

Electronic supplementary Information:

**Can we quantitatively evaluate the mutual impacts of
intramolecular metal-ligand bonds the same as intermolecular
noncovalent bonds?**

*Samaneh Sanei Movafagh and Sadegh Salehzadeh**

Department of Inorganic Chemistry, Faculty of Chemistry and Petroleum Sciences, Bu-Ali Sina
University, Hamedan, Iran.

*Corresponding author. E-mail addresses: saleh@basu.ac.ir

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1. Stabilization energies and cooperative energies

On the basis of equation (3) of the paper, the larger difference between the stabilization energy (SE) of the ternary (or three-component) system and the sum of the stabilization energies of related binary (or two-component) systems corresponds to a higher degree of cooperativity or anticooperativity of bonds. Figure 1 of the paper, illustrates the change in energies upon the formation of AB, BC and ABC systems. As can be seen, in agreement with Hess's law, the sum of -BDEs for A-B and AB-C bonds is equal to that of -BDEs for B-C and A-BC bonds and both are equal to the total stabilization energy of a noncyclic ABC system (SE_{ABC}).

Thus, we have:

$$-BDE_{A-B} + (-BDE_{AB-C}) = -BDE_{B-C} + (-BDE_{A-BC}) \quad (S1)$$

$$SE_{ABC} = -BDE_{A-B} + (-BDE_{AB-C}) \quad (S2)$$

$$SE_{ABC} = -BDE_{B-C} + (-BDE_{A-BC}) \quad (S3)$$

The following equation can also be derived from the summation of eqs. (S2) and (S3):

$$SE_{ABC} = \frac{1}{2} \{(-BDE_{AB-C}) + (-BDE_{A-BC}) + (-BDE_{A-B}) + (-BDE_{B-C})\} \quad (S4)$$

As it is clear in the Figure 1 of the paper, $-BDE_{A-B}$ and $-BDE_{B-C}$ are equal to SE_{AB} and SE_{BC} , respectively, and we can rewrite the eq. (S4) as below:

$$SE_{ABC} = \frac{1}{2} \{-BDE_{AB-C} + (-BDE_{A-BC}) + SE_{AB} + SE_{BC}\} \quad (S5)$$

Obviously, the total stabilization energy of any ABC system, as it is clear in Figure 1, can be simply calculated by the known eq. (4) of the paper. However, the useful eq. (S5), proves that the total stabilization of any noncyclic ABC system regardless of what is the nature of the bond between A, B and C, directly depends on the stability of corresponding AB and BC systems and also BDEs of new bonds A-BC and AB-C bonds.

Thus, the difference between the stabilization energy of an ABC system and the sum of the stabilization energies of corresponding AB and BC systems depends only on the values of BDEs

for A–BC and AB–C bonds. In other words, when the BDEs of new A–BC and AB–C bonds are larger than those of previous A–B and B–C bonds, the stabilization of the ABC system will be larger than the sum of stabilization energies for AB and BC systems. Now, let us to rewrite eq. (S1) as below:

$$BDE_{A-B} - BDE_{A-BC} = BDE_{B-C} - BDE_{AB-C} \quad (S6) \text{ (This is the equation 7 of the paper)}$$

Let us name the left and right sides of the above equation as ΔBDE_{A-B} and ΔBDE_{B-C} , respectively. Now the question is “what can we name the equal differences given by the eq. (S6)?”

We have:

$$\begin{aligned} \Delta BDE_{A-B} &= BDE_{A-B} - BDE_{A-BC} \\ &= [E_A + E_B - E_{AB}] - [E_A + E_{BC} - E_{ABC}] \\ &= E_{ABC} - E_{BC} - E_{AB} + E_B \end{aligned}$$

Also:

$$\begin{aligned} \Delta BDE_{B-C} &= BDE_{B-C} - BDE_{AB-C} \\ &= [E_B + E_C - E_{BC}] - [E_{AB} + E_C - E_{ABC}] \\ &= E_{ABC} - E_{BC} - E_{AB} + E_B \end{aligned}$$

We note that the above results once again confirm the eq. (S6).

On the other hand, we can rewrite/expand the eq. (3) of the paper, as below:

$$\begin{aligned} E_{\text{coop}} &= [E_{ABC} - E_A - E_B - E_C] - \\ &[(E_{AB} - E_A - E_B) + (E_{BC} - E_B - E_C)] \\ &= E_{ABC} - E_{BC} - E_{AB} + E_B \end{aligned}$$

The result is the same with that we obtained above for ΔBDE_{A-B} or ΔBDE_{B-C} differences. Thus, now we can write the important equation below:

$$E_{\text{coop}} = \Delta BDE_{A-B} = \Delta BDE_{B-C} \quad (S7) \text{ (This is the equation 8 of the paper)}$$

2. Interaction energies and cooperative energies

The total interaction energy of an ABC triad can be calculated using the following known equations (see ref.103 of the paper)

$$IE_{\text{total}}^{\text{ABC}} = E_{\text{ABC}} - (E_{\text{A}}^{\text{ABC}} + E_{\text{B}}^{\text{ABC}} + E_{\text{C}}^{\text{ABC}}) \quad (\text{S8})$$

$$IE_{\text{total}}^{\text{ABC}} = \frac{1}{2}(IE_{\text{A-B}}^{\text{ABC}} + IE_{\text{A-BC}}^{\text{ABC}} + IE_{\text{B-C}}^{\text{ABC}} + IE_{\text{AB-C}}^{\text{ABC}}) \quad (\text{S9})$$

The most important advantage of eq. (S9) corresponds to the fact that we can understand better the origin of the cooperativity of bonds as we have a complete list of direct interactions.

We have to admit that in the present work, we accidentally found that the following simple equations also give the total interaction energy of a noncyclic ABC system (i.e. the eqs. (S8) to (S11) all give the same value).

$$IE_{\text{total}}^{\text{ABC}} = IE_{\text{A-B}}^{\text{ABC}} + IE_{\text{AB-C}}^{\text{ABC}} \quad (\text{S10})$$

$$IE_{\text{total}}^{\text{ABC}} = IE_{\text{B-C}}^{\text{ABC}} + IE_{\text{A-BC}}^{\text{ABC}} \quad (\text{S11})$$

However, we could also simply prove the above equations. Let us to rewrite the eq. (S10) as below:

$$\begin{aligned} IE_{\text{total}}^{\text{ABC}} &= [E_{\text{AB}}^{\text{ABC}} - E_{\text{A}}^{\text{ABC}} - E_{\text{B}}^{\text{ABC}}] + [E_{\text{ABC}}^{\text{ABC}} - E_{\text{AB}}^{\text{ABC}} - E_{\text{C}}^{\text{ABC}}] \\ &= E_{\text{ABC}} - E_{\text{A}}^{\text{ABC}} - E_{\text{B}}^{\text{ABC}} - E_{\text{C}}^{\text{ABC}} \end{aligned}$$

Yes, it is the same as eq. (S8). Similarly, we can rewrite the eq. (S11) as below:

$$\begin{aligned} IE_{\text{ABC}}^{\text{total}} &= [E_{\text{BC}}^{\text{ABC}} - E_{\text{B}}^{\text{ABC}} - E_{\text{C}}^{\text{ABC}}] + [E_{\text{ABC}} - E_{\text{A}}^{\text{ABC}} - E_{\text{BC}}^{\text{ABC}}] \\ &= E_{\text{ABC}} - E_{\text{A}}^{\text{ABC}} - E_{\text{B}}^{\text{ABC}} - E_{\text{C}}^{\text{ABC}} \end{aligned}$$

Thus, once again we arrived at eq. (S8), indicating that eqs. (S8) to (S11) all give the same value for the total interaction energy of a noncyclic ABC system. Obviously, from eqs. (S10) and (S11) we can conclude that always there is the following relation:

$$IE_{\text{B-C}}^{\text{ABC}} + IE_{\text{A-BC}}^{\text{ABC}} = IE_{\text{A-B}}^{\text{ABC}} + IE_{\text{AB-C}}^{\text{ABC}} \quad (\text{S12})$$

Now we can rewrite it as below:

$$IE_{A-BC}^{ABC} - IE_{A-B}^{ABC} = IE_{AB-C}^{ABC} - IE_{B-C}^{ABC}$$

(S13) (This is the equation 9 of the paper)

Table S1 Corrected^a bond dissociation energies, cooperative energies (kcal/mol) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds upon the formation of H₃N...ClF...HF (**1**) and H₃N...HF...ClF (**1'**) triads compared here^b

Compound	$-\text{BDE}_{\text{A-B}}$	$-\text{BDE}_{\text{A-BC}}$	$-\text{BDE}_{\text{B-C}}$	$-\text{BDE}_{\text{AB-C}}$	$\text{SE}_{\text{ABC}}^{\text{c}}$	$\text{E}_{\text{coop}}^{\text{d}}$	$\% \Delta \text{BDE}_{\text{A-B}}^{\text{e}}$	$\% \Delta \text{BDE}_{\text{B-C}}^{\text{e}}$
1	-17.84	-25.65	-1.65	-9.46	-27.30	-7.81	44%	473%
	<i>-17.42</i>	<i>-25.18</i>	<i>-1.64</i>	<i>-9.40</i>	<i>-26.82</i>	<i>-7.76</i>	<i>44%</i>	<i>473%</i>
1'	-14.15	-20.35	-2.45	-8.65	-22.80	-6.20	44%	253%
	<i>-13.87</i>	<i>-20.27</i>	<i>-2.78</i>	<i>-9.18</i>	<i>-23.05</i>	<i>-6.40</i>	<i>46%</i>	<i>230%</i>

^a Corrected for basis set superposition errors (BSSE).

^b The data calculated at BP86-D3(BJ)/aug-cc-pVTZ level of theory are shown as plain text and those at BP86-D3(BJ)/def2-TZVP level are in italic.

^c See eqs. (4) of the paper, (S2), (S3), (S4) and (S5) that all give the same value.

^d See eqs. (3) and (8) of the paper.

^e $\% \Delta \text{BDE}_{\text{A-B}} = \frac{|\text{E}_{\text{coop}}|}{\text{BDE}_{\text{A-B}}} \times 100$, $\% \Delta \text{BDE}_{\text{B-C}} = \frac{|\text{E}_{\text{coop}}|}{\text{BDE}_{\text{B-C}}} \times 100$

Table S2. Corrected^a calculated values for interaction energies (IE, kcal/mol) between the defined fragments frozen in the optimized geometry of the H₃N...ClF...HF (**1**) and H₃N...HF...ClF (**1'**) triads compared here, and related IE_{total}^{ABC}, ΔIE_{coop}, %ΔIE_{A-B} and %ΔIE_{B-C} values^b

Compound	IE _{A-B} ^{ABC}	IE _{A-BC} ^{ABC}	IE _{B-C} ^{ABC}	IE _{AB-C} ^{ABC}	IE _{total} ^{ABC} ^c	ΔIE _{coop} ^d	%ΔIE _{A-B} ^e	%ΔIE _{B-C} ^e
1	-24.28	-33.23	-1.94	-10.89	-35.17	-8.95	37%	461%
	<i>-23.11</i>	<i>-32.27</i>	<i>-1.68</i>	<i>-10.84</i>	<i>-33.95</i>	<i>-9.16</i>	40%	545%
1'	-18.72	-27.31	-2.22	-10.81	-29.53	-8.59	46%	387%
	<i>-22.85</i>	<i>-31.89</i>	<i>-1.71</i>	<i>-10.75</i>	<i>-33.60</i>	<i>-9.04</i>	40%	529%

^a Corrected for basis set superposition errors (BSSE).

^b The data calculated at BP86-D3(BJ)/aug-cc-pVTZ level of theory are shown as plain text and those at BP86-D3(BJ)/def2-TZVP level are in italic

^c See the eqs. (S8), (S9), (S10) and (S11) that all give the same value.

^d See eq. (10) of the paper.

$$\text{e } \% \Delta \text{IE}_{A-B} = \frac{|\Delta \text{IE}_{\text{coop}}|}{\text{IE}_{A-B}^{\text{ABC}}} \times 100, \% \Delta \text{IE}_{B-C} = \frac{|\Delta \text{IE}_{\text{coop}}|}{\text{IE}_{B-C}^{\text{ABC}}} \times 100$$

Table S3. The calculated A–B and B–C bond lengths (Å), in the triads **1** to **6** and related dyads, along with their differences (Δr)

<i>Mp2/aug-cc-pVTZ</i>						
compound	Triad		Dyad		Δr	
	$r_{(A-B)}$	$r_{(B-C)}$	$r_{(A-B)}$	$r_{(B-C)}$	$\Delta r_{(A-B)}$	$\Delta r_{(B-C)}$
1	2.074	1.646	2.232	1.939	-0.158	-0.293
2	1.748	1.552	2.361	1.773	-0.613	-0.221
3	1.769	1.552	1.835	1.773	-0.066	-0.221
4	2.423	2.317	2.538	2.411	-0.115	-0.094
5	2.024	1.765	2.044	1.990	-0.020	-0.225
6	1.743	1.966	1.712	1.933	0.031	0.033
<i>BP86-D3(BJ)/aug-cc-pVTZ</i>						
1	2.104	1.601	2.208	1.924	-0.104	-0.323
2	1.723	1.409	2.350	1.668	-0.627	-0.259
3	1.706	1.555	1.778	1.668	-0.072	-0.113
4	2.392	2.280	2.469	2.387	-0.077	-0.107
5	2.008	1.646	2.033	1.825	-0.025	-0.179
6	1.752	1.942	1.712	1.904	0.040	0.038

Table S4. Corrected^a bond dissociation energies, cooperative energies (kcal/mol) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds upon the formation of triads studied here^b

Compound	$-BDE_{A-B}$	$-BDE_{A-BC}$	$-BDE_{B-C}$	$-BDE_{AB-C}$	SE_{ABC}^c	E_{coop}^d	$\% \Delta BDE_{A-B}^e$	$\% \Delta BDE_{B-C}^e$
1	-17.42	-25.18	-1.64	-9.40	-26.82	-7.76	44%	473%
	-9.70	-15.19	-1.69	-7.18	-16.88	-5.49	56%	325%
2	-4.84	-9.74	-9.43	-14.33	-19.17	-4.90	101%	52%
	-4.68	-8.05	-8.11	-11.48	-16.16	-3.37	72%	41%
3	-7.41	-10.75	-8.82	-12.16	-19.57	-3.34	45%	38%
	-6.82	-9.46	-8.10	-10.74	-17.56	-2.64	39%	33%
4	-12.40	-16.10	-2.39	-6.09	-18.49	-3.70	30%	155%
	-6.18	-8.34	-1.38	-3.54	-9.72	-2.16	35%	156%
5	-17.73	-20.96	-3.79	-7.02	-24.75	-3.23	18%	85%
	-17.65	-20.32	-3.47	-6.14	-23.80	-2.67	15%	77%
6	-30.90	-24.19	-38.54	-31.83	-62.73	6.71	22%	17%
	-30.55	-24.66	-36.18	-30.29	-60.84	5.89	19%	16%

^a Corrected for basis set superposition errors (BSSE).

^b The data calculated at BP86-D3(BJ)/def2-TZVP level of theory are shown as plain text and those at MP2/def2-TZVP level are in bold.

^c See eqs. (4) of the paper, (S2), (S3), (S4) and (S5), that all give the same value.

^d See eqs. (3) and (8) of the paper, that both give the same value.

$$^e \% \Delta BDE_{A-B} = \frac{|E_{coop}|}{BDE_{A-B}} \times 100, \% \Delta BDE_{B-C} = \frac{|E_{coop}|}{BDE_{B-C}} \times 100$$

Table S5. Corrected^a calculated values for interaction energies (IE, kcal/mol) between the defined fragments frozen in the optimized geometry of the triads studied here, and related $IE_{\text{total}}^{\text{ABC}}$, ΔIE_{coop} , $\% \Delta IE_{\text{A-B}}$ and $\% \Delta IE_{\text{B-C}}$ values^b

Compound	$IE_{\text{A-B}}^{\text{ABC}}$	$IE_{\text{A-BC}}^{\text{ABC}}$	$IE_{\text{B-C}}^{\text{ABC}}$	$IE_{\text{AB-C}}^{\text{ABC}}$	$IE_{\text{total}}^{\text{ABC}}$ ^c	ΔIE_{coop} ^d	$\% \Delta IE_{\text{A-B}}$ ^e	$\% \Delta IE_{\text{B-C}}$ ^e
1	-23.11	-32.27	-1.68	-10.84	-33.95	-9.16	40%	545%
	-12.88	-20.81	-1.21	-9.14	-22.02	-7.93	61%	655%
2	-20.13	-29.00	-9.83	-18.70	-38.83	-8.87	44%	90%
	-19.12	-26.62	-7.98	-15.48	-34.60	-7.50	39%	94%
3	-7.68	-11.38	-9.48	-13.18	-20.86	-3.70	48%	39%
	-6.89	-9.85	-8.23	-11.19	-18.08	-2.96	43%	36%
4	-14.50	-18.77	-2.26	-6.53	-21.03	-4.27	29%	189%
	-6.70	-9.67	-1.15	-4.12	-10.82	-2.97	44%	258%
5	-17.87	-21.42	-3.82	-7.37	-25.24	-3.55	20%	93%
	-17.79	-20.74	-3.33	-6.28	-24.07	-2.95	17%	89%
6	-31.16	-24.61	-38.72	-32.17	-63.33	6.55	21%	17%
	-30.84	-25.07	-36.35	-30.58	-61.42	5.77	19%	16%

^a Corrected for basis set superposition errors (BSSE).

^b The data calculated at BP86-D3(BJ)/def2-TZVP level of theory are shown as plain text and those at MP2/def2-TZVP level are in bold.

^c See the eqs. (S8), (S9), (S10) and (S11) that all give the same value.

^d See eq. (10) of the paper.

$$\text{}^e \% \Delta IE_{\text{A-B}} = \frac{|\Delta IE_{\text{coop}}|}{IE_{\text{A-B}}^{\text{ABC}}} \times 100, \text{}^e \% \Delta IE_{\text{B-C}} = \frac{|\Delta IE_{\text{coop}}|}{IE_{\text{B-C}}^{\text{ABC}}} \times 100$$

Table S6. Uncorrected bond dissociation energies, cooperative energies (kcal/mol) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds upon the formation of triads studied here^a

Compound	$-BDE_{A-B}$	$-BDE_{A-BC}$	$-BDE_{B-C}$	$-BDE_{AB-C}$	SE_{ABC}^b	E_{coop}^c	$\% \Delta BDE_{A-B}^d$	$\% \Delta BDE_{B-C}^d$
1	-18.01	-25.86	-1.78	-9.63	-27.64	-7.85	44%	441%
	-11.82	-18.28	-2.59	-9.05	-20.87	-6.46	55%	249%
2	-4.66	-10.73	-9.02	-15.09	-19.75	-6.07	130%	67%
	-6.29	-11.16	-9.03	-13.90	-20.19	-4.87	77%	54%
3	-7.84	-11.27	-9.02	-12.45	-20.29	-3.43	43%	38%
	-7.95	-10.73	-9.03	-11.81	-19.76	-2.78	35%	31%
4	-12.27	-15.94	-2.74	-6.41	-18.68	-3.67	30%	134%
	-8.60	-11.36	-3.37	-6.13	-14.73	-2.76	32%	82%
5	-18.36	-21.69	-4.03	-7.36	-25.72	-3.33	18%	83%
	-18.67	-21.64	-4.18	-7.15	-25.82	-2.97	16%	71%
6	-31.56	-24.78	-39.01	-32.23	-63.79	6.78	21%	17%
	-31.31	-25.56	-36.83	-31.08	-62.39	5.75	18%	16%

^a The data calculated at BP86-D3(BJ)/aug-cc-pVTZ level of theory are shown as plain text and those at MP2/aug-cc-pVTZ level are in bold.

^b See eqs. (4) of the paper, (S2), (S3), (S4) and (S5), that all give the same value.

^c See eqs. (3) and (8) of the paper, that both give the same value.

$$^d \% \Delta BDE_{A-B} = \frac{|E_{coop}|}{BDE_{A-B}} \times 100, \quad \% \Delta BDE_{B-C} = \frac{|E_{coop}|}{BDE_{B-C}} \times 100$$

Table S7. Uncorrected calculated values for interaction energies (IE, kcal/mol) between the defined fragments frozen in the optimized geometry of the triads studied here, and related $IE_{\text{total}}^{\text{ABC}}$, ΔIE_{coop} , $\% \Delta IE_{\text{A-B}}$ and $\% \Delta IE_{\text{B-C}}$ values^a

Compound	$IE_{\text{A-B}}^{\text{ABC}}$	$IE_{\text{A-BC}}^{\text{ABC}}$	$IE_{\text{B-C}}^{\text{ABC}}$	$IE_{\text{AB-C}}^{\text{ABC}}$	$IE_{\text{total}}^{\text{ABC}}$ ^b	ΔIE_{coop} ^c	$\% \Delta IE_{\text{A-B}}$ ^d	$\% \Delta IE_{\text{B-C}}$ ^d
1	-24.48 -16.38	-33.41 -24.33	-2.11 -2.60	-11.04 -10.55	-35.52 -26.93	-8.93 -7.95	36% 48%	423% 306%
2	-21.39 -22.15	-30.42 -29.60	-10.18 -9.14	-19.21 -16.59	-40.60 -38.74	-9.03 -7.45	42% 34%	89% 82%
3	-8.21 -8.14	-11.93 -11.08	-9.73 -9.26	-13.45 -12.20	-21.66 -20.34	-3.72 -2.94	45% 36%	38% 32%
4	-14.47 -9.55	-18.55 -12.72	-2.74 -3.34	-6.82 -6.51	-21.29 -16.06	-4.08 -3.17	28% 33%	149% 95%
5	-18.53 -18.83	-22.16 -21.88	-4.09 -4.24	-7.72 -7.29	-26.25 -26.12	-3.63 -3.05	20% 16%	89% 72%
6	-31.78 -31.57	-25.17 -25.96	-39.19 -36.98	-32.58 -31.37	-64.36 -62.94	6.61 5.61	21% 18%	17% 15%

^a The data calculated at BP86-D3(BJ)/aug-cc-pVTZ level of theory are shown as plain text and those at MP2/aug-cc-pVTZ level are in bold.

^c See the eqs. (S8), (S9), (S10) and (S11) that all give the same value.

^d See eq. (10) of the paper.

$$\text{d } \% \Delta IE_{\text{A-B}} = \frac{|\Delta IE_{\text{coop}}|}{IE_{\text{A-B}}^{\text{ABC}}} \times 100, \% \Delta IE_{\text{B-C}} = \frac{|\Delta IE_{\text{coop}}|}{IE_{\text{B-C}}^{\text{ABC}}} \times 100$$

Table S8. Uncorrected bond dissociation energies, cooperative energies (kcal/mol) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds upon the formation of metal complexes studied here^a

Compound	$-BDE_{A-B}$	$-BDE_{A-BC}$	$-BDE_{B-C}$	$-BDE_{AB-C}$	SE_{ABC}^b	E_{coop}^c	$\% \Delta BDE_{A-B}^d$	$\% \Delta BDE_{B-C}^d$
7	-200.55	-210.08	-48.02	-57.55	-258.10	-9.53	5%	20%
	-191.48	-210.55	-34.95	-54.02	-245.50	-19.07	10%	55%
8^e	-	-	-	-	-322.06	-	-	-
	-	-	-	-	-456.36	-	-	-
9	-35.14	-20.05	-58.15	-43.06	-78.20	15.09	43%	26%
	-36.31	-23.33	-64.91	-51.93	-88.24	12.98	36%	20%
10	-200.33	-169.11	-75.71	-44.49	-244.82	31.22	16%	41%
	-183.24	-167.59	-59.81	-44.16	-227.40	15.65	9%	26%
11	-94.80	-52.48	-229.34	-187.02	-281.82	42.32	45%	18%
	-86.55	-59.88	-221.16	-194.49	-281.04	26.67	31%	12%
12	-198.76	-63.17	-525.54	-389.95	-588.71	135.59	68%	26%
	-176.22	-64.55	-516.08	-404.41	-580.63	111.67	63%	22%

^a The data calculated at BP86-D3(BJ)/def2-TZVP level of theory are shown as plain text and those at MP2/def2-TZVP level are in bold.

^b See eqs. (4) of the paper, (S2), (S3), (S4) and (S5), that all give the same value.

^c See eqs. (3) and (8) of the paper, that both give the same value.

^d $\% \Delta BDE_{A-B} = \frac{|E_{coop}|}{BDE_{A-B}} \times 100$, $\% \Delta BDE_{B-C} = \frac{|E_{coop}|}{BDE_{B-C}} \times 100$

^e The MP2 calculations for this compound were performed using the def2-SVP basis set.

Table S9. Uncorrected calculated values for interaction energies (IE, kcal/mol) between the defined fragments frozen in the optimized geometry of metal complexes studied here, and related $IE_{\text{total}}^{\text{ABC}}$, ΔIE_{coop} , $\% \Delta IE_{\text{A-B}}$ and $\% \Delta IE_{\text{B-C}}$ values^a

Compound	$IE_{\text{A-B}}^{\text{ABC}}$	$IE_{\text{A-BC}}^{\text{ABC}}$	$IE_{\text{B-C}}^{\text{ABC}}$	$IE_{\text{AB-C}}^{\text{ABC}}$	$IE_{\text{total}}^{\text{ABC}}$ ^b	ΔIE_{coop} ^c	$\% \Delta IE_{\text{A-B}}$ ^d	$\% \Delta IE_{\text{B-C}}$ ^d
7	-200.67	-212.32	-46.47	-58.12	-258.79	-11.65	6%	25%
	-191.61	-210.97	-35.23	-54.59	-246.20	-19.36	10%	55%
8^e	-146.12	-208.04	-152.61	-214.53	-360.65	-61.92	42%	41%
	-240.34	-266.09	-243.19	-268.94	-509.28	-25.75	11%	11%
9	-35.77	-23.62	-58.07	-45.92	-81.69	12.15	34%	21%
	-35.98	-27.13	-64.75	-55.90	-91.88	8.85	25%	14%
10	-202.52	-171.87	-75.88	-45.23	-247.75	30.65	15%	40%
	-184.91	-169.50	-60.04	-44.63	-229.54	15.41	8%	26%
11	-94.38	-53.54	-229.31	-188.47	-282.85	40.84	43%	18%
	-86.10	-61.08	-220.92	-195.90	-282.00	25.02	29%	11%
12	-197.32	-66.01	-525.08	-393.77	-591.09	131.31	66%	25%
	-174.24	-67.63	-514.92	-408.31	-582.55	106.61	61%	21%

^a The data calculated at BP86-D3(BJ)/def2-TZVP level of theory are shown as plain text and those at MP2/def2-TZVP level are in bold.

^b See the eqs. (S8), (S9), (S10) and (S11) that all give the same value.

^c See eq. (10) of the paper.

$$\text{d } \% \Delta IE_{\text{A-B}} = \frac{|\Delta IE_{\text{coop}}|}{IE_{\text{A-B}}^{\text{ABC}}} \times 100, \% \Delta IE_{\text{B-C}} = \frac{|\Delta IE_{\text{coop}}|}{IE_{\text{B-C}}^{\text{ABC}}} \times 100$$

^e The MP2 calculations for this compound were performed using the def2-SVP basis set.

Table S10. Uncorrected bond dissociation energies, cooperative energies (kcal/mol) and the percentages of changes in the bond dissociation energies of A–B and B–C bonds upon the formation of triads studied here^a

Compound	–BDE _{A–B}	–BDE _{A–BC}	–BDE _{B–C}	–BDE _{AB–C}	SE _{ABC} ^b	E _{Coop} ^c	%ΔBDE _{A–B} ^d	%ΔBDE _{B–C} ^d
1	–18.39	–26.32	–2.12	–10.05	–28.44	–7.93	43%	374%
	–11.48	–17.73	–2.22	–8.47	–19.95	–6.25	54%	281%
2	–5.16	–10.28	–9.84	–14.96	–20.12	–5.12	99%	52%
	–5.50	–10.17	–8.84	–13.51	–19.01	–4.67	85%	53%
3	–7.98	–11.40	–9.23	–12.65	–20.63	–3.42	43%	37%
	–7.44	–10.23	–8.84	–11.63	–19.07	–2.79	37%	32%
4	–13.33	–17.17	–2.90	–6.74	–20.07	–3.84	29%	132%
	–8.04	–10.58	–1.99	–4.53	–12.57	–2.54	32%	128%
5	–18.13	–21.39	–3.89	–7.15	–25.28	–3.26	18%	84%
	–18.22	–20.95	–3.69	–6.42	–24.64	–2.73	15%	74%
6	–30.97	–24.28	–38.69	–32.00	–62.97	6.69	22%	17%
	–30.74	–24.92	–36.44	–30.62	–61.36	5.82	19%	16%

^a The data calculated at BP86-D3(BJ)/def2-TZVP level of theory are shown as plain text and those at MP2/def2-TZVP level are in bold.

^b See eqs. (4) of the paper, (S2), (S3), (S4) and (S5), that all give the same value.

^c See eqs. (3) and (8) of the paper, that both give the same value.

$$\text{d } \% \Delta \text{BDE}_{\text{A–B}} = \frac{|E_{\text{coop}}|}{\text{BDE}_{\text{A–B}}} \times 100, \text{ \% } \Delta \text{BDE}_{\text{B–C}} = \frac{|E_{\text{coop}}|}{\text{BDE}_{\text{B–C}}} \times 100$$

Table S11. Uncorrected calculated values for interaction energies (IE, kcal/mol) between the defined fragments frozen in the optimized geometry of the triads studied here, and related $IE_{\text{total}}^{\text{ABC}}$, ΔIE_{coop} , $\% \Delta IE_{\text{A-B}}$ and $\% \Delta IE_{\text{B-C}}$ values^a

Compound	$IE_{\text{A-B}}^{\text{ABC}}$	$IE_{\text{A-BC}}^{\text{ABC}}$	$IE_{\text{B-C}}^{\text{ABC}}$	$IE_{\text{AB-C}}^{\text{ABC}}$	$IE_{\text{total}}^{\text{ABC}}$ ^b	ΔIE_{coop} ^c	$\% \Delta IE_{\text{A-B}}$ ^d	$\% \Delta IE_{\text{B-C}}$ ^d
1	-24.16	-33.28	-2.30	-11.42	-35.58	-9.12	38%	396%
	-15.09	-22.98	-2.11	-10.00	-25.09	-7.89	52%	374%
2	-20.57	-29.48	-10.31	-19.22	-39.79	-8.91	43%	86%
	-20.98	-28.55	-8.90	-16.47	-37.45	-7.57	36%	85%
3	-8.29	-12.00	-9.92	-13.63	-21.92	-3.71	45%	37%
	-7.58	-10.55	-9.04	-12.01	-19.59	-2.97	39%	33%
4	-15.52	-19.77	-2.85	-7.10	-22.62	-4.25	27%	149%
	-8.82	-11.75	-1.91	-4.84	-13.66	-2.93	33%	153%
5	-18.28	-21.84	-3.93	-7.49	-25.77	-3.56	19%	91%
	-18.36	-21.31	-3.59	-6.54	-24.90	-2.95	16%	82%
6	-31.22	-24.70	-38.88	-32.36	-63.58	6.52	21%	17%
	-31.02	-25.35	-36.60	-30.93	-61.95	5.67	18%	15%

^a The data calculated at BP86-D3(BJ)/def2-TZVP level of theory are shown as plain text and those at MP2/def2-TZVP level are in bold.

^b See the eqs. (S8), (S9), (S10) and (S11) that all give the same value.

^c See eq. (10) of the paper.

$$\text{d } \% \Delta IE_{\text{A-B}} = \frac{|\Delta IE_{\text{coop}}|}{IE_{\text{A-B}}^{\text{ABC}}} \times 100, \% \Delta IE_{\text{B-C}} = \frac{|\Delta IE_{\text{coop}}|}{IE_{\text{B-C}}^{\text{ABC}}} \times 100$$

Table S12. The theoretical^a and available experimental^b A–B and B–C bond lengths (Å) in triads along with Δr values^c, and also theoretical A–B and B–C bond lengths (Å) in related dyads

Compound	Bond length							
	<i>BP86-D3(BJ)/def2-TZVP</i>							
	Triad				Related dyad		Δr	
	$r_{(A-B)}$	exp.	$r_{(B-C)}$	exp.	$r_{(A-B)}$	$r_{(B-C)}$	$\Delta r_{(A-B)}$	$\Delta r_{(B-C)}$
7	1.827	-	1.762	-	1.803	1.847	0.024	-0.085
8	1.651	1.667	1.649	1.665	-	-	-	-
9	1.839	-	2.428	-	1.705	2.348	0.134	0.080
10	1.887	1.888	1.903	1.897	1.871	1.880	0.016	0.023
11	2.115	2.074	1.946	1.977	2.047	1.914	0.068	0.032
12	2.167	2.120	2.072	2.044	2.138	2.156	0.029	-0.084
<i>MP2/def2-TZVP</i>								
7	1.740	-	1.706	-	1.753	1.876	-0.013	-0.170
8	-	1.667	-	1.665	-	-	-	-
9	1.836	-	2.374	-	1.691	2.297	0.145	0.077
10	1.854	1.888	1.884	1.897	1.858	1.892	-0.004	-0.008
11	2.056	2.074	1.913	1.977	1.987	1.873	0.069	0.040
12	2.106	2.120	2.020	2.044	2.029	2.091	0.077	-0.071

^a The data obtained at BP86-D3(BJ)/def2-TZVP and MP2/def2-TZVP levels of theory.

^b For experimental data see refs. 108-111 in the paper.

^c $\Delta r = r_{\text{triad}} - r_{\text{dyad}}$

Table S13. Corrected calculated values for interaction energies in the optimized structures of AB and BC dyads related to triads **1** to **6** studied in this work at different levels of theory

Related ABC complex	<i>BP86-D3(BJ)/aug-cc-pVTZ</i>		<i>MP2/aug-cc-pVTZ</i>	
	IE _{A-B}	IE _{B-C}	IE _{A-B}	IE _{B-C}
1	-21.21	-1.68	-12.75	-2.03
2	-6.17	-9.25	-6.75	-8.76
3	-7.93	-9.26	-7.48	-8.76
4	-13.80	-2.66	-7.38	-1.80
5	-18.08	-3.93	-18.06	-3.81
6	-31.98	-39.08	-31.13	-36.62
	<i>BP86-D3(BJ)/def2-TZVP</i>		<i>MP2/def2-TZVP</i>	
	IE _{A-B}	IE _{B-C}	IE _{A-B}	IE _{B-C}
1	-21.21	-2.03	-11.09	-1.71
2	-5.73	-8.81	-6.06	-8.27
3	-7.63	-9.25	-6.93	-8.27
4	-14.04	-3.74	-6.65	-1.39
5	-17.85	-3.87	-17.77	-3.60
6	-31.52	-38.88	-31.15	-36.47

Table S14. Corrected calculated values for interaction energies in optimized structures of AB and BC metal complexes related to compounds **7** to **12** studied here

Compound	<i>BP86-D3(BJ)/def2-TZVP</i>		<i>MP2/def2-TZVP</i>	
	IE _{A-B}	IE _{B-C}	IE _{A-B}	IE _{B-C}
7	-199.19	-47.59	-185.23	-32.80
8	-	-	-	-
9	-42.62	-58.87	-42.28	-63.23
10	-202.09	-76.28	-180.96	-58.13
11	-96.77	-227.98	-83.61	-214.84
12	-203.45	-521.98	-177.79	-510.29

Table S15. Calculated values for deformation (strain) energies (E_s , kcal/mol) of interacted A, B and C species in the ABC triads **1** to **6** and the related AB and BC dyads studied in this work

Compound	ABC triad			Related AB dyad		Related BC dyad	
	E_s^{ABC} _A	E_s^{ABC} _B	E_s^{ABC} _C	E_s^{AB} _A	E_s^{AB} _B	E_s^{BC} _B	E_s^{BC} _C
<i>BP86-D3(BJ)/aug-cc-pVTZ</i>							
1	0.55	6.91	0.42	0.42	2.94	0.02	0.02
2	18.54	2.30	0.00	1.86	0.02	0.42	0.00
3	0.47	0.89	0.00	0.21	0.02	0.42	0.00
4	0.38	2.03	0.19	0.33	1.28	0.00	0.06
5	0.13	0.36	0.03	0.08	0.04	0.07	0.00
6	0.31	0.00	0.26	0.57	0.00	0.00	0.34
<i>MP2/aug-cc-pVTZ</i>							
1	0.29	5.55	0.22	0.13	1.67	0.02	0.00
2	17.66	0.90	0.00	1.57	0.01	0.17	0.00
3	0.24	0.34	0.00	0.11	0.02	0.17	0.00
4	0.10	1.15	0.08	0.05	0.52	0.00	0.02
5	0.10	0.17	0.03	0.07	0.05	0.07	0.05
6	0.33	0.00	0.22	0.55	0.00	0.00	0.29

Table S16. Calculated values for deformation (strain) energies (E_s , kcal/mol) of fragments in the ABC metal complexes **7** to **12** and the related AB and BC metal complexes studied in this work

Compound	ABC complex			Related AB complex		Related BC complex	
	E_s^{ABC} _A	E_s^{ABC} _B	E_s^{ABC} _C	E_s^{AB} _A	E_s^{AB} _B	E_s^{BC} _B	E_s^{BC} _C
<i>BP86-D3(BJ)/def2-TZVP</i>							
7	0.35	0.00	0.29	0.90	0.00	0.00	0.09
8	6.97	24.80	6.82	-	-	-	-
9	2.60	0.15	0.74	7.40	0.23	0.37	0.83
10	2.44	0.00	0.48	3.52	0.00	0.00	1.29
11	0.83	0.00	0.19	2.54	0.00	0.00	0.19
12	0.86	0.00	1.53	4.95	0.00	0.00	3.50
<i>MP2/def2-TZVP</i>							
7	0.42	0.00	0.28	0.10	0.00	0.00	0.42
8^a	8.83	35.25	8.83	-	-	-	-
9	2.57	0.54	0.52	7.87	0.38	1.69	0.56
10	1.76	0.00	0.38	2.42	0.00	0.00	0.81
11	0.80	0.00	0.16	2.31	0.00	0.00	0.21
12	0.84	0.00	1.09	4.92	0.00	0.00	3.19

^a In this case, the calculations for this compound were performed using the def2-SVP basis set.

Table S17. Corrected calculated values^a for interaction energy (IE^b, kcal/mol) and stabilization energy (SE^c, kcal/mol) between the A and C species in the ABC triads **1** to **6**

<i>aug-cc-pVTZ</i>				
Compound	BP86-D3(BJ)		MP2	
	IE _{A-C} ^{ABC}	SE _{AC} ^{ABC}	IE _{A-C} ^{ABC}	SE _{AC} ^{ABC}
1	-0.72	+0.25	-0.81	-0.30
2	-1.34	+17.21	-1.44	+16.22
3	-0.95	-0.47	-0.96	-0.72
4	-0.41	0.16	-0.48	-0.30
5	-0.98	-0.82	-1.01	-0.88
6	+1.15	+1.73	+1.01	+1.56

^a We, ourselves, do not believe that the data in this Table represent the actual values of the stabilization energy or interaction energy of A...C pair frozen in the structure of ABC systems (the nature and strength of the interaction of two species A and C, where B exists and has isolated them, is never the same as when B does not exist and they have a direct contact with each other).

$$^b \text{IE}_{\text{A-C}}^{\text{ABC}} = E_{\text{AC}}^{\text{ABC}} - (E_{\text{A}}^{\text{ABC}} + E_{\text{C}}^{\text{ABC}})$$

$$^c \text{SE}_{\text{AC}}^{\text{ABC}} = E_{\text{AC}}^{\text{ABC}} - (E_{\text{A}} + E_{\text{C}})$$

Table S18. Corrected calculated values^a for interaction energy (IE^b, kcal/mol) and stabilization energy (SE^c, kcal/mol) between the A and C species of metal complexes studied here

Compound	<i>def-2/TZVP</i>			
	BP86-D3(BJ)		MP2	
	IE _{A-C} ^{ABC}	SE _{AC} ^{ABC}	IE _{A-C} ^{ABC}	SE _{AC} ^{ABC}
7	-2.90	-2.20	-0.70	-0.01
8	+5.64	+8.15	+5.95 ^d	+23.62 ^d
9	+0.13	+3.47	+0.12	+3.21
10	+3.78	+6.71	+4.25	+6.39
11	+5.98	+7.00	+6.86	+7.83
12	-0.84	+1.54	+8.86	+10.79

^a We, ourselves, do not believe that the data in this Table represent the actual values of the stabilization energy or interaction energy of A...C pair frozen in the structure of ABC systems (the nature and strength of the interaction of two species A and C, where B exists and has isolated them, is never the same as when B does not exist and they have a direct contact with each other).

$$^b \text{IE}_{\text{A-C}}^{\text{ABC}} = E_{\text{AC}}^{\text{ABC}} - (E_{\text{A}}^{\text{ABC}} + E_{\text{C}}^{\text{ABC}})$$

$$^c \text{SE}_{\text{AC}}^{\text{ABC}} = E_{\text{AC}}^{\text{ABC}} - (E_{\text{A}} + E_{\text{C}})$$

^d In this case, the calculations for this compound were performed using the def2-SVP basis set.

Table S19. Calculated values for interaction energies (IE, kcal/mol), stabilization energies (SE, kcal/mol) and cooperative energies (E_{coop} , kcal/mol) for triad **2** ($\text{F}_3\text{B}\dots\text{NCH}\dots\text{HLi}$), at MP2/aug-cc-pVTZ level of theory

$\text{IE}_{\text{A-B}}^{\text{ABC}}$	-20.25	SE_{AB}	-5.17
$\text{IE}_{\text{A-B}}$	-6.75	SE_{BC}	-8.58
$\text{IE}_{\text{B-C}}^{\text{ABC}}$	-8.58	$\text{SE}_{\text{AC}}^{\text{ABC}}$	+16.22 ^a
$\text{IE}_{\text{B-C}}$	-8.76	$\text{SE}_{\text{A-BC}}$	-9.18
$\text{IE}_{\text{A-C}}^{\text{ABC}}$	-1.44	$\text{SE}_{\text{AB-C}}$	-12.59
$\text{IE}_{\text{A-BC}}^{\text{ABC}}$	-27.74	SE_{ABC}	-17.76
$\text{IE}_{\text{AB-C}}^{\text{ABC}}$	-16.07	$E_{\text{coop}}^{\text{b}}$	-20.22
$\text{IE}_{\text{total}}^{\text{ABC}}$	-36.32	$E_{\text{coop}}^{\text{c}}$	-4.01

^a $\text{SE}_{\text{AC}}^{\text{ABC}} = E_{\text{AC}}^{\text{ABC}} - (E_{\text{A}} + E_{\text{C}})$

^b See eq (2) of the paper: $E_{\text{coop}} = \text{SE}_{\text{ABC}} - (\text{SE}_{\text{AB}} + \text{SE}_{\text{BC}} + \text{SE}_{\text{AC}}^{\text{ABC}})$

^c See eq (3) or (8) of the paper: $E_{\text{coop}} = \text{SE}_{\text{ABC}} - (\text{SE}_{\text{AB}} + \text{SE}_{\text{BC}}) = \Delta\text{BDE}_{\text{A-B}} = \Delta\text{BDE}_{\text{B-C}}$

As can be seen, equation (2) gives a value of -20.22 kcal/mol for the stabilization-based cooperative energy (E_{coop}) of triad **2** which is surprisingly larger than the total stabilization energy (SE_{ABC}) of this molecule (-17.76 kcal/mol). Obviously, this is quite illogical and clearly proves that equations (3) or (8) of the paper give the more accurate data for noncyclic ABC systems. We note that the large positive value (+16.22 kcal/mol) of $\text{SE}_{\text{AC}}^{\text{ABC}}$ is due to the large value of the deformation energy of species A (E_{s} for BF_3 molecule is 17.66 kcal/mol), so it is illogical to consider it as the result of a repulsive interaction between A and C. Indeed, the value of interaction between A and C ($\text{IE}_{\text{A-C}}^{\text{ABC}}$) is -1.44 kcal/mol and seems to be attractive. However, we note that even the value of -1.44 kcal/mol for $\text{IE}_{\text{A-C}}^{\text{ABC}}$ is not an accurate value for a real interaction. We can only say that if the species B (herein, NCH molecule) did not exist between the species A and C (herein F_3B and HLi molecules), then there was a real interaction (with a value of -1.44 kcal/mol) between them. But we emphasize that such real and direct interaction does not exist in non-cyclic $\text{F}_3\text{B}\dots\text{NCH}\dots\text{HLi}$ triad, and in this case both $\text{SE}_{\text{AC}}^{\text{ABC}}$ and $\text{IE}_{\text{A-C}}^{\text{ABC}}$ values will be misleading.

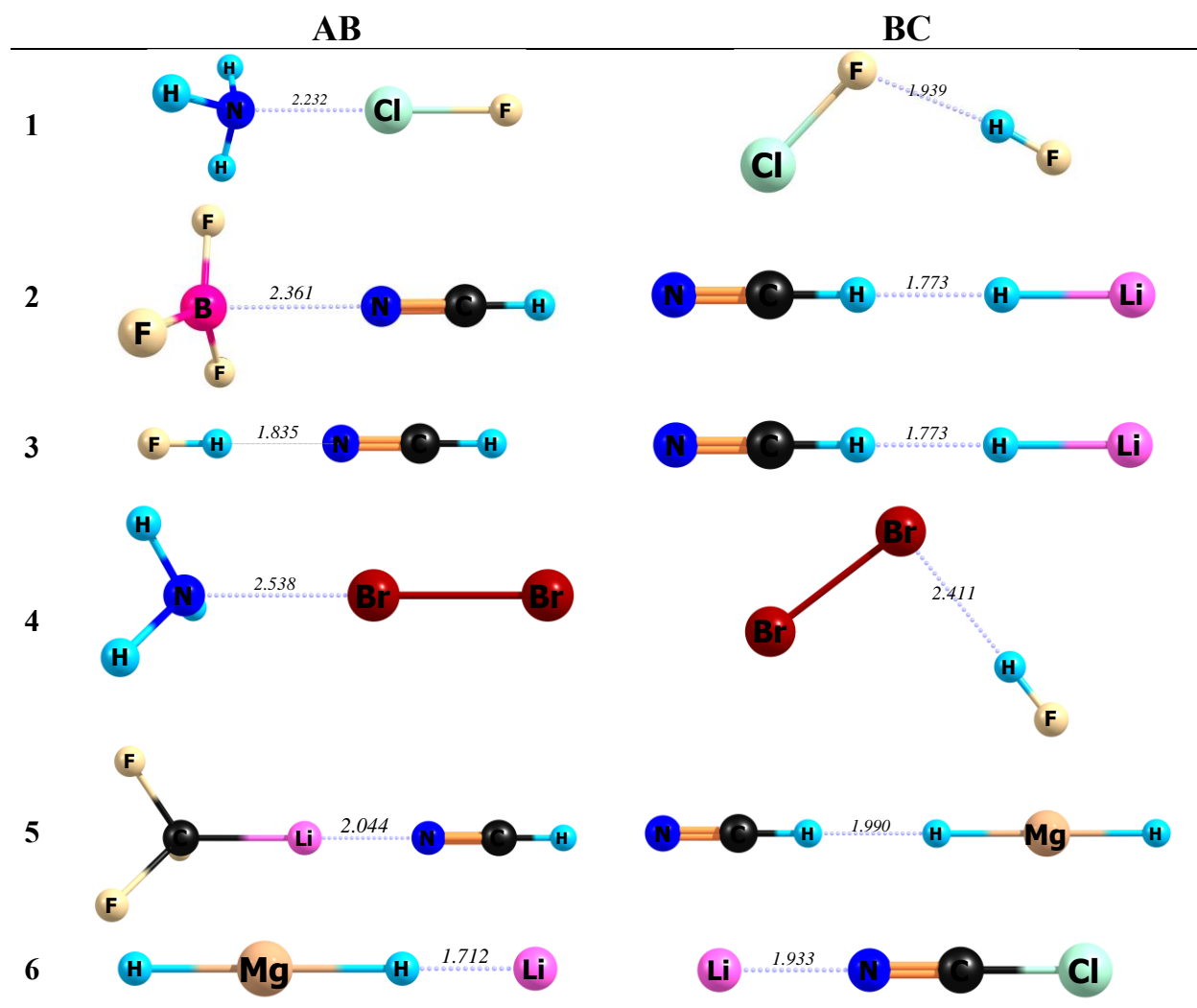


Figure S1. The optimized structures and bonds length(\AA) of AB and BC dyads related to triads **1** to **6** studied here, at the MP2/aug-cc-pVTZ level of theory.

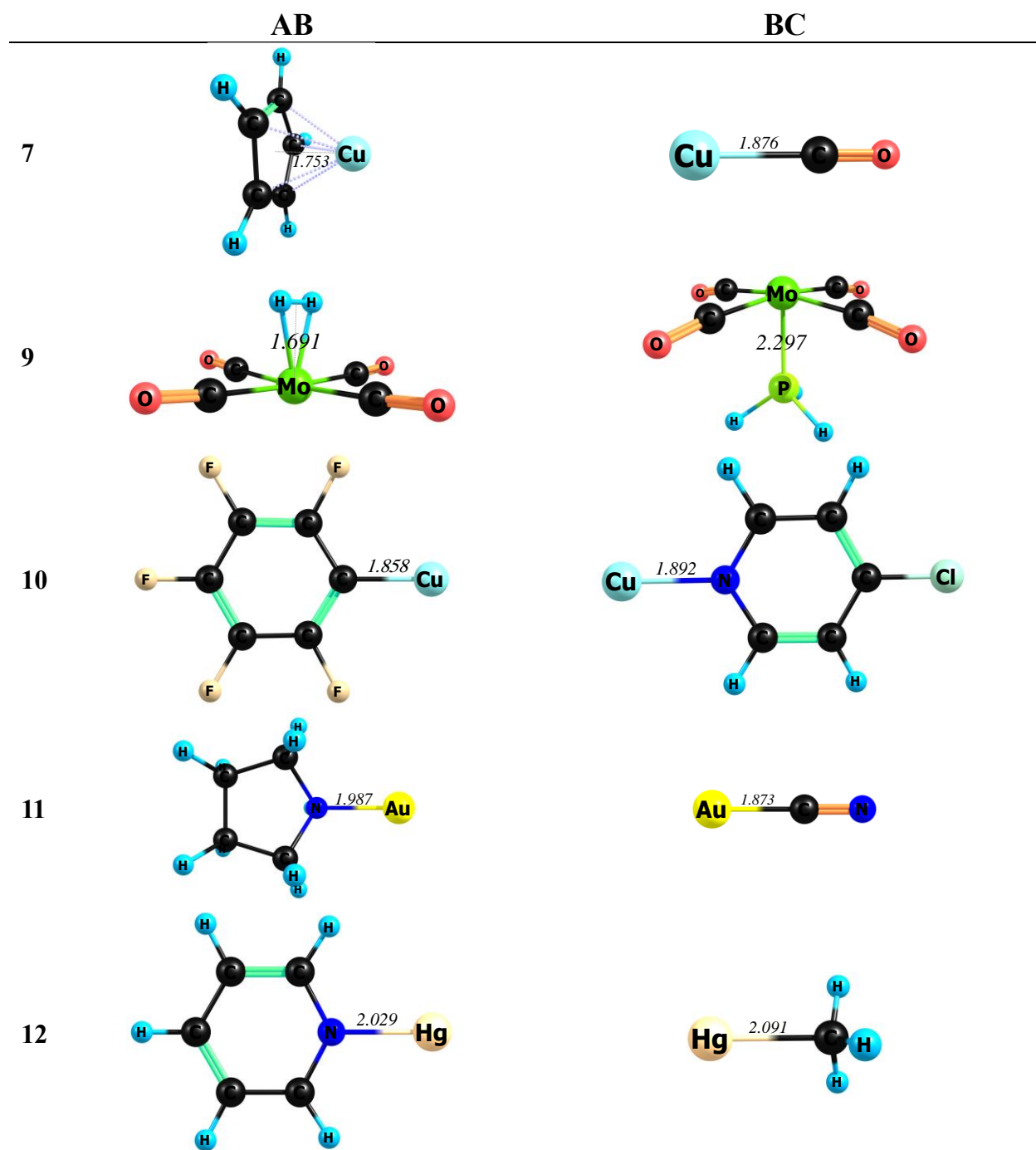


Figure S2. The optimized structures and bonds length(Å) of AB and BC metal complexes related to complexes 7 to 12 (except 8), at the MP2/def2-TZVP level of theory.

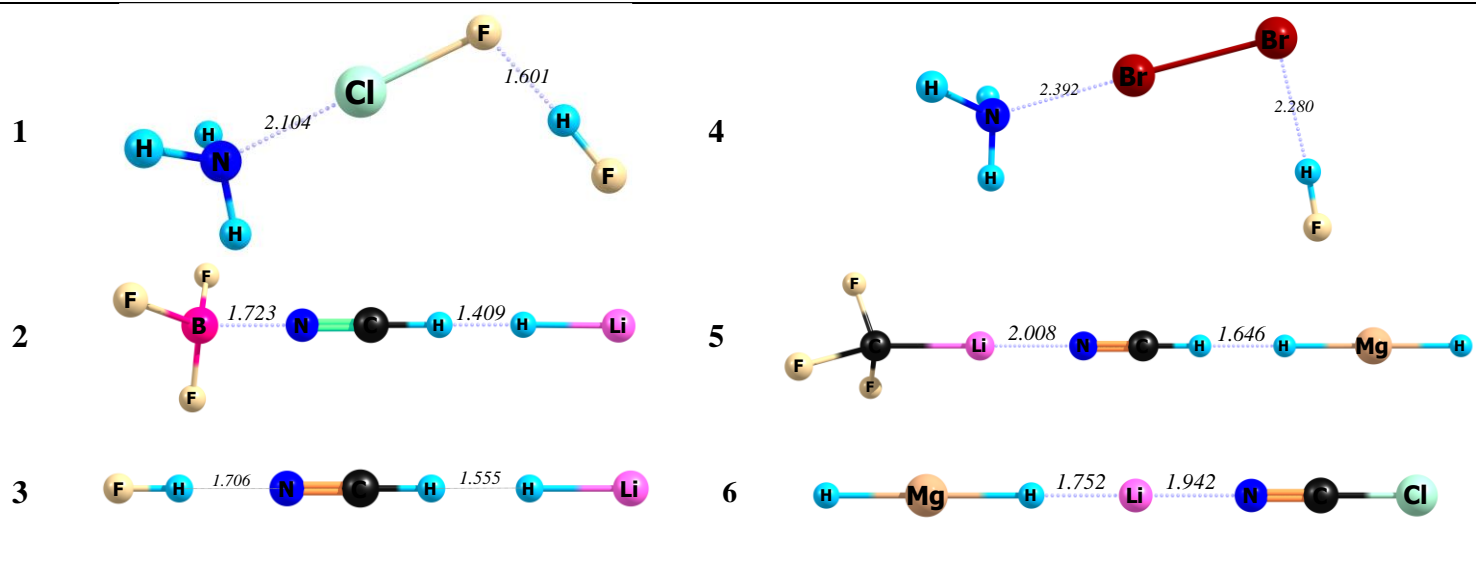


Figure S3. The optimized structures and related A–B and B–C bonds length(Å), of the triads **1** to **6** studied here, at the BP86-D3(BJ)/aug-cc-pVTZ level of theory.

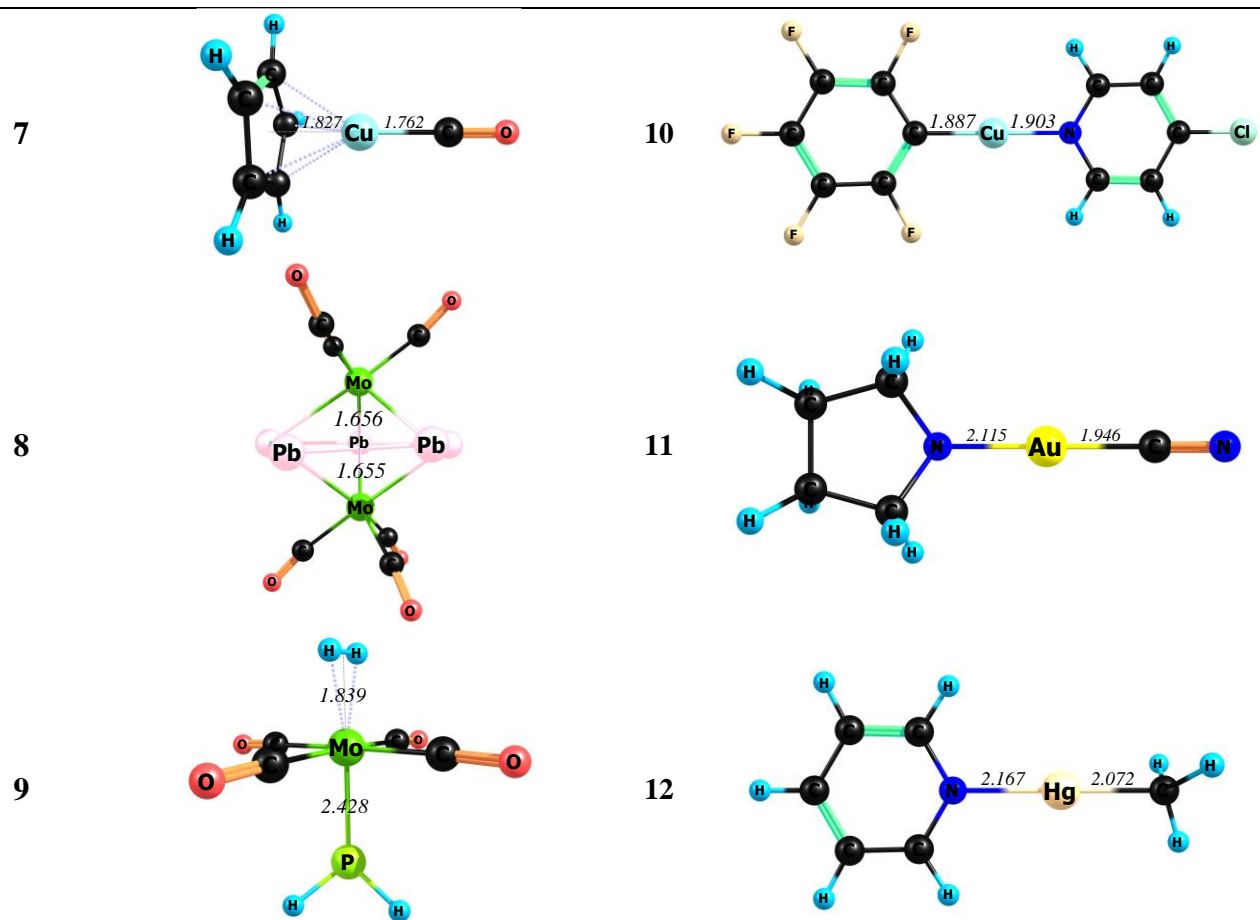
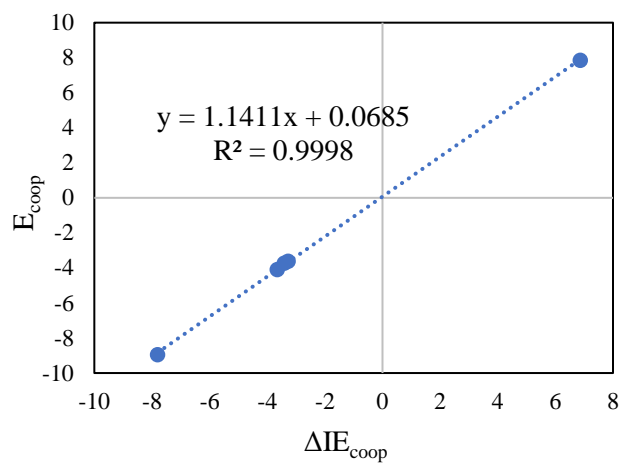
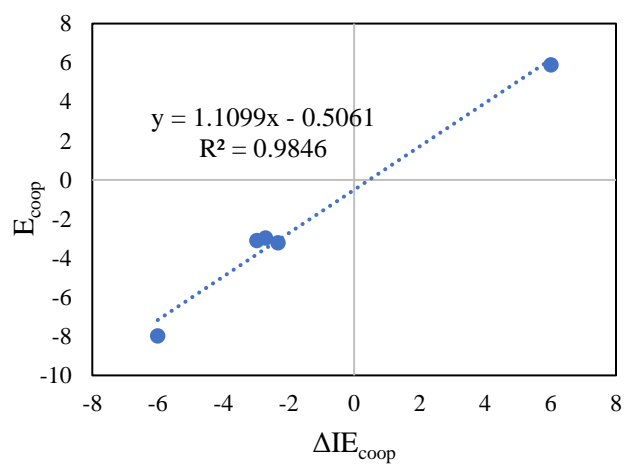


Figure S4. The optimized structures and related A-B and B-C bonds length(Å), of the metal complexes 7 to 12, at the BP86-D3(BJ)/def2-TZVP level of theory.

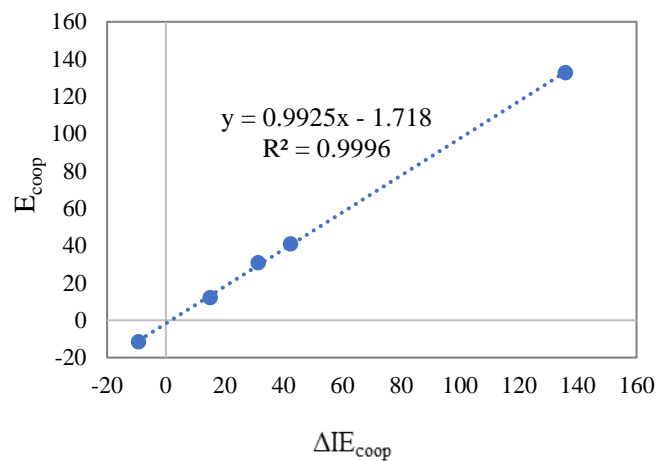


(a)

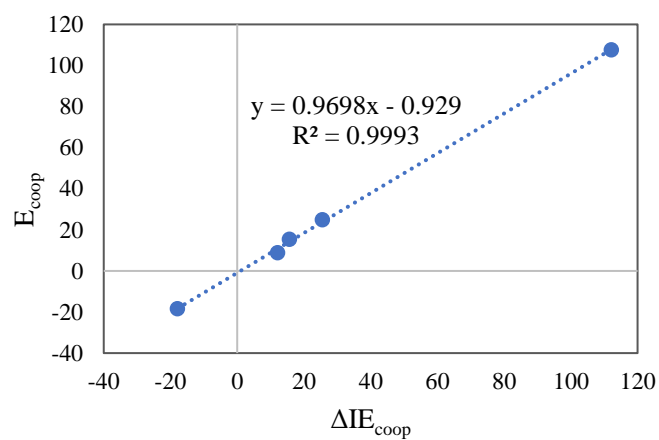


(b)

Figure S5. Correlation between E_{coop} and ΔIE_{coop} (kcal/mol) values for the triads studied here (except triad **2**), at (a) BP86-D3(BJ)/aug-cc-pVTZ and (b) MP2/aug-cc-pVTZ level of theory.



(a)



(b)

Figure S6. Correlation between E_{coop} and ΔIE_{coop} (kcal/mol) values for metal complexes studied here (except complex **8**), at (a) BP86-D3(BJ)/def2-TZVP and (b) MP2/def2-TZVP level of theory.