Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Breaking Hoff/Le Bel Rule by Electron-compensation Strategy: the global minimum of $NGa_4S_4^+$

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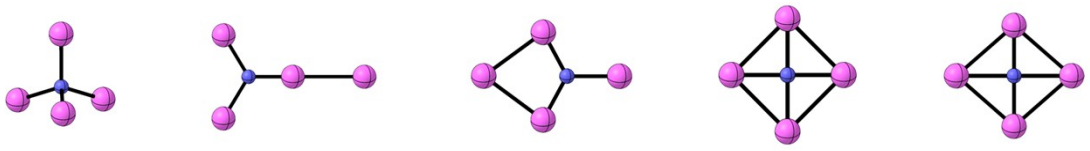

Fig. S1 Structures and relative energies (ΔE, in kcal mol^{-1} at the CCSD(T) + ZPE$_{B2PLYP\text{-}D3(BJ)}$ level) of **0a** and its low-energy isomers.

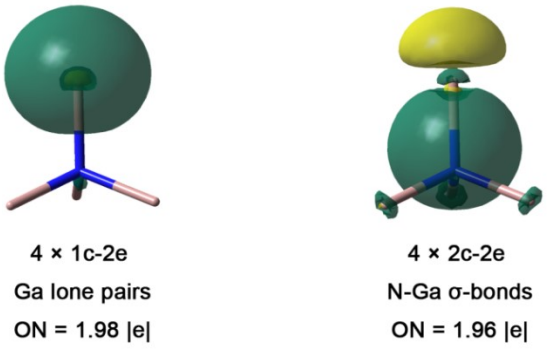

Fig. S2 AdNDP bonding patterns of **0a** with occupation numbers (ONs).

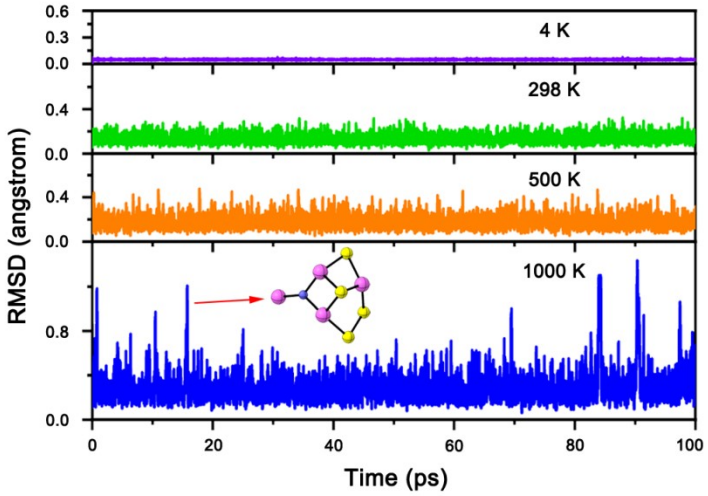

Fig. S3 The RMSD plots for the BOMD simulations of **1c** at 4 K, 298 K, 500 K and 1000 K, respectively.

SI-2

Cartesian Coordinates of the B2PLYP-D3(BJ)/aug-cc-pVTZ-optimized structures shown in **Fig. 2**

1a

N	0.00000000	0.00000000	0.00000000
Ga	0.00000000	1.93735900	0.00000000
Ga	1.93735900	0.00000000	0.00000000
Ga	0.00000000	-1.93735900	0.00000000
Ga	-1.93735900	0.00000000	0.00000000
S	2.21177700	-2.21177700	0.00000000
S	2.21177700	2.21177700	0.00000000
S	-2.21177700	2.21177700	0.00000000
S	-2.21177700	-2.21177700	0.00000000

1b

N	1.13320300	-2.44207700	-0.40960800
S	-2.58382000	-1.41271500	-0.57286800
S	-1.04335300	2.45762800	-0.86947200
S	2.81214600	1.07652300	-0.22317400
S	-0.41710500	0.16600600	1.67811000
Ga	-1.95928100	0.62798700	0.01660500
Ga	-0.48999400	-1.80996600	0.08792800
Ga	2.15300200	-1.01088400	-0.23974600
Ga	0.67632800	1.56368500	0.22120300

1c

N	0.46029500	0.68428600	-0.19170200
Ga	1.17920800	2.46789700	-0.80850500
Ga	-0.92242000	0.49571400	1.19113000
Ga	1.44988800	-0.77981300	0.73312800

Ga	-0.14123700	-0.72535000	-1.40478600
S	-2.32851800	-1.03392000	-1.12518000
S	-2.87544000	0.59606000	0.13384600
S	1.59722200	-2.11546000	-1.03947600
S	0.37231800	-0.57179800	2.67468200

1d

N	0.00000000	0.16577400	0.00000000
Ga	1.78520300	0.78887400	0.00000000
Ga	-0.09117800	2.26426400	0.00000000
Ga	-0.05111300	-1.73772000	0.00000000
Ga	-1.96115000	0.20429100	0.00000000
S	-2.31734500	2.39276900	0.00000000
S	-2.28684600	-1.97331200	0.00000000
S	1.98494500	-2.57924600	0.00000000
S	3.23583200	-0.85717500	0.00000000

1e

N	-0.75876300	-0.54972100	0.69224100
Ga	-3.27311800	-1.03025300	-0.58095700
Ga	-1.38501500	1.25343900	0.33509600
Ga	4.60044300	0.05529300	-0.40948200
Ga	1.10605400	-0.11155600	0.26401200
S	-1.64100900	-1.93500900	0.74463500
S	2.74109400	-1.44508100	0.02001000
S	-3.43461200	1.20768000	-0.46499200
S	0.63528200	2.08949900	0.15569300

Cartesian Coordinates of the B2PLYP-D3(BJ)/aug-cc-pVTZ-optimized structures shown in **Fig. S1**.

0a

N	0.00000000	0.00000000	0.00000000
Ga	1.20472300	1.20472300	1.20472300
Ga	-1.20472300	-1.20472300	1.20472300
Ga	1.20472300	-1.20472300	-1.20472300
Ga	-1.20472300	1.20472300	-1.20472300

0b

N	0.00000000	0.00000000	-1.06264900
Ga	0.00000000	0.00000000	3.65664000
Ga	0.00000000	1.70454900	-2.07907100
Ga	0.00000000	0.00000000	0.74145500
Ga	0.00000000	-1.70454900	-2.07907100

0c

N	0.00000000	0.00000000	0.70630400
Ga	0.00000000	0.00000000	2.72737100
Ga	0.00000000	0.00000000	-2.48075200
Ga	0.00000000	1.66599200	-0.20305400
Ga	0.00000000	-1.66599200	-0.20305400

0d

N	0.00000000	0.00000000	0.00000000
Ga	0.00000000	2.10267600	0.00000000
Ga	2.10267600	0.00000000	0.00000000
Ga	0.00000000	-2.10267600	0.00000000
Ga	-2.10267600	0.00000000	0.00000000

0e

N	0.00000000	0.00000000	0.00000000
Ga	0.00000000	0.00000000	2.22313000
Ga	0.00000000	1.93363100	0.00000000
Ga	0.00000000	0.00000000	-2.22313000
Ga	0.00000000	-1.93363100	0.00000000