Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for

The E≡E Triple Bonds (E = Group 13) Promoted by Charge Transfer From Alkali Metals

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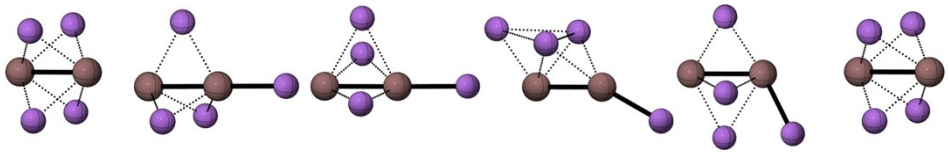
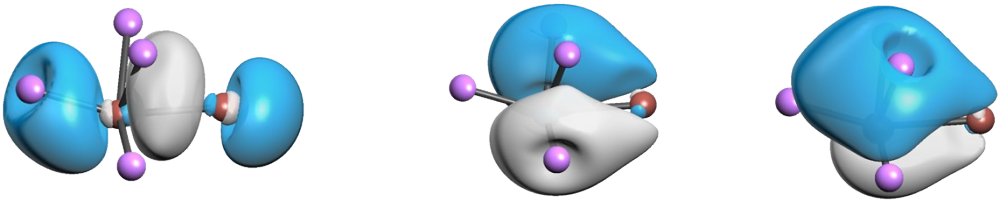


	I (D_{4h} $^1A_{1g}$)	**II** (C_{3v} $^1A_1$)	**III** (C_s $^1A'$)	**IV** (C_s $^1A'$)	**V** (C_s $^3A'$)	**VI** (D_{4h} $^3A_{1g}$)
E=B	0.0	1.1	–	–	22.0	22.7
E=Al	0.0	2.2	2.7	7.0	13.4	17.9*
E=Ga	0.0	1.8	2.8	7.5	14.0	7.9*
E=In	1.7	0.02	0.0	4.8	10.4	4.3*
E=Tl	4.8	1.5	0.0	–	10.4	3.1*

Figure S1. The low-lying energy isomers of E_2Na_4 are obtained at the PBE0/def2-TZVP level, and their relative energies in kcal/mol are computed at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level and corrected by zero-point corrections of PBE0/def2-TZVP. The point group and spectroscopic states were given in parenthesis. "–" represents that the structure does not exist. *Lower symmetry compared to D_{4h}.



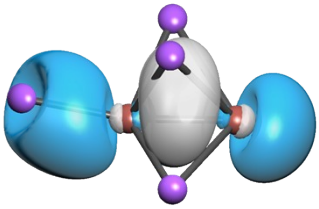
6c-2e σ bond
ON=1.90

2 × 6c-2e π bond
ON=1.88,1.90

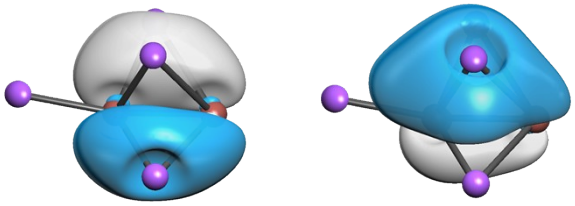
6c-2e σ bond
ON=1.96

6c-2e σ bond
ON=1.94

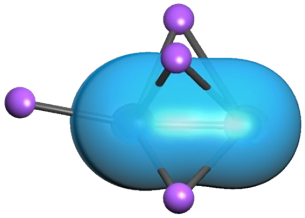
Figure S2. AdNDP of C_s symmetry global minimum Tl_2Li_4 (**II**) computed at the CCSD/def2-TZVP level. ON refers to the occupation number.



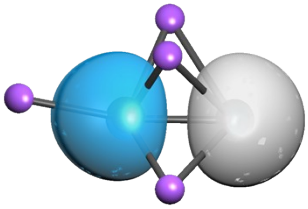
6c-2e σ bond
ON=1.89



2 × 6c-2e π bond
ON=1.88~1.89



6c-2e σ bond
ON=1.95



6c-2e σ bond
ON=1.92~1.94

Figure S3. AdNDP of C_s symmetry global minimum Tl_2Na_4 (**III**) computed at the CCSD/def2-TZVP level. ON refers to the occupation number.

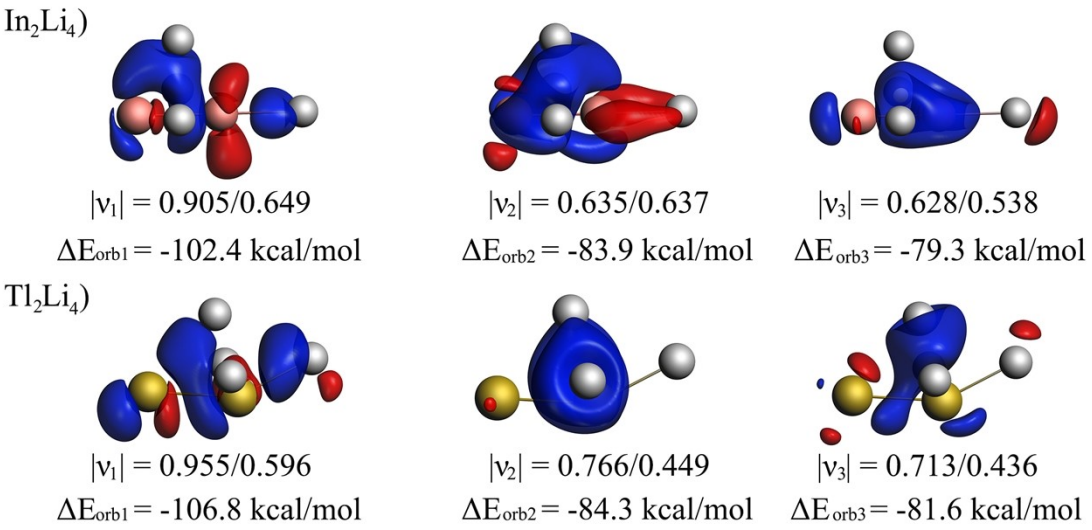


Figure S4. Plot of deformation densities $\Delta\rho_{1\text{-}3}$ of the pairwise orbital interactions among E^{2-} (Quartet), ELi^{-} (Quartet), Li_3^{3+} (Singlet) fragments in E_2Li_4 (E = In, Tl), associated interaction energies ΔE_{orb} (in kcal/mol) and eigenvalues ν and the alpha and beta eigenvalues are given in before and after slash. The eigenvalues ν indicate the size of the charge flow, and the direction of charge flow is red→blue.

Table S1. EDA-NOCV results of E_2Li_4 using the interacting fragments (two E^{2-} and one Li_4^{4+}) at the BP86/TZ2P level of theory. Energy values are given in kcal/mol.

	E^{2-} (Doublet) + E^{2-} (Doublet) + Li_4^{4+} (Singlet)				
	E = B	E = Al	E = Ga	E = In	E = Tl
ΔE_{int}	-1682.6	-1352.9	-1368.8	-1311.1	-1301.0
ΔE_{Pauli}	796.1	401.3	475.6	441.0	413.5
ΔE_{elstat}[a]	-1954.9 (78.9%)	-1381.4 (78.7%)	-1466.8 (79.5%)	-1372.1 (78.4%)	-1340.7 (78.2%)
ΔE_{orb}[a]	-523.8 (21.1%)	-372.6 (21.3%)	-377.5 (19.5%)	-380.0 (21.6%)	-373.7 (21.8%)
ΔE_{orb1}[b]	-327.2 (62.5%)	-149.3 (40.1%)	-174.0 (46.1%)	-143.1 (37.7%)	-153.9 (41.2%)
ΔE_{orb2}[b]	-92.9 (17.7%)	-113.6 (30.5%)	-92.9 (24.6%)	-133.6 (35.2%)	-106.2 (28.4%)
ΔE_{orb3}[b]	-63.4 (12.1%)	-96.3 (25.8%)	-91.1 (24.1%)	-88.3 (23.2%)	-97.7 (26.1%)
$\Delta E_{orb(rest)}$[b]	-40.2 (7.7%)	-13.7 (3.6%)	-19.8 (5.2%)	-15.6 (4.0%)	-16.8 (4.4%)

[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$

[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}

Table S2. EDA-NOCV results of E_2Li_4 using the interacting fragments (two E^{2-} and one Li_4^{4+}) at the PBE0/TZ2P level of theory. Energy values are given in kcal/mol.

	E^{2-} (Quartet) + E^{2-} (Quartet) + Li_4^{4+} (Singlet)				
	E = B	E = Al	E = Ga	E = In	E = Tl
ΔE_{int}	-1673.5	-1359.6	-1372.8	-1317.2	-1306.3
ΔE_{Pauli}	718.6	402.3	463.0	419.2	400.8
ΔE_{elstat}[a]	-1960.2 (81.9%)	-1408.8 (80.0%)	-1487.2 (81.0%)	-1398.0 (80.5%)	-1360.2 (79.7%)
ΔE_{orb}[a]	-431.9 (18.1%)	-353.0 (20.0%)	-348.6 (19.0%)	-338.4 (19.5%)	-346.9 (20.3%)
ΔE_{orb1}[b]	-253.7 (58.7%)	-149.3 (42.3%)	-145.9 (41.9%)	-134.0 (39.6%)	-130.9 (37.7%)
ΔE_{orb2}[b]	-71.3 (16.5%)	-95.5 (27.1%)	-93.6 (26.8%)	-95.6 (28.2%)	-100.8 (29.1%)
ΔE_{orb3}[b]	-71.3 (16.5%)	-95.5 (27.1%)	-93.6 (26.8%)	-95.6 (28.2%)	-100.8 (29.1%)
$\Delta E_{orb(rest)}$[b]	-35.6 (8.3%)	-12.8 (3.6%)	-15.6 (4.5%)	-13.5 (4.0%)	-14.4 (4.2%)

[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.

[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

Table S3. EDA-NOCV results of E_2Li_4 using the interacting fragments (two E^{2-} and one Li_4^{4+}) at the PBE0/TZ2P level of theory. Energy values are given in kcal/mol.

	E^{2-} (Doublet) + E^{2-} (Doublet) + Li_4^{4+} (Singlet)				
	E=B	E=Al	E=Ga	E=In	E=Tl
ΔE_{int}	-1709.0	-1388.5	-1401.9	-1343.3	-1323.0
ΔE_{Pauli}	836.7	395.6	423.0	401.4	401.7
ΔE_{elstat}[a]	-1980.6 (77.8%)	-1398.1 (77.9%)	-1424.9 (78.1%)	-1351.9 (77.5%)	-1341.8 (77.8%)
ΔE_{orb}[a]	-565.3 (22.2%)	-386.0 (22.1%)	-399.9 (21.9%)	-392.8 (22.5%)	-383.0 (22.2%)
ΔE_{orb1}[b]	-351.9 (62.3%)	-142.2 (36.8%)	-157.4 (39.4%)	-156.7 (39.9%)	-162.9 (42.5%)
ΔE_{orb2}[b]	-105.2 (18.6%)	-118.3 (30.7%)	-135.5 (33.9%)	-125.7 (32.0%)	-102.8 (26.8%)
ΔE_{orb3}[b]	-74.8 (13.2%)	-112.6 (29.2%)	-90.6 (22.7%)	-94.7 (24.1%)	-98.6 (25.7%)
$\Delta E_{orb(rest)}$[b]	-33.4 (5.9%)	-13.0 (3.4%)	-15.6 (4.0%)	-16.2 (4.1%)	-18.7 (4.9%)

[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$.

[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

Table S4. EDA-NOCV results of E_2Li_4 using the interacting fragments (one E^{2-}, one ELi^- and one Li_3^{3+}) at the BP86/TZ2P level of theory. Energy values are given in kcal/mol.

	E^{2-} (Doublet) + ELi^- (Doublet) + Li_3^{3+} (Singlet)	
	E = In	E = Tl
ΔE_{int}	-836.5	-836.6
ΔE_{Pauli}	335.6	276.5
ΔE_{elstat}[a]	-841.0 (71.8%)	-800.1 (71.9%)
ΔE_{orb}[a]	-331.0 (28.2%)	-312.9 (28.1%)
ΔE_{orb1}[b]	-173.0 (52.3%)	-169.9 (54.3%)
ΔE_{orb2}[b]	-78.0 (23.5%)	-83.1 (26.5%)
ΔE_{orb3}[b]	-66.8 (20.2%)	-48.1 (15.4%)
$\Delta E_{orb(rest)}$[b]	-13.8 (4.1%)	-12.5 (3.9%)

[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$

[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}

Table S5. Smallest frequencies (V_{min}, cm^{-1}), NPA charges (Q, |e|), Bonding properties (B, Wiberg bond index (WBI) in parenthesis and bond distances (Å)) of the D_{4h} symmetry E_2Na_4 obtained at the CCSD/def2-TZVP level.

E_2Na_4	V_{min}	Q_E	Q_{Na}	B_{E-E}	B_{E-Na}	B_{Na-Na}
E=B	48.3	-1.26	0.63	1.561 (2.64)	2.601 (0.17)	3.508 (0.08)
E=Al	54.0	-1.12	0.56	2.472 (2.15)	3.081 (0.22)	3.991 (0.07)
E=Ga	55.1	-1.07	0.54	2.391 (2.15)	3.034 (0.22)	3.943 (0.08)
E=In	41.2	-1.21	0.60	2.736 (2.22)	3.183 (0.20)	4.065 (0.07)
E=Tl	34.8	-1.04	0.52	3.757 (1.18)	3.262 (0.28)	3.771 (0.03)

Table S6. Vibrational spectrum of B_2Li_4 calculated by PBE0/def2-TZVP and CCSD(T)/def2-TZVP (in parenthesis).

Frequency, cm^{-1}	IR intensities (KM/Mole),
148.4461(141.9035)	0.0000(0.0000)
226.2009(219.0153)	0.2196(0.0000)
226.2009(219.0167)	0.2196(0.0000)
254.1325(247.6765)	90.1915(0.0000)
270.8825(266.8881)	0.0000(0.0000)
340.2450(344.2427)	0.0000(0.0000)
340.2450(344.2429)	0.0000(0.0000)
450.9756(431.0406)	0.0000(0.0000)
466.3722(449.6721)	0.0000(0.0000)
558.9979(543.8807)	264.8556(0.0000)
558.9979(543.8813)	264.8556(0.0000)
1190.6582(1154.2719)	0.0000(0.0000)

Table S7. Vibrational spectrum of Al_2Li_4 calculated by PBE0/def2-TZVP and CCSD(T)/def2-TZVP (in parenthesis).

Frequency, cm^{-1}	IR intensities (KM/Mole),
116.6634(116.5702)	0.1557(0.0000)
116.6634(116.5711)	0.1557(0.0000)
162.3540(158.7801)	0.0000(0.0000)
167.6475(160.3224)	0.0000(0.0000)
173.3738(175.6397)	0.0000(0.0000)
173.3739(195.9869)	0.0000(0.0000)
178.0446(195.9875)	2.8691(0.0000)
296.6174(290.4548)	0.0000(0.0000)
350.5615(331.7219)	0.0000(0.0000)
362.9617(356.0872)	176.0876(0.0000)
362.9617(356.0872)	176.0876(0.0000)
397.1194(391.7274)	0.0000(0.0000)

Table S8. Vibrational spectrum of Ga_2Li_4 calculated by PBE0/def2-TZVP and CCSD(T)/def2-TZVP (in parenthesis).

Frequency, cm^{-1}	IR intensities (KM/Mole),
119.4709(122.3917)	0.1042(0.0000)
119.4709(122.4072)	0.1042(0.0000)
134.1475(140.3968)	0.0000(0.0000)
134.1475(150.3889)	0.0000(0.0000)
134.9629(155.3284)	0.3210(0.0000)
158.1822(155.3492)	0.0000(0.0000)
171.1501(169.5822)	0.0000(0.0000)
214.9063(230.0906)	0.0000(0.0000)
341.5126(333.1456)	142.6419(0.0000)
341.5126(338.0040)	142.6419(0.0000)
349.0849(338.0066)	0.0000(0.0000)
357.0215(347.2164)	0.0000(0.0000)

Table S9. Vibrational spectrum of In_2Li_4 calculated by PBE0/def2-TZVP and CCSD(T)/def2-TZVP (in parenthesis).

Frequency, cm^{-1}	IR intensities (KM/Mole),
92.2437(97.7062)	0.0000(0.0000)
92.2437(97.7158)	0.0000(0.0000)
95.6407(121.9416)	0.0000(0.0000)
101.6047(135.5019)	0.0267(0.0000)
101.6048(137.4641)	0.0267(0.0000)
127.5439(137.4738)	0.0029(0.0000)
162.7177(150.7678)	0.0000(0.0000)
186.0464(167.6527)	0.0000(0.0000)
314.7260(310.9896)	107.1652(0.0000)
314.7260(310.9912)	107.1653(0.0000)
334.0436(314.7015)	0.0000(0.0000)
340.5494(324.2662)	0.0000(0.0000)

Table S10. Vibrational spectrum of Tl_2Li_4 calculated by PBE0/def2-TZVP and CCSD(T)/def2-TZVP (in parenthesis).

Frequency, cm^{-1}	IR intensities (KM/Mole),
41.3281(45.3668)	0.0000(0.0000)
83.2822(97.9906)	1.2871(0.0000)
130.8934(98.0017)	0.3924(0.0000)
130.8934(108.2840)	0.3924(0.0000)
160.6110(108.3016)	0.0000(0.0000)
179.4269(111.4199)	0.0000(0.0000)
179.4269(143.0439)	0.0000(0.0000)
228.6324(190.4997)	0.0000(0.0000)
232.5106(299.7020)	0.0000(0.0000)
258.3857(299.7044)	36.8665(0.0000)
258.3857(305.2934)	36.8666(0.0000)
264.9977(313.0689)	0.0000(0.0000)

II. Coordinates obtained at the CCSD(T)/def2-TZVP level.

I-B_2Li_4

5	0.000000000	0.000000000	0.772029000
5	0.000000000	0.000000000	-0.772029000
3	0.000000000	2.078571000	0.000000000
3	2.078571000	0.000000000	0.000000000
3	0.000000000	-2.078571000	0.000000000
3	-2.078571000	0.000000000	0.000000000

I-Al_2Li_4

13	0.000000000	0.000000000	1.250270000
13	0.000000000	0.000000000	-1.250270000
3	0.000000000	2.396899000	0.000000000
3	2.396899000	0.000000000	0.000000000
3	0.000000000	-2.396899000	0.000000000
3	-2.396899000	0.000000000	0.000000000

I-Ga_2Li_4

31	0.000000000	0.000000000	1.204830000
31	0.000000000	0.000000000	-1.204830000
3	0.000000000	2.366619000	0.000000000
3	2.366619000	0.000000000	0.000000000
3	0.000000000	-2.366619000	0.000000000
3	-2.366619000	0.000000000	0.000000000

I-In_2Li_4

49	0.000000000	0.000000000	1.405634000
49	0.000000000	0.000000000	-1.405634000
3	1.719015000	-1.719015000	0.000000000
3	-1.719015000	-1.719015000	0.000000000
3	-1.719015000	1.719015000	0.000000000
3	1.719015000	1.719015000	0.000000000

I-Tl_2Li_4

81	0.000000000	0.000000000	1.456532000
81	0.000000000	0.000000000	-1.456532000
3	1.694921000	-1.694921000	0.000000000
3	-1.694921000	-1.694921000	0.000000000
3	-1.694921000	1.694921000	0.000000000
3	1.694921000	1.694921000	0.000000000

II-In_2Li_4

49	0.383635000	1.234226000	0.000000000

49	-0.265487000	-1.498422000	0.000000000
3	0.990204000	3.887718000	0.000000000
3	-2.388986000	0.496973000	0.000000000
3	-0.265487000	-0.034741000	2.418032000
3	-0.265487000	-0.034741000	-2.418032000

III-Tl_2Li_4

81	0.357924000	1.293919000	0.000000000
81	-0.209082000	-1.551049000	0.000000000
3	-0.541112000	3.831285000	0.000000000
3	-2.395402000	0.934680000	0.000000000
3	-0.541112000	1.088271000	2.490134000
3	-0.541112000	1.088271000	-2.490134000

I-B_2Na_4

5	0.000000000	0.000000000	0.780585000
5	0.000000000	0.000000000	-0.780585000
11	0.000000000	2.480699000	0.000000000
11	2.480699000	0.000000000	0.000000000
11	0.000000000	-2.480699000	0.000000000
11	-2.480699000	0.000000000	0.000000000

I-Al_2Na_4

13	0.000000000	0.000000000	1.235969000
13	0.000000000	0.000000000	-1.235969000
11	0.000000000	2.821898000	0.000000000
11	2.821898000	0.000000000	0.000000000
11	0.000000000	-2.821898000	0.000000000
11	-2.821898000	0.000000000	0.000000000

I-Ga_2Na_4

31	0.000000000	0.000000000	1.195345000
31	0.000000000	0.000000000	-1.195345000
11	0.000000000	2.788275000	0.000000000
11	2.788275000	0.000000000	0.000000000
11	0.000000000	-2.788275000	0.000000000
11	-2.788275000	0.000000000	0.000000000

I-In_2Na_4

49	0.000000000	0.000000000	1.367853000
49	0.000000000	0.000000000	-1.367853000
11	2.032602000	-2.032602000	0.000000000
11	-2.032602000	-2.032602000	0.000000000
11	-2.032602000	2.032602000	0.000000000

11	2.032602000	2.032602000	0.000000000

I-Tl_2Na_4

81	0.000000000	0.000000000	1.878708000
81	0.000000000	0.000000000	-1.878708000
11	1.885451000	-1.885451000	0.000000000
11	-1.885451000	-1.885451000	0.000000000
11	-1.885451000	1.885451000	0.000000000
11	1.885451000	1.885451000	0.000000000

III-In_2Na_4

49	0.615490000	0.892765000	0.000000000
49	-0.236109000	-1.794824000	0.000000000
11	1.350863000	3.844916000	0.000000000
11	-2.568614000	0.598113000	0.000000000
11	-0.236109000	-0.212383000	2.792737000
11	-0.236109000	-0.212383000	-2.792737000

III-Tl_2Na_4

81	0.704428000	0.972723000	0.000000000
81	-0.395848000	-1.717959000	0.000000000
11	0.985804000	3.993314000	0.000000000
11	-2.466383000	1.153277000	0.000000000
11	-0.395848000	0.170527000	2.775936000
11	-0.395848000	0.170527000	-2.775936000