Electronic supplementary information

Group 13 Five- and Six-Membered Rings with Rare 2π Aromaticity

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Table S1 Relative energies (kcal/mol) with different spin multiplicities (*M*) at the M06-2X/def2-TZVP level of theory. The results at the higher M06-2X/def2-QZVP level of theory are given in parentheses.

M	1	3	5
$Na_2(AlH)_5$	**0.00(0.00)**	26.99(27.17)	34.78(34.69)
$Na_2(InH)_5$	**0.00(0.00)**	20.97(21.09)	27.02(27.08)
$Ca(AlH)_5$	**0.00(0.00)**	13.65(13.69)	45.75(45.19)
$Ca(GaH)_5$	**0.00(0.00)**	20.63(20.76)	46.00(32.86)
$Ca(InH)_5$	**0.00(0.00)**	14.07(16.18)	25.51(25.77)
$Ca(AlH)_6$	**0.00(0.00)**	13.49(13.11)	30.50(29.44)
$Ca(InH)_6$	**0.00(0.00)**	7.64(7.53)	21.13(20.88)

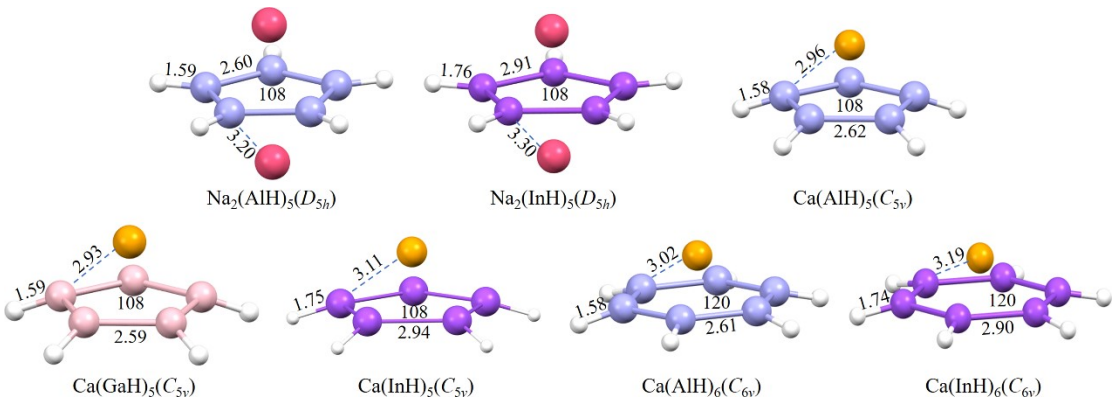

Fig. S1 Optimized structures at the M06-2X/def2-QZVP level of theory. Bond distances and interior angles are given in Å and degree, respectively. Al: blue, Ga: pink, In: purple, Na: red, Ca: orange, H: white.

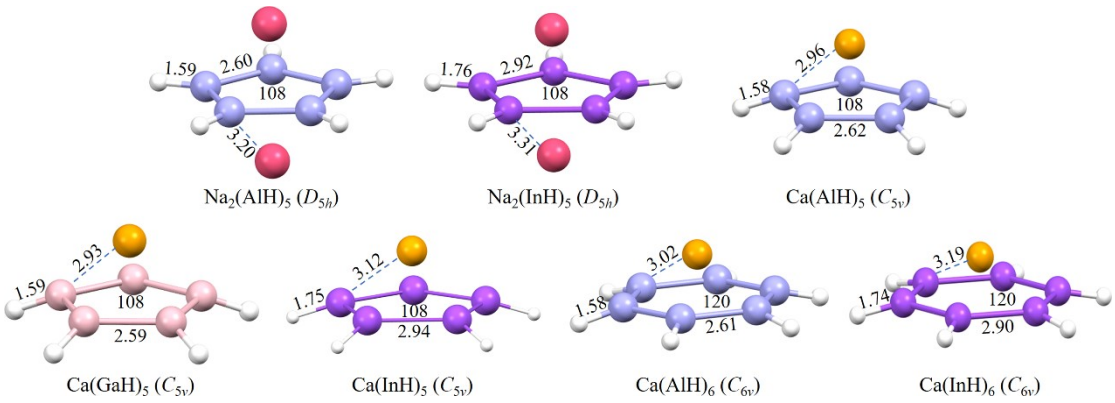

Fig. S2 Optimized structures at the M06-2X/def2-TZVPPD level of theory. Bond distances and interior angles are given in Å and degree, respectively. Al: blue, Ga: pink, In: purple, Na: red, Ca: orange, H: white.

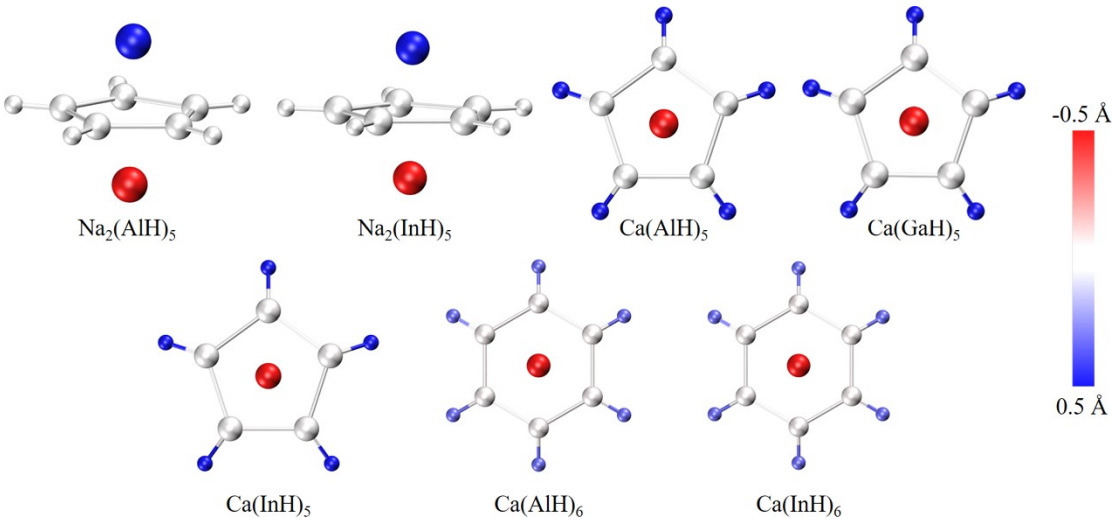

Fig. S3 Calculated molecular planarity parameter (MPP) and span of deviation from plane (SDP). The MPP and SDP values for the central rings are all zero.

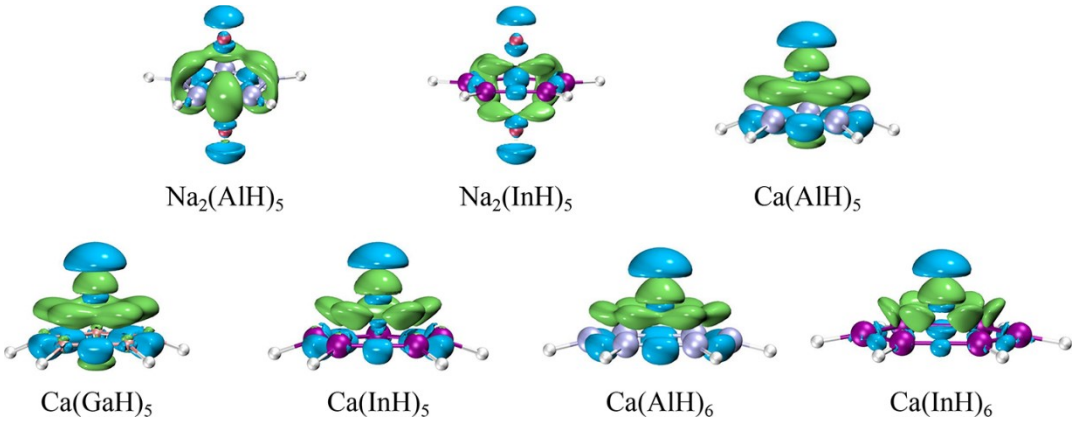

Fig. S4 Charge density difference for the formation of all complexes from Na_2/Ca and $(MH)_{5/6}$ ring. The green and blue colors represent charge accumulation and depletion, respectively.

Table S2 IQA interaction energy (kcal/mol) and its interatomic exchange-correlation and Coulombic energy components between Na/Ca(M1) and one M or H atom in the central ring, V_{Int}(M1,M) and V_{Int}(M1,H), V_{XC}(M1,M) and V_{XC}(M1,H), V_C(M1,M) and V_C(M1,H). All data are computed at M06-2X/def2-TZVP level.

Species	V_{Int}(M1,M)	V_{Int}(M1,H)	V_{XC}(M1,M)	V_{XC}(M1,H)	V_C(M1,M)	V_C(M1,H)
$Na_2(AlH)_5$	89.9	-43.7	-4.8	-0.2	94.7	-43.5
$Na_2(InH)_5$	-6.8	-21.8	-9.6	-0.2	2.8	-21.6
$Ca(AlH)_5$	127.4	-68.0	-17.6	-1.0	145.0	-67.0
$Ca(AlH)_6$	157.7	-70.6	-13.1	-0.9	170.8	-69.7
$Ca(GaH)_5$	-20.6	-42.0	-25.3	-0.9	4.7	-41.1
$Ca(InH)_5$	-21.0	-34.0	-26.3	-0.8	5.3	-33.2
$Ca(InH)_6$	-15.0	-35.8	-20.8	-0.8	5.8	-35.0

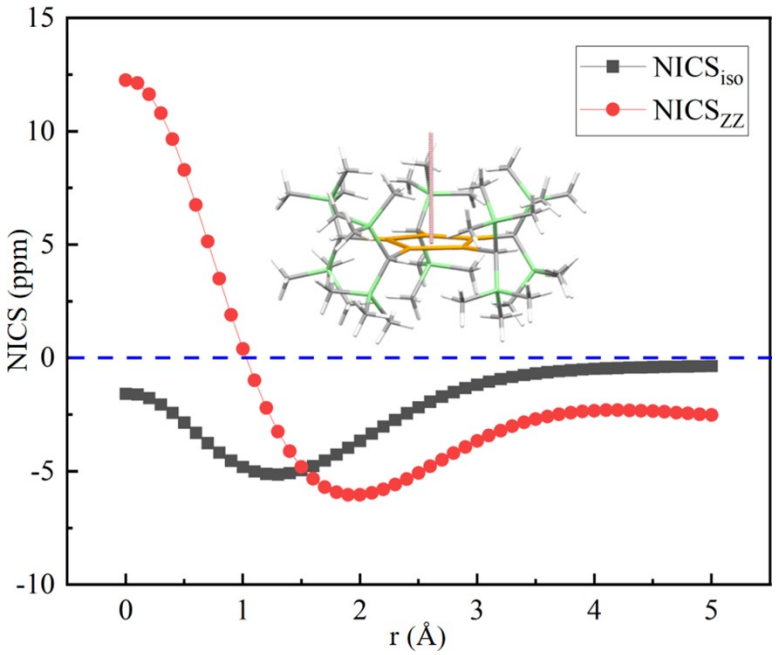

Fig. S5 NICS profiles along the direction perpendicular to the ring plane of $Ga_5[CH(SiMe_3)_2]_5^{2-}$ reported in experiment. Ga: orange, C: gray, Si: green, H: white. Bq (ghost atom): pink.

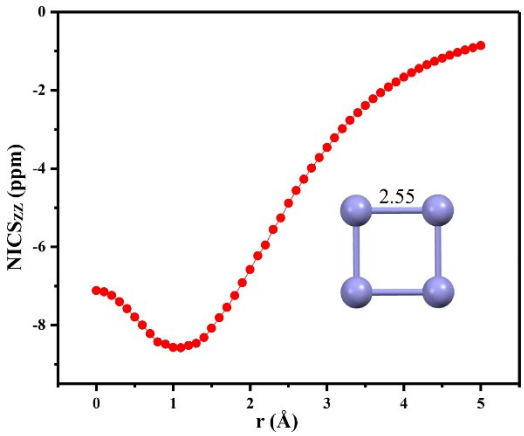

Fig. S6 π orbital contribution to the NICS$_{zz}$ profile along the direction perpendicular to the ring plane of Al_4^{2-}. The bond length is given in Å.

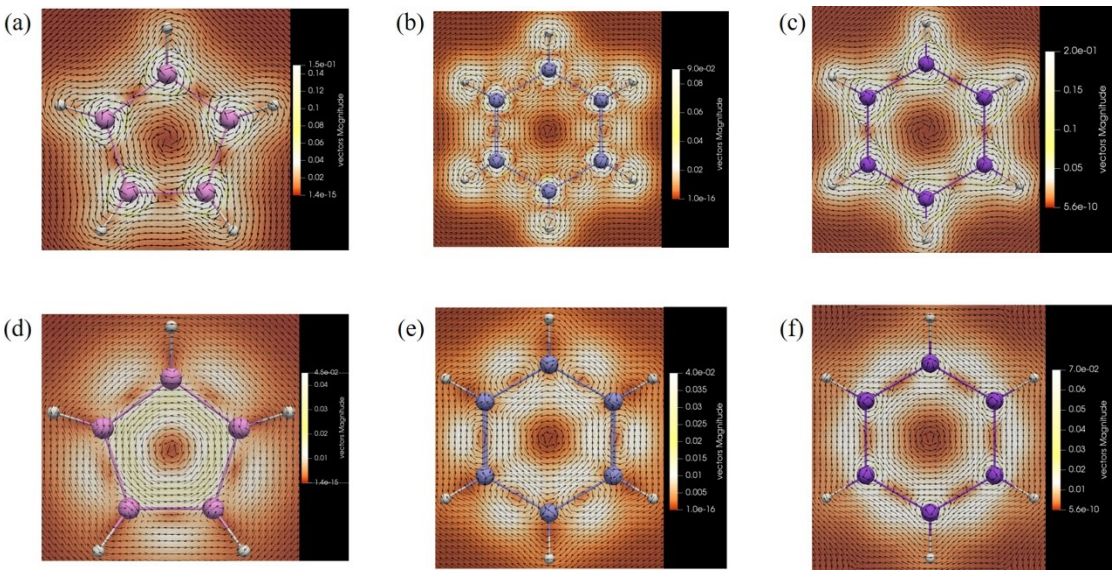

Fig. S7 Induced ring currents (height: 0 and 1 Å; black arrows denote current density vectors) of (a)(d) $(GaH)_5^{2-}$, (b)(e) $(AlH)_6^{2-}$ and (c)(f) $(InH)_6^{2-}$. The external magnetic field is perpendicular to the ring plane and points towards the reader, and clockwise currents thus mean diatropic.

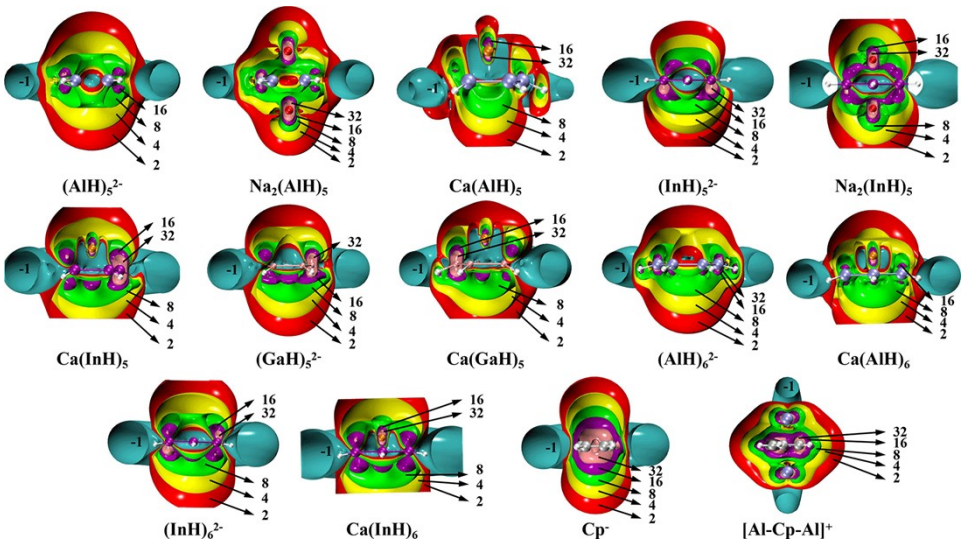

Fig. S8 $ICSS_{ZZ}$ isosurfaces and shielding values (denoted by different colors) for our systems as compared to conventional sandwich molecule.

Optimized Cartesian coordinates with the lowest vibrational frequency

$Na_2(AlH)_5$ (42.57 cm^{-1})

Al	0.00000000	2.20884400	0.00000000
Al	2.10073600	0.68257000	0.00000000
Al	1.29832600	-1.78699200	0.00000000
Al	-1.29832600	-1.78699200	0.00000000
Al	-2.10073600	0.68257000	0.00000000
Na	0.00000000	0.00000000	2.32305800
Na	0.00000000	0.00000000	-2.32305800
H	0.00000000	3.80331600	0.00000000
H	3.61716900	1.17528900	0.00000000
H	2.23553300	-3.07694800	0.00000000
H	-2.23553300	-3.07694800	0.00000000
H	-3.61716900	1.17528900	0.00000000

$Na_2(InH)_5$ (22.40 cm^{-1})

In	0.00000000	2.48003300	0.00000000
In	2.35865200	0.76637200	0.00000000
In	1.45772700	-2.00638900	0.00000000
In	-1.45772700	-2.00638900	0.00000000
In	-2.35865200	0.76637200	0.00000000
H	0.00000000	4.23873700	0.00000000
H	-4.03127900	1.30984200	0.00000000
H	-2.49146700	-3.42921000	0.00000000
H	2.49146700	-3.42921000	0.00000000
H	4.03127900	1.30984200	0.00000000
Na	0.00000000	0.00000000	2.18623500
Na	0.00000000	0.00000000	-2.18623500

$Ca(AlH)_5$ (24.06 cm^{-1})

H	0.00000000	3.70482000	-0.98113400
H	3.52349400	1.14485200	-0.98113400
H	2.17763900	-2.99726300	-0.98113400
H	-2.17763900	-2.99726300	-0.98113400
H	-3.52349400	1.14485200	-0.98113400
Al	0.00000000	2.22800500	-0.40222400
Al	-2.11895900	0.68849100	-0.40222400
Al	-1.30958800	-1.80249400	-0.40222400
Al	1.30958800	-1.80249400	-0.40222400
Al	2.11895900	0.68849100	-0.40222400
Ca	0.00000000	0.00000000	1.55251200

$Ca(GaH)_5$ (23.21 cm^{-1})

H	-3.49011821	1.13400815	-0.81589802

H	-2.15701168	-2.96887188	-0.81589802
H	2.15701168	-2.96887188	-0.81589802
H	3.49011821	1.13400815	-0.81589802
H	0.00000000	3.66972746	-0.81589802
Ga	-0.00000000	2.20432443	-0.19745330
Ga	2.09643711	0.68117371	-0.19745330
Ga	1.29566939	-1.78333592	-0.19745330
Ga	-1.29566939	-1.78333592	-0.19745330
Ga	-2.09643711	0.68117371	-0.19745330
Ca	0.00000000	0.00000000	1.73423758

$Ca(InH)_5$ (20.01 cm^{-1})

H	2.44087000	-3.35957000	-0.70949700
H	-2.44087000	-3.35957000	-0.70949700
H	-3.94941100	1.28324100	-0.70949700
H	0.00000000	4.15265700	-0.70949700
H	3.94941100	1.28324100	-0.70949700
Ca	0.00000000	0.00000000	1.73077200
In	0.00000000	2.50200100	-0.12680800
In	2.37954500	0.77316100	-0.12680800
In	1.47063900	-2.02416200	-0.12680800
In	-1.47063900	-2.02416200	-0.12680800
In	-2.37954500	0.77316100	-0.12680800

$Ca(AlH)_6$ (22.05 cm^{-1})

H	3.59303700	-2.07444100	-0.65527000
H	3.59303700	2.07444100	-0.65527000
H	0.00000000	4.14888100	-0.65527000
H	-3.59303700	2.07444100	-0.65527000
H	-3.59303700	-2.07444100	-0.65527000
H	0.00000000	-4.14888100	-0.65527000
Al	0.00000000	2.61284000	-0.26801400
Al	-2.26278600	1.30642000	-0.26801400
Al	-2.26278600	-1.30642000	-0.26801400
Al	0.00000000	-2.61284000	-0.26801400
Al	2.26278600	-1.30642000	-0.26801400
Al	2.26278600	1.30642000	-0.26801400
Ca	0.00000000	0.00000000	1.24183700

$Ca(InH)_6$ (18.04 cm^{-1})

H	0.00000000	-4.62064300	-0.37765600
H	4.00159400	-2.31032100	-0.37765600
H	4.00159400	2.31032100	-0.37765600
H	0.00000000	4.62064300	-0.37765600

H	-4.00159400	2.31032100	-0.37765600
H	-4.00159400	-2.31032100	-0.37765600
Ca	0.00000000	0.00000000	1.24038800
In	0.00000000	2.90364200	-0.07667300
In	-2.51462800	1.45182100	-0.07667300
In	-2.51462800	-1.45182100	-0.07667300
In	0.00000000	-2.90364200	-0.07667300
In	2.51462800	-1.45182100	-0.07667300
In	2.51462800	1.45182100	-0.07667300