8)	165.0 (13.4)	179.2 (17.5)	192.3 (6.3)	279.6 (61.5)	628.8 (302.3)	869.8 (61.6)
CGa_2Tl_2	Isomer-01	20.6 (0.9)	55.2 (0.4)	56.5 (0.5)	107.1 (2.7)	121.0 (7.4)	174.1 (7.3)	192.1 (17.4)	567.4 (360.1)	743.1 (109.6)
	Isomer-02	39.4 (0.00)	46.9 (0.00)	74.2 (2.6)	78.2 (1.6)	81.7 (0.6)	161.9 (0.5)	387.7 (232.0)	493.2 (252.6)	582.0 (264.3)
CAl_2GaTl	Isomer-01	28.4 (0.2)	70.1 (2.7)	95.8 (0.8)	168.5 (10.9)	185.6 (7.0)	198.4 (4.2)	338.4 (33.5)	687.6 (313.4)	851.0 (66.3)
	Isomer-02	55.3 (0.01)	65.4 (0.1)	103.3 (8.4)	127.0 (4.9)	133.3 (2.1)	254.4 (5.7)	422.0 (174.4)	607.2 (261.2)	680.5 (275.7)
CAl_2InTl	Isomer-01	23.7 (0.7)	62.0 (1.5)	82.7 (0.8)	166.4 (12.5)	183.2 (12.4)	193.7 (5.1)	303.0 (50.4)	653.4 (305.8)	860.9 (61.1)
	Isomer-02	49.0 (0.00)	66.9 (0.02)	102.1 (7.9)	115.8 (5.9)	120.6 (1.4)	239.7 (3.5)	393.8 (194.0)	578.6 (240.3)	700.3 (256.6)
$CAlGa_2Tl$	Isomer-01	27.0 (0.2)	70.0 (2.0)	81.7 (1.3)	114.5 (2.1)	181.2 (8.5)	194.8 (4.6)	288.4 (17.2)	653.8 (320.5)	807.6 (100.7)
	Isomer-02	53.2 (0.01)	57.0 (0.06)	94.8 (5.7)	111.4 (1.5)	115.2 (3.9)	226.0 (2.4)	420.4 (198.5)	559.0 (261.4)	652.6 (278.1)
$CAlGaTl_2$	Isomer-01	23.2 (1.0)	55.4 (0.7)	63.6 (0.5)	110.6 (4.6)	175.6 (16.1)	184.2 (6.9)	243.2 (34.6)	582.9 (330.9)	819.6 (88.2)
	Isomer-02	41.2 (0.01)	52.7 (0.01)	87.9 (1.1)	90.3 (5.4)	99.6 (3.2)	202.4 (2.1)	380.1 (214.3)	508.8 (245.5)	671.5 (265.0)
CGa_2InTl	Isomer-01	19.8 (0.6)	60.8 (0.3)	64.7 (1.2)	108.5 (2.4)	123.8 (5.3)	176.1 (5.9)	208.7 (13.1)	600.1 (352.9)	734.0 (108.2)
	Isomer-02	45.1 (0.01)	50.3 (0.00)	78.7 (2.6)	87.4 (0.9)	88.9 (2.1)	173.1 (0.3)	414.5 (229.1)	511.2 (255.1)	578.0 (258.5)
CAlGaInTl	Isomer-01	21.8 (0.7)	62.1 (1.1)	70.7 (0.8)	112.5 (3.7)	179.8 (12.3)	185.9 (5.5)	261.4 (26.8)	611.5 (326.6)	812.0 (89.8)
	Isomer-02	47.8 (0.01)	55.6 (0.02)	92.4 (3.9)	98.3 (2.6)	106.8 (4.0)	212.8 (1.3)	406.5 (214.1)	518.1 (245.4)	659.4 (260.8)

11. Decomposition stability of CAl_3Tl

In general, six kinds of feasible decomposition reactions of CAl_3Tl were considered:

$CAl_3Tl \rightarrow CAl_3 + Tl$ (1)
$CAl_3Tl \rightarrow CAl_2Tl + Al$ (2)

$CAl_3Tl \rightarrow CAl_3^- + Tl^+$ (3)
$CAl_3Tl \rightarrow CAl_2Tl^- + Al^+$ (4)

$CAl_3Tl \rightarrow CAlTl + Al_2$ (5)
$CAl_3Tl \rightarrow CAl_2 + AlTl$ (6)

The dissociation energies are as high as 58.73, 74.83, 123.29, 161.98, 153.94, and 164.12 kcal/mol, respectively, indicating the good thermodynamic stability of GM ptC.

12. Table S5 T1 diagnostic values of these nine GM ptC structures in $CX_aY_bZ_cK_d$.

	T1 diagnostic		T1 diagnostic
CAl_3Tl	0.024	$CAlGaTl_2$	0.021
CGa_3Tl	0.022	CAl_2InTl	0.024
CGa_2Tl_2	0.021	CGa_2InTl	0.022
$CAlGa_2Tl$	0.022	CAlGaInTl	0.023
CAl_2GaTl	0.023		

"T1 has been used to estimate the reliability of CCSD(T) values in other ptC studies,[1,2] and the CCSD(T) result is reliable when the T1 value is around or smaller than 0.02. The T1 diagnostic of nine GM ptC structures in $CX_aY_bZ_cK_d$ are listed in Table S5. Clearly, with the T1 values of around 0.02, it seems that these structures have little multi-reference natures.

1. T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.*, **1989**, 199.
2. R. Grande-Aztatzi, J. L. Cabellos, R. Islas, I. Infante, J. M. Mercero, A. Restrepo and G. Merino, *Phys. Chem. Chem. Phys.*, 2012, **17**, 4620-4624.

13. Table S6 Bond order analysis between the central carbon and the distant Tl atom. Wiberg bond index (WBI), Mayer bond index (MBI), fuzzy bond order[3] (FBO) and NAO bond order.

CAl_3Tl	WBI	0.304	$CAlGaTl_2$	WBI	0.378
	MBI	0.303		MBI	0.383
	FBO	0.480		FBO	0.465
	NAO bond order	0.122		NAO bond order	0.172
CGa_3Tl	WBI	0.347	CAl_2InTl	WBI	0.342
	MBI	0.373		MBI	0.337
	FBO	0.439		FBO	0.469
	NAO bond order	0.149		NAO bond order	0.132
CGa_2Tl_2	WBI	0.391	CGa_2InTl	WBI	0.372
	MBI	0.419		MBI	0.406
	FBO	0.446		FBO	0.440
	NAO bond order	0.167		NAO bond order	0.156
$CAlGa_2Tl$	WBI	0.332	CAlGaInTl	WBI	0.358
	MBI	0.342		MBI	0.371
	FBO	0.456		FBO	0.456
	NAO bond order	0.151		NAO bond order	0.133
CAl_2GaTl	WBI	0.313			
	MBI	0.313			
	FBO	0.469			
	NAO bond order	0.134			

3. Mayer, I.; Salvador, P. Overlap Populations, Bond Orders and Valences for 'Fuzzy' Atoms. *Chem. Phys. Lett.* **2004**, 383, 368−375.

14. Table S7 Key cartesian coordinates of the lowest energy ptC and thC isomers of $CX_aY_bZ_cK_d$ (X, Y, Z, K=Al/Ga/In/Tl; $0 \leq a, b, c, d \leq 4$, a+b+c+d=4) at the level of B3LYP/def2-QZVP.

CGa_3Tl-^{1}01 (ptC)			
6	**0.000000**	**1.350867**	**0.000000**
31	**-1.747533**	**0.527006**	**0.000000**
31	**-0.000016**	**3.349511**	**0.000000**
81	**-0.000006**	**-1.785380**	**0.000000**
31	**1.747566**	**0.527051**	**0.000000**
CGa_3Tl-^{1}02 (thC)			
31	**-1.387308**	**-0.965249**	**1.671037**
6	**-0.761010**	**-0.000869**	**0.000000**
31	**-1.387308**	**1.928219**	**0.000000**
31	**-1.387308**	**-0.965249**	**-1.671037**
81	**1.649206**	**0.000936**	**0.000000**
CAl_2Tl_2-^{1}01 (thC)			
13	**-0.000245**	**2.076314**	**-1.628184**
6	**-0.000050**	**1.007137**	**0.000017**
13	**0.000478**	**2.076118**	**1.628344**
81	**1.956735**	**-0.370543**	**-0.000091**
81	**-1.956768**	**-0.370499**	**0.000064**
CAl_2Tl_2-^{1}02 (thC)			
6	**0.000000**	**0.452011**	**0.000000**
13	**-1.706242**	**-0.342076**	**0.000000**
81	**-0.003960**	**2.763278**	**0.000000**
81	**0.003672**	**-2.687597**	**0.000000**
13	**1.708036**	**-0.338098**	**0.000000**
CGa_2Tl_2-^{1}01 (ptC)			
31	**-0.310501**	**-1.735581**	**0.000055**
6	**0.518383**	**0.000002**	**0.000055**
81	**2.826557**	**-0.000001**	**-0.000015**
81	**-2.627288**	**-0.000001**	**-0.000031**
31	**-0.310502**	**1.735585**	**0.000055**
CGa_2Tl_2-^{1}01 (thC)			
31	**0.000127**	**1.790249**	**-1.668396**
6	**-0.000007**	**0.669226**	**-0.000003**
31	**-0.000077**	**1.790229**	**1.668407**
81	**1.936626**	**-0.709951**	**0.000041**
81	**-1.936644**	**-0.709927**	**-0.000046**
CAl_2GaTl-^{1}01 (ptC)			
6	**-1.476238**	**0.000415**	**0.008264**
13	**-0.686020**	**-1.714759**	**0.008984**
13	**-0.685527**	**1.715351**	**0.008979**
31	**-3.473127**	**-0.000093**	**-0.004418**
81	**1.658697**	**-0.000090**	**-0.001804**
CAl_2GaTl-^{1}03 (thC)			

6 1.009015 0.570493 -0.000002
13 1.270229 1.635069 -1.628347
13 1.267384 1.635380 1.628641
31 2.189169 -1.085042 0.000463
81 -1.319843 -0.151883 -0.000224
CAl_2InTl-^{1}01 (ptC)
6 1.034071 0.000193 0.001947
13 0.232435 -1.704657 0.001713
13 0.232417 1.705072 0.001712
49 3.252768 -0.000061 -0.000538
81 -2.118927 -0.000044 -0.000368
CAl_2InTl-^{1}02 (thC)
6 0.531651 0.871028 0.000136
13 0.606134 1.948632 1.626672
13 0.605555 1.950818 -1.624988
49 2.227654 -0.653233 -0.000378
81 -1.581443 -0.295193 -0.000052
$CAlGa_2Tl$-^{1}01 (ptC)
6 0.000000 1.417233 0.000000
31 1.632101 0.375874 0.000000
31 0.254783 3.398094 0.000000
81 -0.433228 -1.686487 0.000000
13 -1.800149 0.854538 0.000000
$CAlGa_2Tl$-^{1}03 (thC)
13 -1.047452 -0.000220 2.352161
6 -0.865121 0.000003 0.398944
31 -1.671807 1.671444 -0.425175
31 -1.672254 -1.671136 -0.425373
81 1.512018 -0.000083 -0.081540
$CAlGaTl_2$-^{1}01 (ptC)
6 -0.485508 -0.144237 -0.005257
13 0.299186 -1.854104 -0.008332
31 0.343067 1.593222 -0.003396
81 -2.794968 -0.123767 0.001353
81 2.651617 -0.177728 0.001674
$CAlGaTl_2$-^{1}02 (thC)
6 -0.000031 0.691293 0.480470
13 0.000526 0.980872 2.406407
31 -0.000290 2.408501 -0.563960
81 -1.942370 -0.565254 -0.102916
81 1.942399 -0.565149 -0.103051
CGa_2InTl-^{1}01 (ptC)

6 -1.000602 -0.000009 0.003954
31 -0.166891 1.736617 0.004052
31 -0.166885 -1.736633 0.004051
49 -3.218268 0.000004 -0.002496
81 2.148714 0.000005 -0.001884
CGa_2InTl-^{1}02 (thC)
6 0.490157 0.419015 -0.000069
31 0.771026 1.520075 -1.667150
31 0.771206 1.517364 1.668880
49 1.891352 -1.365482 -0.000806
81 -1.770696 -0.367483 -0.000169
CAlGaInTl-^{1}01 (ptC)
6 -1.010683 -0.180340 -0.004998
13 -0.189100 -1.874492 -0.008582
31 -0.203139 1.571256 -0.003473
49 -3.227847 -0.204955 0.002304
81 2.135608 -0.163157 0.001683
CAlGaInTl-^{1}02 (thC)
6 0.510207 0.462796 0.457056
13 0.580782 0.698716 2.395402
31 0.811260 2.199993 -0.527723
49 2.055009 -1.074487 -0.195005
81 -1.684641 -0.338395 -0.098369