Electronic Supplementary Information

Energy decomposition analysis of cationic carbene analogues with groups 13 and 16 elements as a central atom: a comparative study

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Table S1: The analytic interaction energies ΔE_{int} of the $(\text{P}t\text{Bu}_3)_2\text{M}^+$ reactions with (a) methane and (b) ethene are calculated by subtracting the strain energies ΔE_{str} from the activation energies and reaction enthalpies ΔE of the transition states and products, respectively[a]. $\Delta E_{\text{str, carb}}$, $\Delta E_{\text{str, meth}}$, and $\Delta E_{\text{str, eth}}$ are the strain energies of the carbene, methane, and ethene fragments, respectively. Energies are in the unit of Kcal/mol.

(a) Reactions : $(\text{P}t\text{Bu}_3)_2\text{M}^+ + \text{CH}_4 \longrightarrow$ **TS-M-CH$_4$** $\longrightarrow$ **Pro-M-CH$_4$** (**M = B, Al, Ga, In, Tl**)

	Transition States **TS-M-CH$_4$**					Products **Pro-M-CH$_4$**				
Energy	**TS-B-CH$_4$**	**TS-Al-CH$_4$**	**TS-Ga-CH$_4$**	**TS-In-CH$_4$**	**TS-Tl-CH$_4$**	**Pro-B-CH$_4$**	**Pro-Al-CH$_4$**	**Pro-Ga-CH$_4$**	**Pro-In-CH$_4$**	**Pro-Tl-CH$_4$**
ΔE	28.37	44.62	58.75	72.26	90.11	−47.45	−20.25	1.68	20.74	44.54
ΔE_{str}	24.21	66.11	83.12	95.76	112.06	147.60	152.27	151.69	153.67	150.55
$\Delta E_{\text{str, carb}}$	22.65	13.64	14.82	11.74	11.36	31.97	10.32	11.08	7.35	3.63
$\Delta E_{\text{str, meth}}$	1.56	52.47	68.31	84.02	100.70	115.64	141.95	140.61	146.32	146.91
ΔE_{int}	4.16	−21.49	−24.37	−23.50	−21.94	−195.06	−172.53	−150.01	−132.93	−106.01

(b) Reactions : $(\text{P}t\text{Bu}_3)_2\text{M}^+ + \text{C}_2\text{H}_4 \longrightarrow$ **TS-M-C$_2$H$_4$** $\longrightarrow$ **Pro-M-C$_2$H$_4$** (**M = B, Al, Ga, In, Tl**)

	Transition States **TS-M-C$_2$H$_4$**					Products **Pro-M-C$_2$H$_4$**				
Energy	**TS-B-C$_2$H$_4$**	**TS-Al-C$_2$H$_4$**	**TS-Ga-C$_2$H$_4$**	**TS-In-C$_2$H$_4$**	**TS-Tl-C$_2$H$_4$**	**Pro-B-C$_2$H$_4$**	**Pro-Al-C$_2$H$_4$**	**Pro-Ga-C$_2$H$_4$**	**Pro-In-C$_2$H$_4$**	**Pro-Tl-C$_2$H$_4$**
ΔE	33.81	3.01	19.23	37.52	65.57	−39.01	−8.74	16.72	37.06	65.57
ΔE_{str}	29.33	18.47	35.16	47.83	49.68	66.81	53.19	54.44	50.28	49.68
$\Delta E_{\text{str, carb}}$	28.19	9.67	17.84	18.20	17.68	36.91	16.14	20.58	20.03	17.68
$\Delta E_{\text{str, eth}}$	1.14	8.80	17.32	29.63	32.00	29.90	37.05	33.86	30.26	32.00
ΔE_{int}	4.48	−15.46	−15.93	−10.31	15.89	−105.82	−61.92	−37.71	−13.22	15.89

[a] All energies are calculated at the BP86/Def2-SVP theory level.

Table S2: The analytic and EDA interaction energies of the $(PtBu_3)_2M^+$ reactions with (a) methane and (b) ethene partitioned by the ETS-NOCV[a] and NEDA[b] schemes are tabulated in the unit of Kcal/mol.

(a) Reactions : $(PtBu_3)_2M^+ + CH_4 \longrightarrow$ **TS-M-CH$_4$** $\longrightarrow$ **Pro-M-CH$_4$** (**M = B, Al, Ga, In, Tl**)

	Transition States **TS-M-CH$_4$**					Products **Pro-M-CH$_4$**				
Energy	**TS-B-CH$_4$**	**TS-Al-CH$_4$**	**TS-Ga-CH$_4$**	**TS-In-CH$_4$**	**TS-Tl-CH$_4$**	**Pro-B-CH$_4$**	**Pro-Al-CH$_4$**	**Pro-Ga-CH$_4$**	**Pro-In-CH$_4$**	**Pro-Tl-CH$_4$**
ΔE_{int}	4.16	−21.49	−24.37	−23.50	−21.94	−195.06	−172.53	−150.01	−132.93	−106.01
$\Delta E_{\text{int}}^{\text{ETS}}$	0.47	−19.66	−16.95	−20.76	−21.73	−192.68	−169.28	−131.34	−124.87	−104.14
$\Delta E_{\text{Pauli}}^{\text{ETS}}$	113.84	170.76	189.08	187.27	204.56	733.93	451.94	472.65	396.87	416.23
$\Delta E_{\text{elstat}}^{\text{ETS}}$	−44.00	−76.81	−89.01	−95.09	−110.84	−239.11	−164.73	−193.92	−180.86	−203.87
$\Delta E_{\text{orb}}^{\text{ETS}}$	−69.37	−113.61	−117.02	−112.94	−115.45	−687.50	−456.49	−410.07	−340.88	−316.49
$\left\lvert\Delta E_{\text{int}}^{\text{ETS}} - \Delta E_{\text{int}}\right\rvert$	3.69	1.83	7.42	2.74	0.21	2.38	3.25	18.67	8.06	1.87
$\Delta E_{\text{int}}^{\text{NEDA}}$	6.33	−19.10	−23.41	−21.21	−19.77	−191.16	−169.20	−146.33	−129.34	−102.78
$\Delta E_{\text{Pauli}}^{\text{NEDA}}$	134.10	243.26	441.39	365.82	275.76	960.48	766.62	872.80	607.36	376.17
$\Delta E_{\text{elstat}}^{\text{NEDA}}$	−39.99	−59.62	−120.86	−78.70	−83.34	−116.38	−119.66	−243.29	−135.69	−126.96
$\Delta E_{\text{orb}}^{\text{NEDA}}$	−87.77	−202.74	−343.94	−308.33	−212.19	−1035.26	−816.17	−775.84	−601.02	−351.99
$\left\lvert\Delta E_{\text{int}}^{\text{NEDA}} - \Delta E_{\text{int}}\right\rvert$	2.18	2.38	0.96	2.29	2.18	3.90	3.32	3.67	3.59	3.23

(b) Reactions : $(PtBu_3)_2M^+ + C_2H_4 \longrightarrow$ **TS-M-C$_2$H$_4$** $\longrightarrow$ **Pro-M-C$_2$H$_4$** (**M = B, Al, Ga, In, Tl**)

	Transition States **TS-M-C$_2$H$_4$**					Products **Pro-M-C$_2$H$_4$**				
Energy	**TS-B-C$_2$H$_4$**	**TS-Al-C$_2$H$_4$**	**TS-Ga-C$_2$H$_4$**	**TS-In-C$_2$H$_4$**	**TS-Tl-C$_2$H$_4$**	**Pro-B-C$_2$H$_4$**	**Pro-Al-C$_2$H$_4$**	**Pro-Ga-C$_2$H$_4$**	**Pro-In-C$_2$H$_4$**	**Pro-Tl-C$_2$H$_4$**
ΔE_{int}	4.48	−15.46	−15.93	−10.31	15.89	−105.82	−61.92	−37.71	−13.22	15.89
$\Delta E_{\text{int}}^{\text{ETS}}$	5.69	−12.90	−2.94	−6.96	15.90	−102.01	−58.99	−19.82	−9.73	15.90
$\Delta E_{\text{Pauli}}^{\text{ETS}}$	50.44	174.35	271.05	315.77	280.19	802.93	447.86	431.05	330.96	280.19
$\Delta E_{\text{elstat}}^{\text{ETS}}$	−21.30	−91.23	−138.71	−164.47	−150.66	−342.11	−218.19	−210.07	−171.88	−150.66
$\Delta E_{\text{orb}}^{\text{ETS}}$	−23.46	−96.01	−135.27	−158.26	−113.63	−562.84	−288.66	−240.80	−168.81	−113.63
$\left\lvert\Delta E_{\text{int}}^{\text{ETS}} - \Delta E_{\text{int}}\right\rvert$	1.21	2.56	12.99	3.35	0.01	3.81	2.93	17.89	3.49	0.01
$\Delta E_{\text{int}}^{\text{NEDA}}$	7.24	−12.34	−12.32	−7.20	18.99	−100.27	−58.24	−33.50	−9.94	18.99
$\Delta E_{\text{Pauli}}^{\text{NEDA}}$	97.26	244.30	506.41	407.77	408.72	786.41	473.57	590.49	407.81	408.72
$\Delta E_{\text{elstat}}^{\text{NEDA}}$	−36.27	−97.27	−196.68	−148.90	−140.63	−224.14	−177.42	−271.07	−154.14	−140.63
$\Delta E_{\text{orb}}^{\text{NEDA}}$	−53.75	−159.37	−322.05	−266.08	−249.10	−662.54	−354.39	−352.91	−263.62	−249.10
$\left\lvert\Delta E_{\text{int}}^{\text{NEDA}} - \Delta E_{\text{int}}\right\rvert$	2.75	3.12	3.61	3.11	3.09	5.55	3.68	4.21	3.28	3.09

[a] The ETS-NOCV decompositions of the interaction energies are obtained at the BP86/TZ2P//BP86/Def2-SVP theory level with ZORA, $\Delta E_{\text{int}}^{\text{ETS}} = \Delta E_{\text{Pauli}}^{\text{ETS}} + \Delta E_{\text{elstat}}^{\text{ETS}} + \Delta E_{\text{orb}}^{\text{ETS}}$

[b] The NEDA decompositions of the interaction energies are calculated at the BP86/Def2-SVP theory level, $\Delta E_{\text{int}}^{\text{NEDA}} = \Delta E_{\text{Pauli}}^{\text{NEDA}} + \Delta E_{\text{elstat}}^{\text{NEDA}} + \Delta E_{\text{orb}}^{\text{NEDA}}$

Table S3: The analytic interaction energies ΔE_{int} of the $(\text{Dipp}_2\text{DAB})\text{M}^{+2}$ reactions with (a) methane and (b) ethene are calculated by subtracting the strain energies ΔE_{str} from the activation energies and reaction enthalpies ΔE of the transition states and products (relative to the reactant energies), respectively[a]. $\Delta E_{\text{str, carb}}$, $\Delta E_{\text{str, meth}}$, and $\Delta E_{\text{str, eth}}$ are the strain energies of the carbene, methane, and ethene fragments, respectively. Energies are in the unit of Kcal/mol.

(a) Reactions : $(\text{Dipp}_2\text{DAB})\text{M}^{+2} + \text{CH}_4 \longrightarrow$ **TS-M-CH$_4$** $\longrightarrow$ **Pro-M-CH$_4$** (**M = O, S, Se, Te**)

	Transition States **TS-M-CH$_4$**				Products **Pro-M-CH$_4$**			
Energy	**TS-O-CH$_4$**	**TS-S-CH$_4$**	**TS-Se-CH$_4$**	**TS-Te-CH$_4$**	**Pro-O-CH$_4$**	**Pro-S-CH$_4$**	**Pro-Se-CH$_4$**	**Pro-Te-CH$_4$**
ΔE	−3.61	35.18	30.27	30.65	−42.61	4.19	6.38	7.01
ΔE_{str}	170.94	73.86	79.12	86.94	170.94	174.96	163.07	147.93
$\Delta E_{\text{str, carb}}$	27.12	27.02	23.06	17.09	34.95	62.47	43.88	21.79
$\Delta E_{\text{str, meth}}$	143.82	46.84	56.05	69.85	135.99	112.48	119.19	126.14
ΔE_{int}	−171.13	−40.65	−43.81	−52.92	−208.48	−171.10	−149.43	−136.50

(b) Reactions : $(\text{Dipp}_2\text{DAB})\text{M}^{+2} + \text{C}_2\text{H}_4 \longrightarrow$ **TS-M-C$_2$H$_4$** $\longrightarrow$ **Pro-M-C$_2$H$_4$** (**M = O, S, Se, Te**)

	Transition States **TS-M-C$_2$H$_4$**				Products **Pro-M-C$_2$H$_4$**			
Energy	**TS-O-C$_2$H$_4$**	**TS-S-C$_2$H$_4$**	**TS-Se-C$_2$H$_4$**	**TS-Te-C$_2$H$_4$**	**Pro-O-C$_2$H$_4$**	**Pro-S-C$_2$H$_4$**	**Pro-Se-C$_2$H$_4$**	**Pro-Te-C$_2$H$_4$**
ΔE	−1.18	−9.11	−17.76	−23.70	−56.51	−13.10	−20.92	−24.56
ΔE_{str}	15.13	25.53	30.09	10.49	137.89	80.90	6.87	10.06
$\Delta E_{\text{str, carb}}$	13.72	22.29	23.10	9.10	37.99	63.37	6.17	8.73
$\Delta E_{\text{str, eth}}$	1.40	3.24	7.00	1.39	99.90	17.52	0.70	1.33
ΔE_{int}	−13.89	−35.52	−43.87	−31.64	−186.11	−94.26	−24.98	−32.04

[a] All energies are calculated at the BP86/Def2-SVP theory level.

Table S4: The analytic and EDA interaction energies of the $(Dipp_2DAB)M^{+2}$ reactions with (a) methane and (b) ethene partitioned by the ETS-NOCV[a] and NEDA[b] schemes are tabulated in the unit of Kcal/mol.

(a) Reactions : $(Dipp_2DAB)M^{+2} + CH_4 \longrightarrow$ **TS-M-CH$_4$** $\longrightarrow$ **Pro-M-CH$_4$** (**M = O, S, Se, Te**)

	Transition States **TS-M-CH$_4$**				Products **Pro-M-CH$_4$**			
Energy	**TS-O-CH$_4$**	**TS-S-CH$_4$**	**TS-Se-CH$_4$**	**TS-Te-CH$_4$**	**Pro-O-CH$_4$**	**Pro-S-CH$_4$**	**Pro-Se-CH$_4$**	**Pro-Te-CH$_4$**
ΔE_{int}	−174.55	−38.68	−48.84	−56.29	−213.54	−170.77	−156.69	−140.92
$\Delta E_{\text{int}}^{\text{ETS}}$	−171.13	−40.65	−43.81	−52.92	−208.48	−171.10	−149.43	−136.50
$\Delta E_{\text{Pauli}}^{\text{ETS}}$	414.01	293.18	265.59	241.13	671.41	623.99	560.48	476.64
$\Delta E_{\text{elstat}}^{\text{ETS}}$	−183.96	−124.79	−126.51	−123.77	−294.05	−247.00	−243.08	−236.14
$\Delta E_{\text{orb}}^{\text{ETS}}$	−392.06	−200.50	−174.40	−161.46	−578.56	−540.84	−459.25	−367.90
$\Delta E_{\text{disp}}^{\text{ETS}}$	−9.12	−8.54	−8.49	−8.82	−7.29	−7.25	−7.58	−9.10
$\lvert\Delta E_{\text{int}}^{\text{ETS}} - \Delta E_{\text{int}}\rvert$	3.42	1.97	5.03	3.37	5.06	0.33	7.26	4.42
$\Delta E_{\text{int}}^{\text{NEDA}}$	−168.47	−34.71	−44.99	−52.61	−207.26	−164.83	−151.05	−136.62
$\Delta E_{\text{Pauli}}^{\text{NEDA}}$	1005.44	422.82	406.45	298.69	1211.91	1065.72	714.85	713.92
$\Delta E_{\text{elstat}}^{\text{NEDA}}$	−189.72	−104.99	−146.31	−85.68	−249.23	−161.89	−181.50	−115.33
$\Delta E_{\text{orb}}^{\text{NEDA}}$	−976.09	−345.56	−298.26	−258.16	−1164.06	−1064.62	−679.99	−727.75
$\Delta E_{\text{disp}}^{\text{NEDA}}$	−8.10	−6.98	−6.86	−7.45	−5.88	−4.04	−4.41	−7.46
$\lvert\Delta E_{\text{int}}^{\text{NEDA}} - \Delta E_{\text{int}}\rvert$	6.08	3.97	3.85	3.68	6.28	5.94	5.64	4.31

(b) Reactions : $(Dipp_2DAB)M^{+2} + C_2H_4 \longrightarrow$ **TS-M-C$_2$H$_4$** $\longrightarrow$ **Pro-M-C$_2$H$_4$** (**M = O, S, Se, Te**)

	Transition States **TS-M-C$_2$H$_4$**				Products **Pro-M-C$_2$H$_4$**			
Energy	**TS-O-C$_2$H$_4$**	**TS-S-C$_2$H$_4$**	**TS-Se-C$_2$H$_4$**	**TS-Te-C$_2$H$_4$**	**Pro-O-C$_2$H$_4$**	**Pro-S-C$_2$H$_4$**	**Pro-Se-C$_2$H$_4$**	**Pro-Te-C$_2$H$_4$**
ΔE_{int}	−16.31	−34.64	−47.85	−34.19	−194.41	−94.00	−27.79	−34.61
$\Delta E_{\text{int}}^{\text{ETS}}$	−13.89	−35.52	−43.87	−31.64	−186.11	−94.26	−24.98	−32.04
$\Delta E_{\text{Pauli}}^{\text{ETS}}$	54.47	178.71	260.29	77.81	815.37	580.21	56.13	76.15
$\Delta E_{\text{elstat}}^{\text{ETS}}$	−23.16	−82.81	−128.86	−43.29	−367.15	−253.57	−30.23	−42.55
$\Delta E_{\text{orb}}^{\text{ETS}}$	−34.56	−120.82	−165.08	−55.28	−623.94	−410.25	−39.76	−54.66
$\Delta E_{\text{disp}}^{\text{ETS}}$	−10.64	−10.60	−10.23	−10.88	−10.38	−10.66	−11.10	−10.98
$\lvert\Delta E_{\text{int}}^{\text{ETS}} - \Delta E_{\text{int}}\rvert$	2.42	0.88	3.98	2.55	8.30	0.26	2.81	2.57
$\Delta E_{\text{int}}^{\text{NEDA}}$	−12.44	−30.71	−43.23	−30.14	−185.81	−87.21	−24.36	−31.02
$\Delta E_{\text{Pauli}}^{\text{NEDA}}$	139.73	267.91	359.13	123.66	1424.17	618.98	110.03	122.34
$\Delta E_{\text{elstat}}^{\text{NEDA}}$	−44.55	−99.62	−141.09	−56.91	−391.45	−185.11	−56.69	−56.21
$\Delta E_{\text{orb}}^{\text{NEDA}}$	−98.03	−189.21	−252.77	−87.60	−1209.75	−513.54	−67.83	−87.33
$\Delta E_{\text{disp}}^{\text{NEDA}}$	−9.58	−9.79	−8.49	−9.29	−8.77	−7.53	−9.88	−9.82
$\lvert\Delta E_{\text{int}}^{\text{NEDA}} - \Delta E_{\text{int}}\rvert$	3.87	3.93	4.63	4.05	8.60	6.79	3.43	3.59

[a] The ETS-NOCV decompostions of the interaction energies are obtained at the BP86/TZ2P//BP86/Def2-SVP theory level with ZORA,
$\Delta E_{\text{int}}^{\text{ETS}} = \Delta E_{\text{Pauli}}^{\text{ETS}} + \Delta E_{\text{elstat}}^{\text{ETS}} + \Delta E_{\text{orb}}^{\text{ETS}} + \Delta E_{\text{disp}}^{\text{ETS}}$

[b] The NEDA decompostions of the interaction energies are calculated at the BP86/Def2-SVP theory level,
$\Delta E_{\text{int}}^{\text{NEDA}} = \Delta E_{\text{Pauli}}^{\text{NEDA}} + \Delta E_{\text{elstat}}^{\text{NEDA}} + \Delta E_{\text{orb}}^{\text{NEDA}} + \Delta E_{\text{disp}}^{\text{NEDA}}$

To qualitatively compare the variation trends of the energies data listed in Tables S1 and S2 (S3 and S4), the numbers in the two tables are converted into the "charts of variation trends" in Tables S5 and S6 (S7 and S8), respectively. The energy entry under the structure ΔE(Complex-M_2) is replaced by one of the four notations {+, −, 0(+), 0(−)}, depending on the value of the energy variation (EV),

$$\mathrm{EV} = \Delta E(\text{Complex-M}_2) - \Delta E(\text{Complex-M}_1) \ ,$$

where Complex-M_1 and Complex-M_2 are the structures with elements M_1 and M_2 as the central atoms, respectively, and M_1 is the lighter neighboring element of M_2 of the same group of elements. The variation trend of Complex-M_2 is denoted by one of the four symbols below,

$$\text{Symbol} = \begin{cases} \quad + & \text{if} \quad \mathrm{EV} \in (0.5, -\infty) \\ 0(+) & \text{if} \quad \mathrm{EV} \in [0, 0.5] \\ 0(-) & \text{if} \quad \mathrm{EV} \in [-0.5, 0) \\ \quad - & \text{if} \quad \mathrm{EV} \in (-\infty, -0.5) \end{cases} \ .$$

Symbols "0(+)" and "0(−)" mean the magnitude of EV is less than 0.5 Kcal/mol., and are considered to be virtually invariant. Symbols "0(+)" and "0(−)" are interchangeable in interpreting the charts of variation trends. Additionaly, at times symbols "0(+)" and "0(−)" flexibly regarded as "+" and "−", respectively. All qualitative comparisons of the $(P\mathit{t}Bu_3)_2M^+$ and $(Dipp_2DAB)M^{+2}$ reactions in the main text are referred to the charts in Tables (S5 and S6) and (S7 and S8), respectively.

Table S5: The charts of variation trends of the analytic interaction energies and related energies are converted from Table S1 for the $(PtBu_3)_2M^+$ reactions with (a) methane and (b) ethene.

(a) Reactions : $(PtBu_3)_2M^+ + CH_4 \longrightarrow$ **TS-M-CH$_4$** $\longrightarrow$ **Pro-M-CH$_4$** (**M = B, Al, Ga, In, Tl**)

	Transition States **TS-M-CH$_4$**					Products **Pro-M-CH$_4$**				
Variation	Remarks	**TS-Al-CH$_4$**	**TS-Ga-CH$_4$**	**TS-In-CH$_4$**	**TS-Tl-CH$_4$**	Remarks	**Pro-Al-CH$_4$**	**Pro-Ga-CH$_4$**	**Pro-In-CH$_4$**	**Pro-Tl-CH$_4$**
ΔE		+	+	+	+		+	+	+	+
ΔE_{str}	*[a]	+	+	+	+		+	−	+	−
$\Delta E_{\text{str, carb}}$		−	+	−	0(−)		−	+	−	−
$\Delta E_{\text{str, meth}}$	#[b]	+	+	+	+		+	−	+	+
ΔE_{int}		−	−	+	+	*	+	+	+	+

(b) Reactions : $(PtBu_3)_2M^+ + C_2H_4 \longrightarrow$ **TS-M-C$_2$H$_4$** $\longrightarrow$ **Pro-M-C$_2$H$_4$** (**M = B, Al, Ga, In, Tl**)

	Transition States **TS-M-C$_2$H$_4$**					Products **Pro-M-C$_2$H$_4$**				
Variation	Remarks	**TS-Al-C$_2$H$_4$**	**TS-Ga-C$_2$H$_4$**	**TS-In-C$_2$H$_4$**	**TS-Tl-C$_2$H$_4$**	Remarks	**Pro-Al-C$_2$H$_4$**	**Pro-Ga-C$_2$H$_4$**	**Pro-In-C$_2$H$_4$**	**Pro-Tl-C$_2$H$_4$**
ΔE		−	+	+	+		+	+	+	+
ΔE_{str}	*	−	+	+	+		−	+	−	−
$\Delta E_{\text{str, carb}}$		−	+	0(+)	−	#	−	+	−	−
$\Delta E_{\text{str, eth}}$		+	+	+	+		+	−	−	+
ΔE_{int}		−	0(−)	+	+	*	+	+	+	+

[a] Symbol "*" means the variation trend of the specified energy is same as ΔE.
[b] Symbol "#" means the variation trend of the specified energy is same as ΔE_{str}.

Table S6: The charts of variation trends of the analytic and EDA interaction energies and their ETS-NOCV and NEDA partitions are converted from Table S2 for the $(PtBu_3)_2M^+$ reactions with (a) methane and (b) ethene.

(a) Reactions : $(PtBu_3)_2M^+ + CH_4 \longrightarrow$ **TS-M-CH$_4$** $\longrightarrow$ **Pro-M-CH$_4$** (**M = B, Al, Ga, In, Tl**)

	Transition States **TS-M-CH$_4$**					Products **Pro-M-CH$_4$**				
Variation	Remarks	**TS-Al-CH$_4$**	**TS-Ga-CH$_4$**	**TS-In-CH$_4$**	**TS-Tl-CH$_4$**	Remarks	**Pro-Al-CH$_4$**	**Pro-Ga-CH$_4$**	**Pro-In-CH$_4$**	**Pro-Tl-CH$_4$**
$\Delta E_{\rm int}$		−	−	+	+		+	+	+	+
$\Delta E_{\rm int}^{\rm ETS}$		−	+	−	−	*[a]	+	+	+	+
$\Delta E_{\rm Pauli}^{\rm ETS}$		+	+	−	+		−	+	−	+
$\Delta E_{\rm elstat}^{\rm ETS}$		−	−	−	−		+	−	+	−
$\Delta E_{\rm orb}^{\rm ETS}$		−	−	+	−	*	+	+	+	+
$\Delta E_{\rm int}^{\rm NEDA}$	*	−	−	+	+	*	+	+	+	+
$\Delta E_{\rm Pauli}^{\rm NEDA}$		+	+	−	−		−	+	−	−
$\Delta E_{\rm elstat}^{\rm NEDA}$		−	−	+	−		−	−	+	+
$\Delta E_{\rm orb}^{\rm NEDA}$	*	−	−	+	+	*	+	+	+	+

(b) Reactions : $(PtBu_3)_2M^+ + C_2H_4 \longrightarrow$ **TS-M-C$_2$H$_4$** $\longrightarrow$ **Pro-M-C$_2$H$_4$** (**M = B, Al, Ga, In, Tl**)

	Transition States **TS-M-C$_2$H$_4$**					Products **Pro-M-C$_2$H$_4$**				
Variation	Remarks	**TS-Al-C$_2$H$_4$**	**TS-Ga-C$_2$H$_4$**	**TS-In-C$_2$H$_4$**	**TS-Tl-C$_2$H$_4$**	Remarks	**Pro-Al-C$_2$H$_4$**	**Pro-Ga-C$_2$H$_4$**	**Pro-In-C$_2$H$_4$**	**Pro-Tl-C$_2$H$_4$**
$\Delta E_{\rm int}$		−	0(−)	+	+		+	+	+	+
$\Delta E_{\rm int}^{\rm ETS}$		−	+	−	+	*	+	+	+	+
$\Delta E_{\rm Pauli}^{\rm ETS}$		+	+	+	−		−	−	−	−
$\Delta E_{\rm elstat}^{\rm ETS}$		−	−	−	+	*	+	+	+	+
$\Delta E_{\rm orb}^{\rm ETS}$		−	−	−	+	*	+	+	+	+
$\Delta E_{\rm int}^{\rm NEDA}$	*	−	0(+)	+	+	*	+	+	+	+
$\Delta E_{\rm Pauli}^{\rm NEDA}$		+	+	−	+		−	+	−	+
$\Delta E_{\rm elstat}^{\rm NEDA}$	*	−	−	+	+		+	−	+	+
$\Delta E_{\rm orb}^{\rm NEDA}$	*	−	−	+	+	*	+	+	+	+

[a] Symbol "*" means the variation trend of the specified energy is same as the analytic interaction energies $\Delta E_{\rm int}$.

Table S7: The charts of variation trends of the analytic interaction energies and related energies are converted from Table S3 for the $(Dipp_2DAB)M^{+2}$ reactions with (a) methane and (b) ethene.

(a) Reactions : $(Dipp_2DAB)M^{+2} + CH_4 \longrightarrow$ **TS-M-CH$_4$** $\longrightarrow$ **Pro-M-CH$_4$** (**M** = **O**, **S**, **Se**, **Te**)

	Transition States **TS-M-CH$_4$**				Products **Pro-M-CH$_4$**			
Variation	Remarks	**TS-S-CH$_4$**	**TS-Se-CH$_4$**	**TS-Te-CH$_4$**	Remarks	**Pro-S-CH$_4$**	**Pro-Se-CH$_4$**	**Pro-Te-CH$_4$**
ΔE		+	−	0(+)		+	+	+
ΔE_{str}		−	+	+		+	−	−
$\Delta E_{\text{str, carb}}$		0(−)	−	−	#[b]	+	−	−
$\Delta E_{\text{str, meth}}$	#	−	+	+		−	+	+
ΔE_{int}		+	−	−	*[a]	+	+	+

(b) Reactions : $(Dipp_2DAB)M^{+2} + C_2H_4 \longrightarrow$ **TS-M-C$_2$H$_4$** $\longrightarrow$ **Pro-M-C$_2$H$_4$** (**M** = **O**, **S**, **Se**, **Te**)

	Transition States **TS-M-C$_2$H$_4$**				Products **Pro-M-C$_2$H$_4$**			
Variation	Remarks	**TS-S-C$_2$H$_4$**	**TS-Se-C$_2$H$_4$**	**TS-Te-C$_2$H$_4$**	Remarks	**Pro-S-C$_2$H$_4$**	**Pro-Se-C$_2$H$_4$**	**Pro-Te-C$_2$H$_4$**
ΔE		−	−	−		+	−	−
ΔE_{str}		+	+	−		−	−	+
$\Delta E_{\text{str, carb}}$	#	+	+	−		+	−	+
$\Delta E_{\text{str, eth}}$	#	+	+	−	#	−	−	+
ΔE_{int}		−	−	+		+	+	−

[a] Symbol "*" means the variation trend of the specified energy is same as ΔE.
[b] Symbol "#" means the variation trend of the specified energy is same as ΔE_{str}.

Table S8: The charts of variation trends of the analytic and EDA interaction energies and their ETS-NOCV and NEDA partitions are converted from Table S4 for the $(Dipp_2DAB)M^{+2}$ reactions with (a) methane and (b) ethene.

(a) Reactions : $(Dipp_2DAB)M^{+2} + CH_4 \longrightarrow$ **TS-M-CH$_4$** $\longrightarrow$ **Pro-M-CH$_4$** (**M** = **O**, **S**, **Se**, **Te**)

	Transition States **TS-M-CH$_4$**				Products **Pro-M-CH$_4$**			
Variation	Remarks	**TS-S-CH$_4$**	**TS-Se-CH$_4$**	**TS-Te-CH$_4$**	Remarks	**Pro-S-CH$_4$**	**Pro-Se-CH$_4$**	**Pro-Te-CH$_4$**
ΔE_{int}		+	−	−		+	+	+
$\Delta E_{\text{int}}^{\text{ETS}}$	*[a]	+	−	−	*	+	+	+
$\Delta E_{\text{Pauli}}^{\text{ETS}}$		−	−	−		−	−	−
$\Delta E_{\text{elstat}}^{\text{ETS}}$		+	−	+	*	+	+	+
$\Delta E_{\text{orb}}^{\text{ETS}}$		+	+	+	*	+	+	+
$\Delta E_{\text{int}}^{\text{NEDA}}$	*	+	−	−	*	+	+	+
$\Delta E_{\text{Pauli}}^{\text{NEDA}}$		−	−	−		−	−	−
$\Delta E_{\text{elstat}}^{\text{NEDA}}$		+	−	+		+	−	+
$\Delta E_{\text{orb}}^{\text{NEDA}}$		+	+	+		+	+	−

(b) Reactions : $(Dipp_2DAB)M^{+2} + C_2H_4 \longrightarrow$ **TS-M-C$_2$H$_4$** $\longrightarrow$ **Pro-M-C$_2$H$_4$** (**M** = **O**, **S**, **Se**, **Te**)

	Transition States **TS-M-C$_2$H$_4$**				Products **Pro-M-C$_2$H$_4$**			
Variation	Remarks	**TS-S-C$_2$H$_4$**	**TS-Se-C$_2$H$_4$**	**TS-Te-C$_2$H$_4$**	Remarks	**Pro-S-C$_2$H$_4$**	**Pro-Se-C$_2$H$_4$**	**Pro-Te-C$_2$H$_4$**
ΔE_{int}		−	−	+		+	+	−
$\Delta E_{\text{int}}^{\text{ETS}}$	*	−	−	+	*	+	+	−
$\Delta E_{\text{Pauli}}^{\text{ETS}}$		+	+	−		−	−	+
$\Delta E_{\text{elstat}}^{\text{ETS}}$	*	−	−	+	*	+	+	−
$\Delta E_{\text{orb}}^{\text{ETS}}$	*	−	−	+	*	+	+	−
$\Delta E_{\text{int}}^{\text{NEDA}}$	*	−	−	+	*	+	+	−
$\Delta E_{\text{Pauli}}^{\text{NEDA}}$		+	+	−		−	−	+
$\Delta E_{\text{elstat}}^{\text{NEDA}}$	*	−	−	+		+	+	0(+)
$\Delta E_{\text{orb}}^{\text{NEDA}}$	*	−	−	+	*	+	+	−

[a] Symbol "*" means the variation trend of the specified energy is same as the analytic interaction energies ΔE_{int}.

Table S9: The main governing effects on the variation trends of the energies listed in the second column are shown in the third column for the $(PtBu_3)_2M^+$ reactions with (a) methane and (b) ethene and the $(Dipp_2DAB)M^{+2}$ reactions with (c) methane and (d) ethene.[a]

(a) Reactions of $(PtBu_3)_2M^+$ with CH_4		
Structures	Energies	Main Governing Components
Transition States	ΔE_{activ}	ΔE_{str}
	ΔE_{str}	$\Delta E_{\text{str, meth}}$
	ETS-NOCV ΔE_{int}	None
	NEDA ΔE_{int}	ΔE_{orb}
Products	ΔE_{react}	ΔE_{int}
	ΔE_{str}	None
	ETS-NOCV ΔE_{int}	ΔE_{orb}
	NEDA ΔE_{int}	ΔE_{orb}
(b) Reactions of $(PtBu_3)_2M^+$ with C_2H_4		
Structures	Energies	Main Governing Components
Transition States	ΔE_{activ}	ΔE_{str}
	ΔE_{str}	None
	ETS-NOCV ΔE_{int}	None
	NEDA ΔE_{int}	ΔE_{elstat} and ΔE_{orb}
Products	ΔE_{react}	ΔE_{int}
	ΔE_{str}	$\Delta E_{\text{str, carb}}$
	ETS-NOCV ΔE_{int}	ΔE_{elstat} and ΔE_{orb}
	NEDA ΔE_{int}	ΔE_{orb}
(c) Reactions of $(Dipp_2DAB)M^{+2}$ with CH_4		
Structures	Energies	Main Governing Components
Transition States	ΔE_{activ}	ΔE_{int}
	ΔE_{str}	$\Delta E_{\text{str, meth}}$
	ETS-NOCV ΔE_{int}	None
	NEDA ΔE_{int}	None
Products	ΔE_{react}	ΔE_{int}
	ΔE_{str}	$\Delta E_{\text{str, carb}}$
	ETS-NOCV ΔE_{int}	ΔE_{elstat} and ΔE_{orb}
	NEDA ΔE_{int}	None
(d) Reactions of $(Dipp_2DAB)M^{+2}$ with C_2H_4		
Structures	Energies	Main Governing Components
Transition States	ΔE_{activ}	None
	ΔE_{str}	$\Delta E_{\text{str, carb}}$ and $\Delta E_{\text{str, eth}}$
	ETS-NOCV ΔE_{int}	ΔE_{elstat} and ΔE_{orb}
	NEDA ΔE_{int}	ΔE_{elstat} and ΔE_{orb}
Products	ΔE_{react}	None
	ΔE_{str}	$\Delta E_{\text{str, eth}}$
	ETS-NOCV ΔE_{int}	ΔE_{elstat} and ΔE_{orb}
	NEDA ΔE_{int}	ΔE_{orb}

[a] ΔE_{activ} and ΔE_{react} are the activation energies and reaction enthalpies of the transition states and products, respectively. All other notations in the table are explicated in Eqs. (1) and (3) of the main text.