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

Supporting information for:

Planar pentacoordinate carbon in $[XC_7H_2]^{2+}$ (X = Be and Mg) and its derivatives

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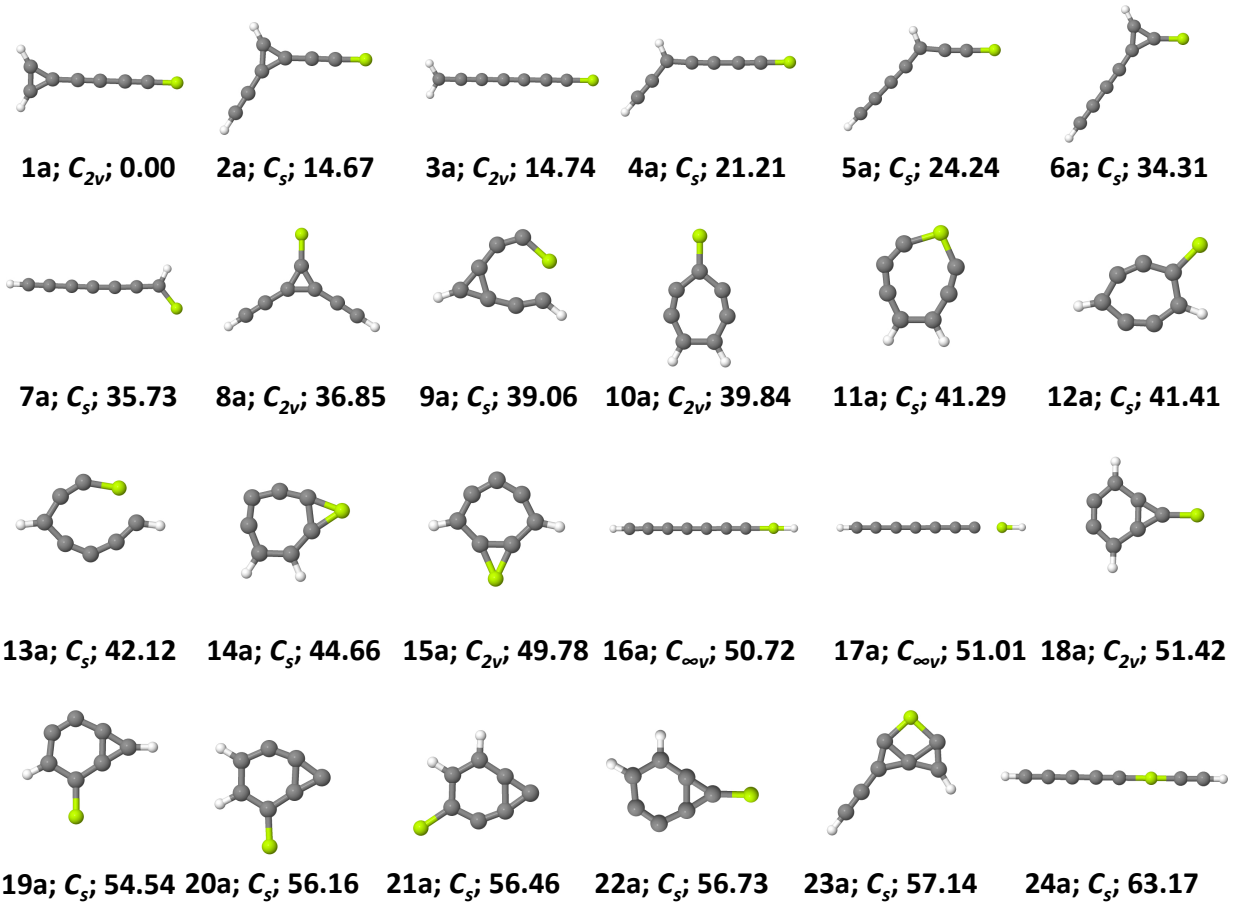

Figure S1: Isomers **1a** to **24a** of $[BeC_7H_2]^{2+}$. ZPVE-corrected relative energies (in kcal mol^{-1}) are calculated at the CBS-QB3 level of theory.

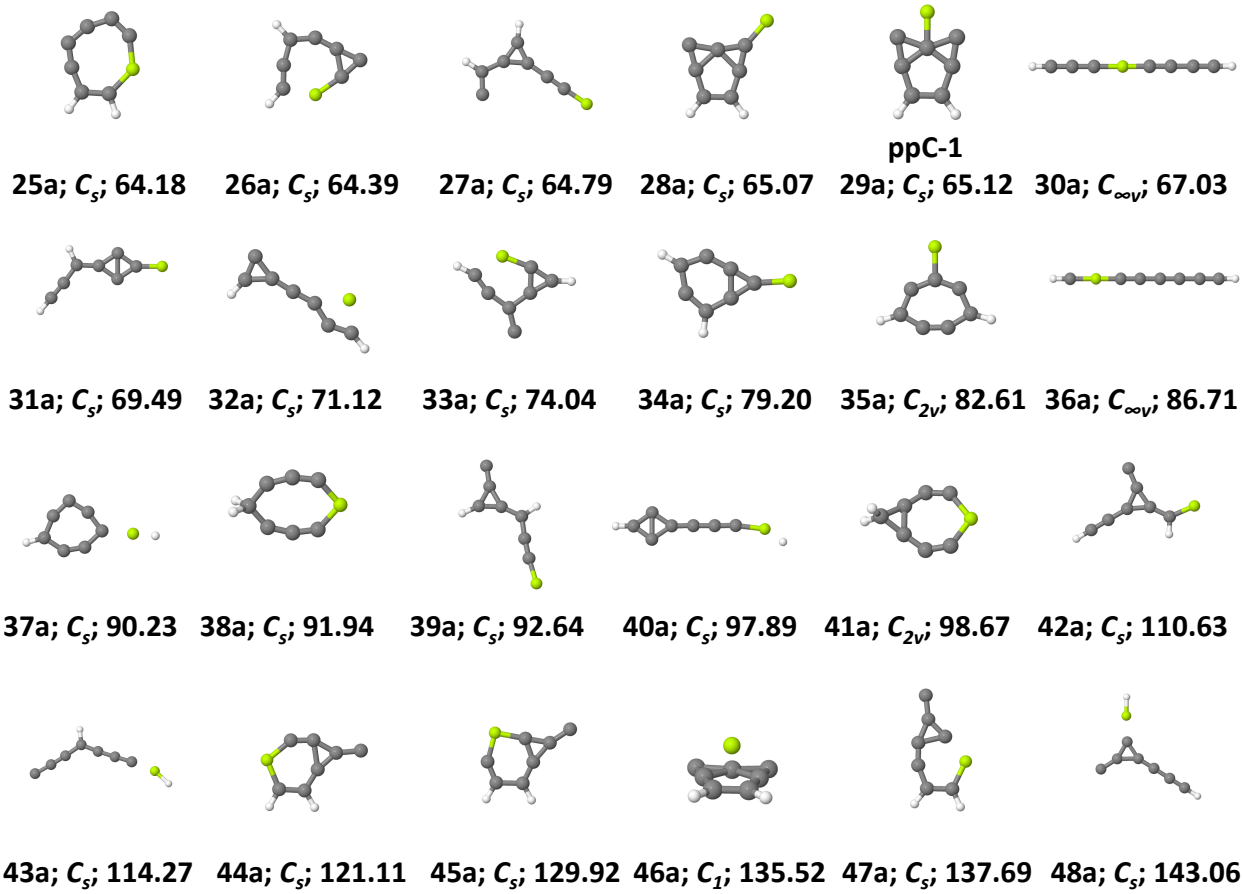

Figure S2: Isomers **25a** to **48a** of $[BeC_7H_2]^{2+}$. ZPVE-corrected relative energies (in kcal mol^{-1}) are calculated at the CBS-QB3 level of theory.

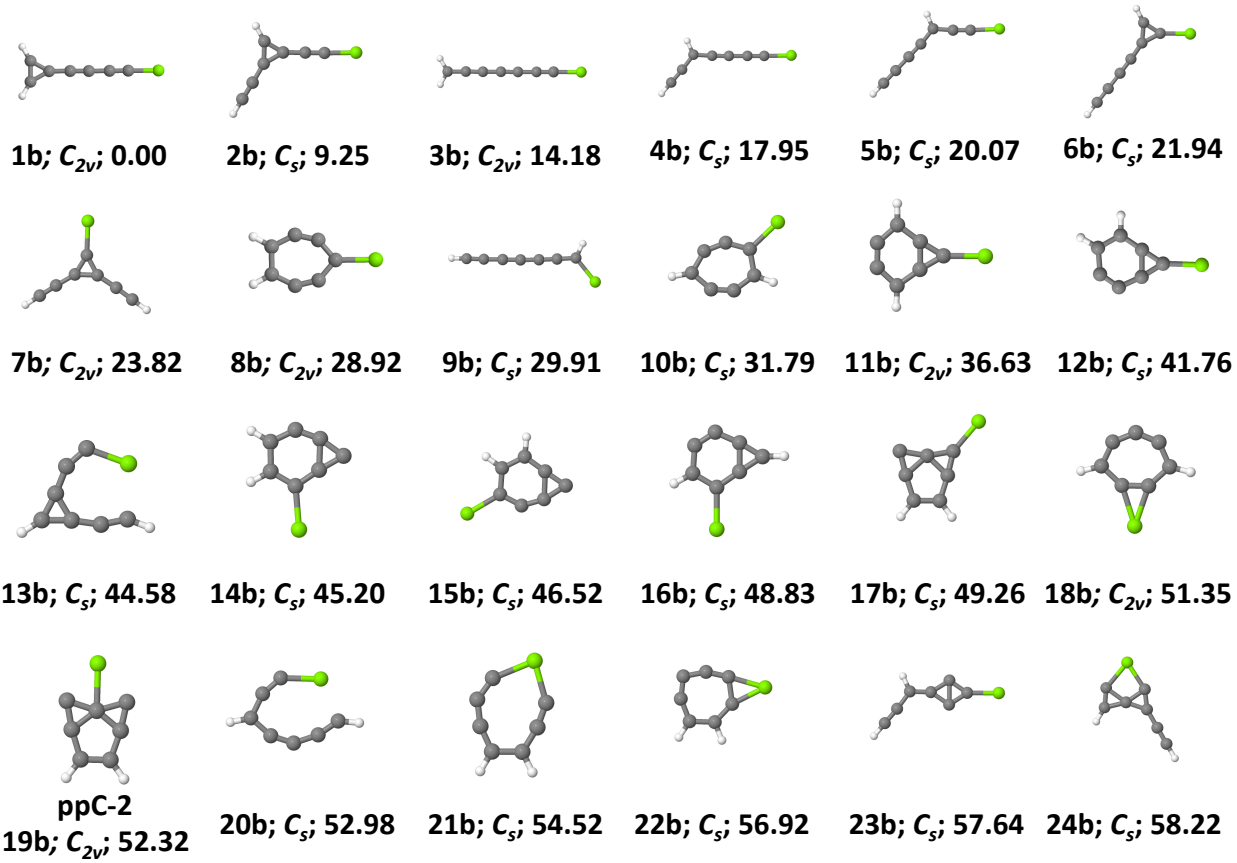

Figure S3: Isomers **1b** to **24b** of $[MgC_7H_2]^{2+}$. ZPVE-corrected relative energies (in kcal mol^{-1}) are calculated at the CBS-QB3 level of theory.

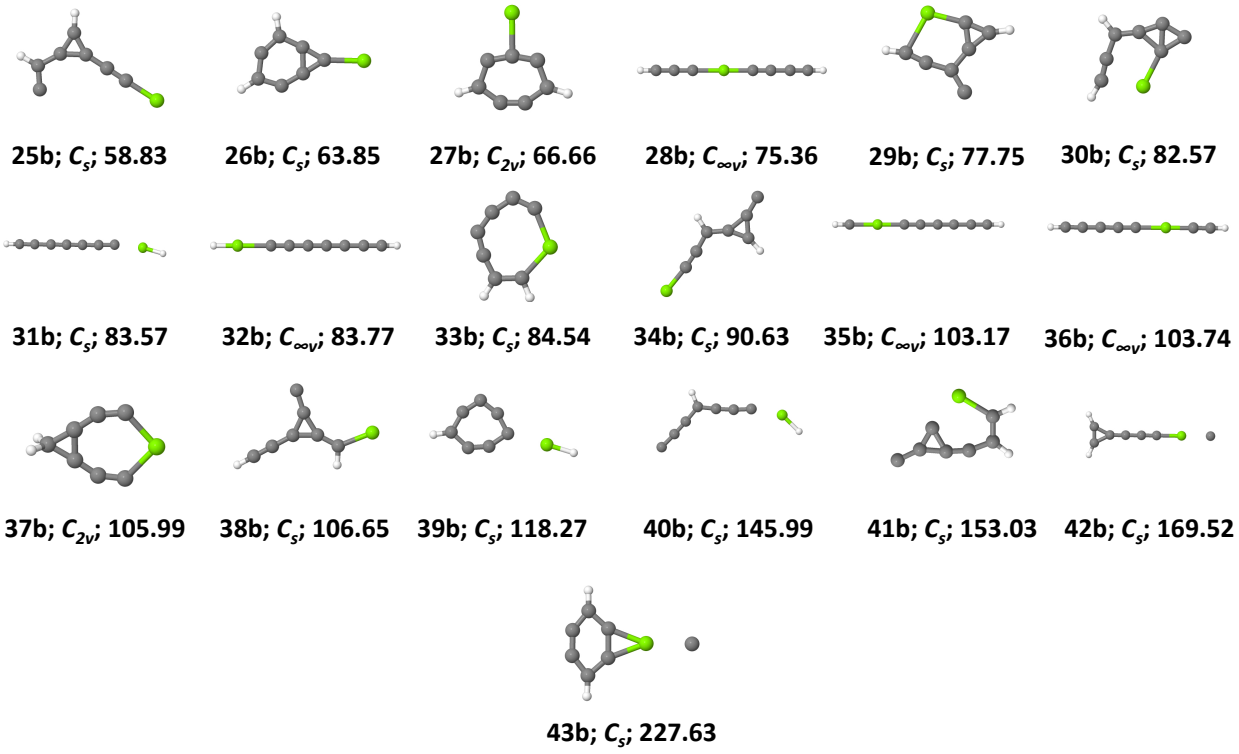

Figure S4: Isomers **25b** to **43b** of $[MgC_7H_2]^{2+}$. ZPVE-corrected relative energies (in kcal mol^{-1}) are calculated at the CBS-QB3 level of theory.

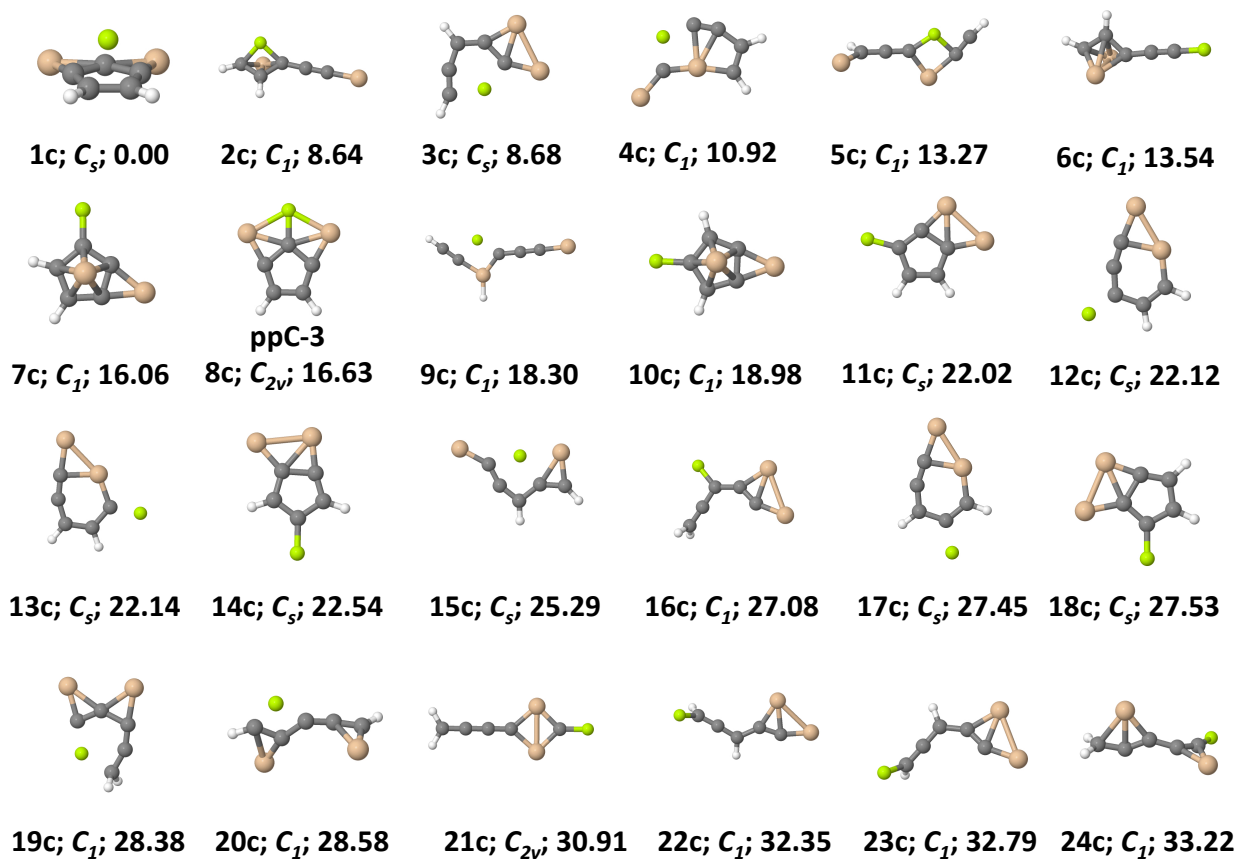

Figure S5: Isomers **1c** to **24c** of $[BeSi_2C_5H_2]^{2+}$. ZPVE-corrected relative energies (in kcal mol^{-1}) are calculated at the CBS-QB3 level of theory.

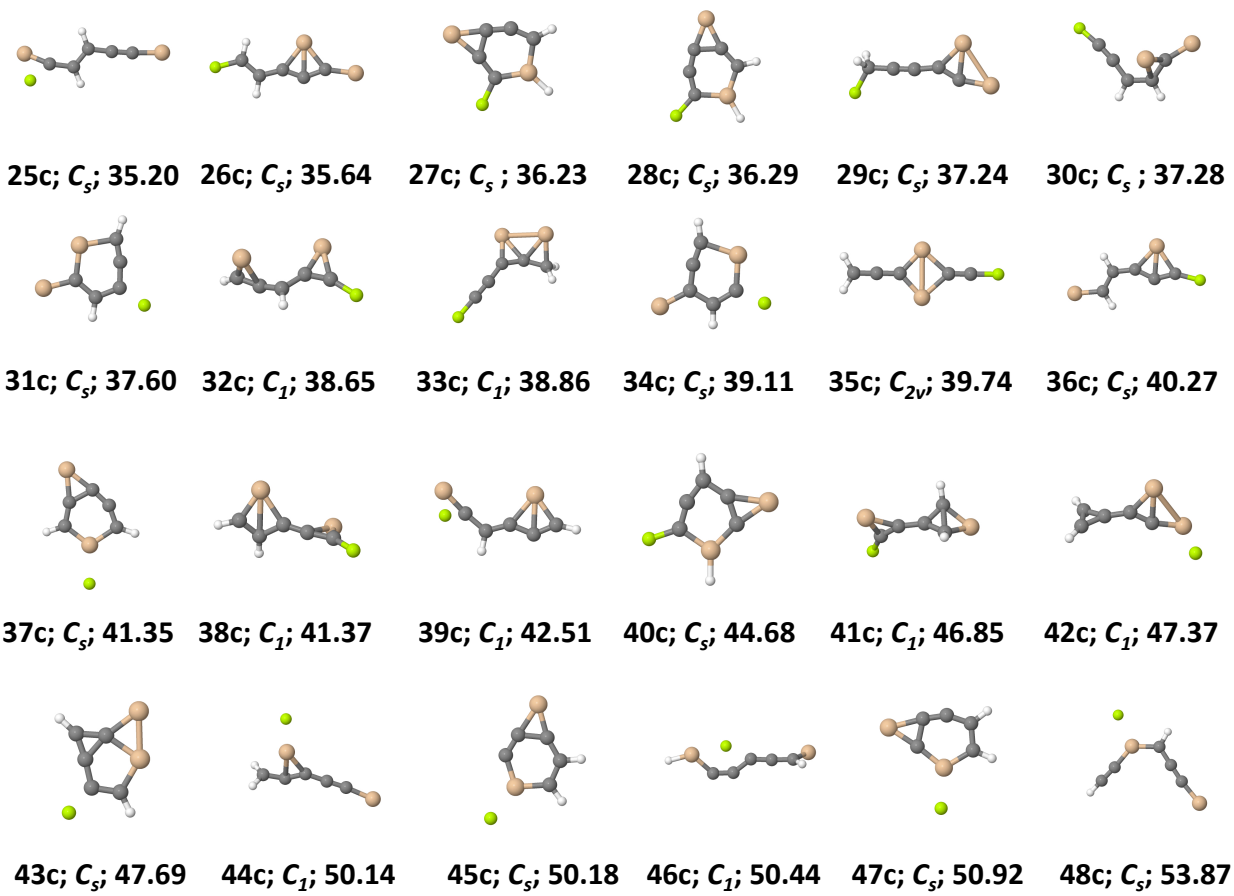

Figure S6: Isomers **25c** to **48c** of $[BeSi_2C_5H_2]^{2+}$. ZPVE-corrected relative energies (in kcal mol^{-1}) are calculated at the CBS-QB3 level of theory.

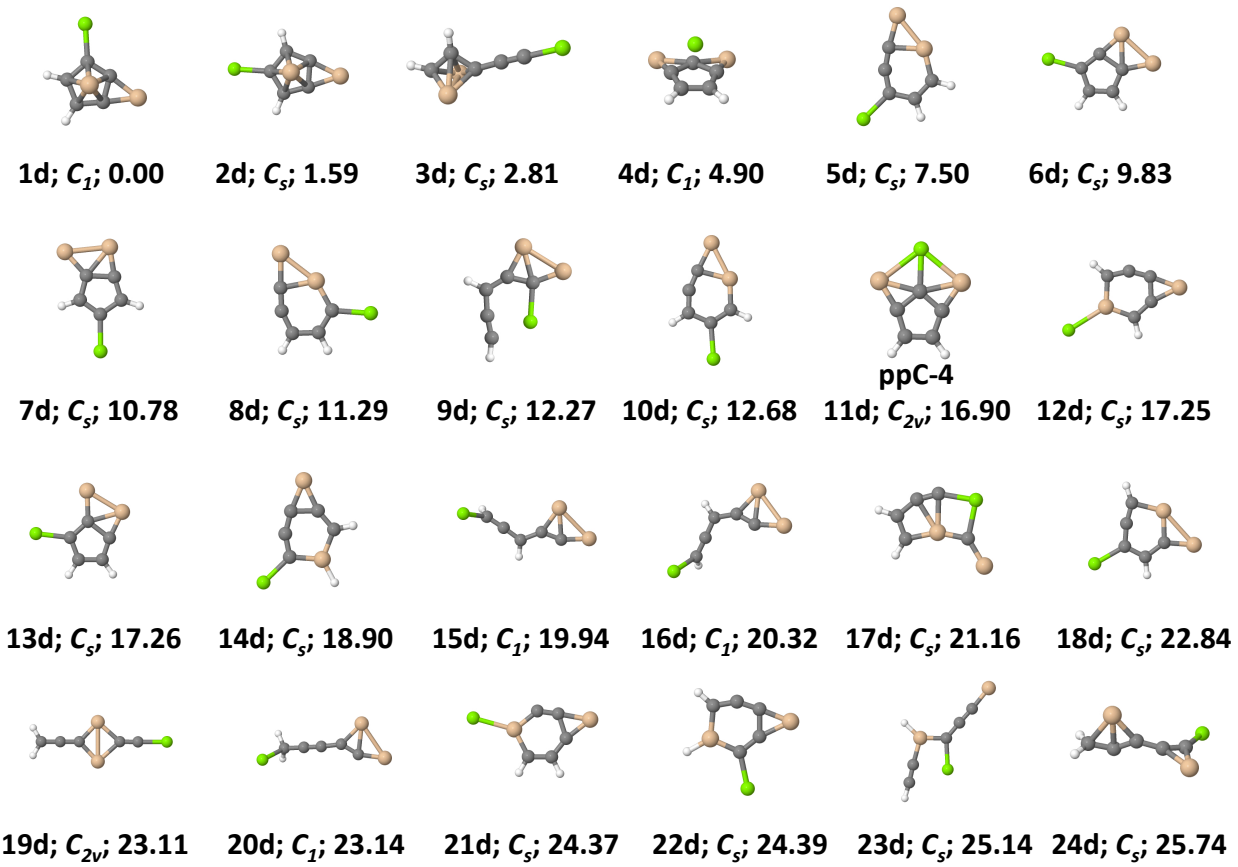

Figure S7: Isomers **1d** to **24d** of $[MgSi_2C_5H_2]^{2+}$. ZPVE-corrected relative energies (in kcal mol^{-1}) are calculated at the CBS-QB3 level of theory.

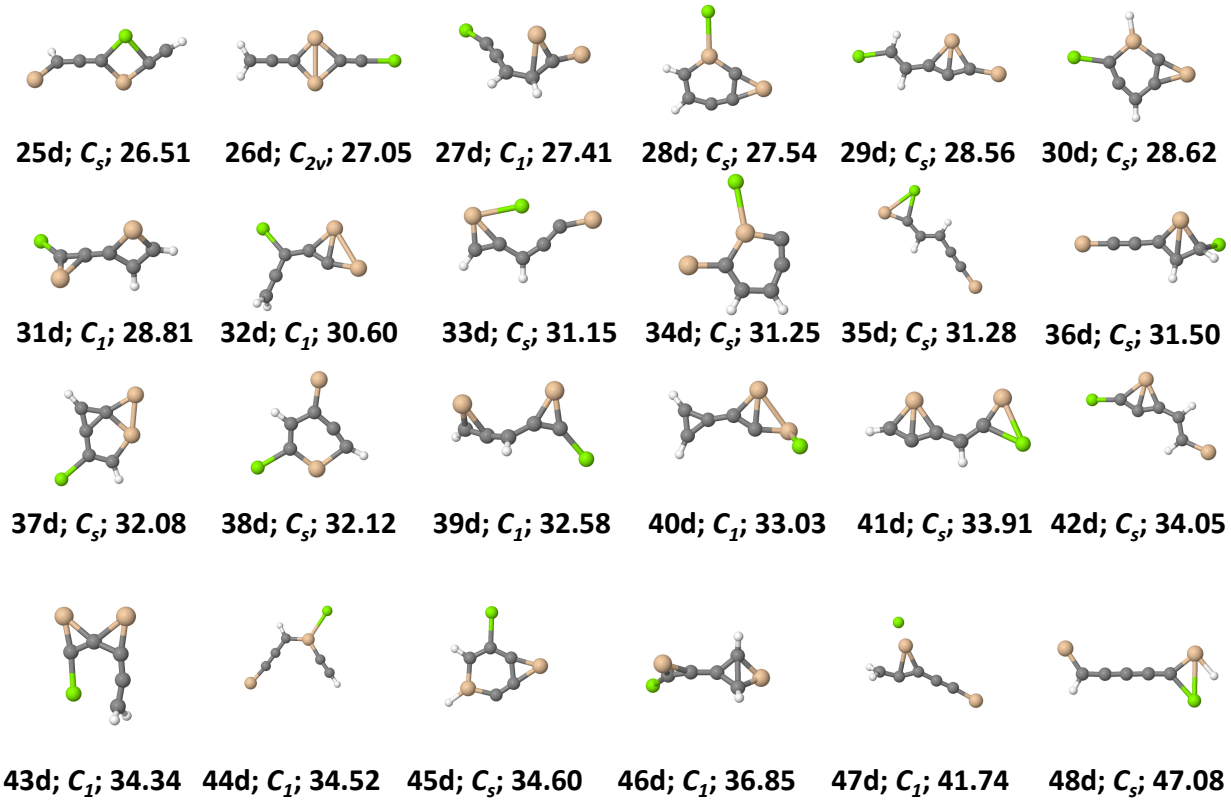

Figure S8: Isomers **25d** to **48d** of $[MgSi_2C_5H_2]^{2+}$. ZPVE-corrected relative energies (in kcal mol^{-1}) are calculated at the CBS-QB3 level of theory.

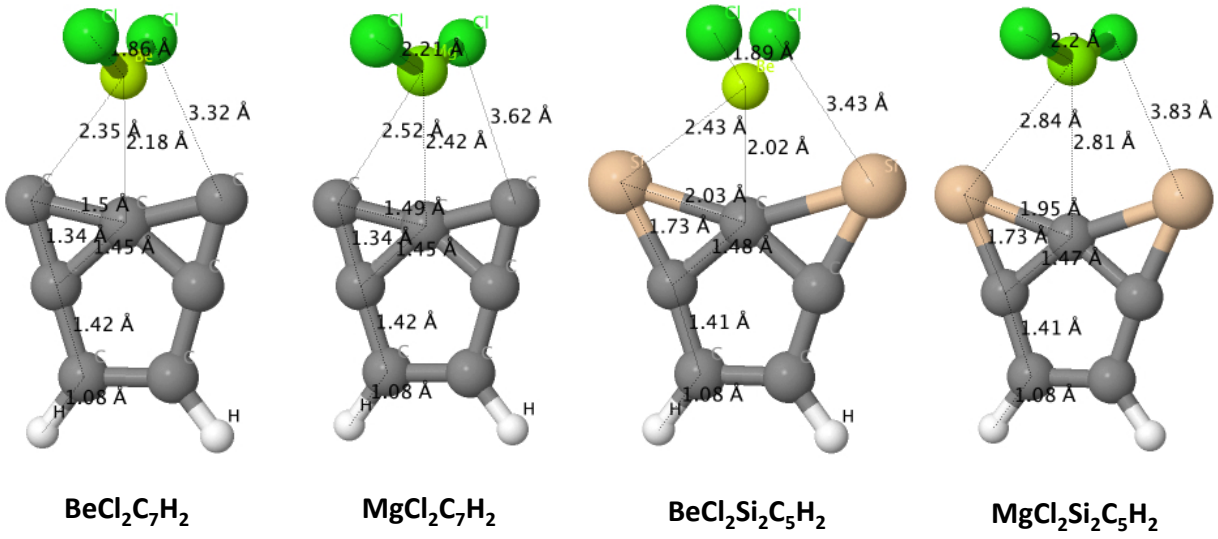

Figure S9: Optimized geometries of neutral $XCl_2C_7H_2$ and $XSi_2C_5H_2$ (X = Be and Mg) in their ground electronic states obtained at the PBE0-D3/def2-TZVP level of theory. All isomers are minima.

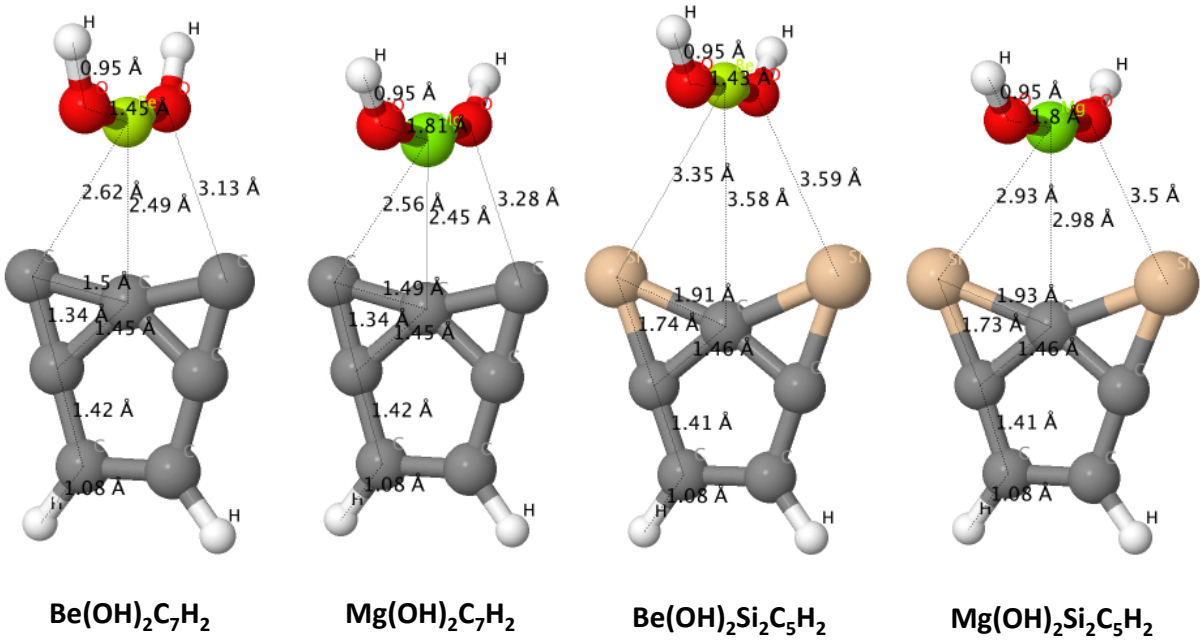

Figure S10: Optimized geometries of neutral $XCl_2C_7H_2$ and $XSi_2C_5H_2$ (X = Be and Mg) in their ground electronic states obtained at the PBE0-D3/def2-TZVP level of theory. All isomers are minima.

Table S1: Electron density descriptors (in a.u.) at the Bond Critical Point (BCP) and Ring Critical Point (RCP) obtained at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory for $[BeC_7H_2]^{2+}$ (ppC-1)

BCP & RCP	$K(r_c)$	$H(r_c)$	ELF	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$-\frac{G(r_c)}{V(r_c)}$	$\frac{G(r_c)}{\rho(r_c)}$
C3-C5	0.357	-0.357	0.878	0.317	-0.794	0.158	-0.515	-0.307	0.498
C1-C3	0.193	-0.193	0.699	0.231	-0.118	0.163	-0.356	-0.458	0.708
C1-C5	0.243	-0.243	0.818	0.263	-0.39	0.146	-0.389	-0.374	0.555
C5-C7	0.255	-0.255	0.937	0.272	-0.68	0.0848	-0.34	-0.249	0.312
C7-H9	0.325	-0.325	0.996	0.297	-1.21	0.0234	-0.348	-0.067	0.0787
C1-Be10	0.0255	-0.0255	0.108	0.0836	0.426	0.132	-0.158	-0.838	1.579
RCP	0.000635	-0.000635	0.0764	0.0536	0.302	0.0761	-0.0767	-0.991	1.419
C6-C7	0.328	-0.328	0.946	0.317	-0.904	0.102	-0.429	-0.236	0.32
C1-C2	0.193	-0.193	0.699	0.231	-0.118	0.163	-0.356	-0.458	0.708
C1-C4	0.243	-0.243	0.818	0.263	-0.39	0.146	-0.389	-0.374	0.555
C4-C6	0.255	-0.255	0.937	0.272	-0.68	0.0848	-0.34	-0.249	0.312
C2-C4	0.357	-0.357	0.878	0.317	-0.794	0.158	-0.515	-0.307	0.498
C6-H8	0.325	-0.325	0.996	0.297	-1.21	0.0234	-0.348	-0.067	0.078

Table S2: Electron density descriptors (in a.u.) at the Bond Critical Point (BCP) and Ring Critical Point (RCP) obtained at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory for $[MgC_7H_2]^{2+}$ (ppC-2)

BCP & RCP	$K(r_c)$	$H(r_c)$	ELF	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$-\frac{G(r_c)}{V(r_c)}$	$\frac{G(r_c)}{\rho(r_c)}$
C3-C5	0.372	-0.372	0.876	0.322	-0.834	0.163	-0.535	-0.305	0.506
C1-C3	0.208	-0.208	0.75	0.239	-0.22	0.153	-0.361	-0.423	0.639
RCP	-0.003	0.003	0.048	0.034	0.203	0.047	-0.044	-1.077	1.357
C1-C5	0.228	-0.228	0.804	0.255	-0.328	0.146	-0.373	-0.39	0.57
C5-C7	0.26	-0.26	0.939	0.276	-0.701	0.085	-0.345	-0.246	0.308
C7-H9	0.324	-0.324	0.996	0.297	-1.19	0.025	-0.349	-0.072	0.084
C1-Mg10	-0.004	0.004	0.042	0.035	0.051	-0.047	-0.047	1.466	-1.344
RCP	-0.0034	0.0034	0.048	0.034	0.203	0.047	-0.044	-1.077	1.357
RCP	0.0007	-0.0007	0.078	0.054	0.3	0.075	-0.076	-0.989	1.403
C6-C7	0.34	-0.34	0.943	0.322	-0.933	0.107	-0.446	-0.238	0.33
C1-C2	0.208	-0.208	0.75	0.239	-0.22	0.153	-0.361	-0.423	0.639
C1-C4	0.228	-0.228	0.804	0.255	-0.328	0.146	-0.373	-0.39	0.57
C4-C6	0.26	-0.26	0.939	0.276	-0.701	0.085	-0.345	-0.246	0.308
C2-C4	0.372	-0.372	0.876	0.322	-0.834	0.163	-0.535	-0.305	0.506
C6-H8	0.324	-0.324	0.996	0.297	-1.19	0.025	-0.349	-0.072	0.084
C2-Mg10	-0.003	0.003	0.05	0.034	0.198	0.046	-0.043	-1.07	1.325
RCP	0.135	-0.135	0.613	0.229	0.242	0.195	-0.33	-0.591	0.852
C3-Mg10	-0.003	0.003	0.05	0.034	0.198	0.046	-0.043	-1.07	1.325
RCP	0.135	-0.135	0.613	0.229	0.242	0.195	-0.33	-0.591	0.852

Table S3: Electron density descriptors (in a.u.) at the Bond Critical Point (BCP) and Ring Critical Point (RCP) obtained at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory for $[BeSi_2C_5H_2]^{2+}$ (ppC-3)

BCP & RCP	$K(r_c)$	$H(r_c)$	ELF	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$-\frac{G(r_c)}{V(r_c)}$	$\frac{G(r_c)}{\rho(r_c)}$
Si3-C5	0.09	-0.09	0.265	0.134	0.314	0.169	-0.259	-0.651	1.254
C1-C5	0.2	-0.2	0.891	0.242	-0.425	0.094	-0.294	-0.319	0.389
C5-C7	0.312	-0.312	0.943	0.305	-0.859	0.097	-0.409	-0.237	0.318
C7-H9	0.322	-0.322	0.995	0.297	-1.18	0.028	-0.35	-0.08	0.094
C1-Be10	0.045	-0.0451	0.167	0.101	0.379	0.14	-0.185	-0.756	1.388
RCP	0.0000721	-0.0000721	0.076	0.052	0.29	0.072	-0.072	-0.999	1.391
C6-C7	0.322	-0.322	0.946	0.314	-0.889	0.099	-0.421	-0.236	0.317
C1-C4	0.2	-0.2	0.891	0.242	-0.425	0.094	-0.294	-0.319	0.389
C4-C6	0.312	-0.312	0.943	0.305	-0.859	0.097	-0.409	-0.237	0.318
Si2-C4	0.09	-0.09	0.265	0.134	0.314	0.169	-0.259	-0.651	1.254
C6-H8	0.322	-0.322	0.995	0.297	-1.18	0.028	-0.35	-0.08	0.094

Table S4: Electron density descriptors (in a.u.) at the Bond Critical Point (BCP) and Ring Critical Point (RCP) obtained at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory for $MgSi_2C_5H_2^{2+}$ (ppC-4)

BCP & RCP	$K(r_c)$	$H(r_c)$	ELF	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$-\frac{G(r_c)}{V(r_c)}$	$\frac{G(r_c)}{\rho(r_c)}$
C4-Si8	0	-0.094	0.262	0.139	0.346	0.181	-0.275	-0.657	1.294
C3-H6	0.321	-0.321	0.994	0.296	-1.17	0.029	-0.351	-0.085	0.1
C3-C4	0.293	-0.293	0.945	0.296	-0.807	0.091	-0.384	-0.237	0.308
C4-C5	0.211	-0.211	0.896	0.248	-0.46	0.095	-0.307	-0.312	0.386
C5-Mg10	0.0014	-0.001	0.091	0.046	0.21	0.054	-0.056	-0.967	1.167
RCP	0.00003	-0.00003	0.075	0.052	0.297	0.074	-0.074	-1	1.413
C1-C3	0.343	-0.343	0.942	0.323	-0.939	0.108	-0.451	-0.239	0.334
C2-C5	0.211	-0.211	0.896	0.248	-0.46	0.095	-0.307	-0.312	0.386
C1-C2	0.293	-0.293	0.945	0.296	-0.807	0.091	-0.384	-0.237	0.308
C1-H7	0.321	-0.321	0.994	0.296	-1.17	0.029	-0.351	-0.085	0.1
C2-Si9	0.094	-0.094	0.262	0.139	0.346	0.181	-0.275	-0.657	1.294

A sample input file for $[BeC_7H_2]^{2+}$ is given below.

```
%mem=10GB
%NprocShared=16
%chk=bec7h2.chk
#P B3LYP/6-311++G(2d,2p) EmpiricalDispersion=GD3BJ pop=nboread gfinput

AIM_analysis

2 1
 C     3.284481    -0.000000     1.000000
 C     3.774452    -0.000000     2.384559
 C     3.774452    -0.000000    -0.384559
 C     2.440165     0.000000     2.162450
 C     2.440165    -0.000000    -0.162450
 C     1.072583     0.000000     1.696429
 C     1.072583     0.000000     0.303571
 H     0.201606     0.000000     2.340235
 H     0.201606     0.000000    -0.340235
Be     4.961606    -0.000000     1.000000
```

Cartesian coordinates of optimized geometries of $[BeC_7H_2]^{2+}$ at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory.

```
   10
scf done:  -281.732956
 C     3.284481    -0.000000     1.000000
 C     3.774452    -0.000000     2.384559
```

C	3.774452	-0.000000	-0.384559
C	2.440165	0.000000	2.162450
C	2.440165	-0.000000	-0.162450
C	1.072583	0.000000	1.696429
C	1.072583	0.000000	0.303571
H	0.201606	0.000000	2.340235
H	0.201606	0.000000	-0.340235
Be	4.961606	-0.000000	1.000000

Cartesian coordinates of optimized geometries of $[BeSi_2C_5H_2]^{2+}$ at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory.

10

scf done: -784.749628

C	3.377945	-0.000000	1.000000
Si	3.941053	0.000000	2.995762
Si	3.941053	-0.000000	-0.995762
C	2.419455	0.000000	2.135647
C	2.419455	-0.000000	-0.135647
C	1.090025	0.000000	1.697549
C	1.090025	-0.000000	0.302451
H	0.222737	0.000000	2.340813
H	0.222737	-0.000000	-0.340813
Be	5.031502	-0.000000	1.000000

Cartesian coordinates of optimized geometries of $[MgC_7H_2]^{2+}$ at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory.

```
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 C     3.701839    -0.000000     2.396746
 C     3.701839    -0.000000    -0.396746
 C     2.381837     0.000000     2.139334
 C     2.381837     0.000000    -0.139334
 C     1.013388     0.000000     1.691649
 C     1.013388     0.000000     0.308351
 H     0.148033     0.000000     2.340259
 H     0.148033     0.000000    -0.340259
Mg     5.458464    -0.000000     1.000000
```

Cartesian coordinates of optimized geometries of $[MgSi_2C_5H_2]^{2+}$ at the B3LYP-D3BJ/6-311++G(2d,2p) level of theory.

```
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scf done:  -970.153405
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 C    -4.179726     0.488024    -0.307436
 C    -6.297254    -0.279969    -0.131651
 C    -5.424231    -1.387988    -0.218114
 C    -4.012326    -0.977308    -0.336035
 H    -7.370248    -0.342837    -0.039373
 H    -5.891806     1.885800    -0.145348
Si    -4.750313    -2.979670    -0.291196
Si    -2.456121     0.478690    -0.455964
Mg    -2.215747    -2.177203    -0.505538
```

Table S5: Computed energies of alkali and alkaline-earth metal ions at different levels.

Ions	B3LYP/6-311++G(2d,2p)	TPSSh/6-311++G(2d,2p)
	a.u	a.u
Li^+	-7.2849178	-7.2854225
Na^+	-162.0875669	-162.0851292
K^+	-599.7609747	-599.7635368
[a]Rb^+	-23.7057810	-23.6979130
[a]Cs^+	-19.7315209	-19.7309192
Be^{2+}	-13.6528851	-13.6611035
Mg^{2+}	-199.2410012	-199.2454218
Ca^{2+}	-676.9057654	-676.9136491
[a]Sr^{2+}	-29.8115699	-29.8034249
[a]Ba^{2+}	-24.6517711	-24.6513191
	PBE0/def2-TZVP	TPSSh/def2-TZVP
	a.u	a.u
Li^+	-7.2623925	-7.2859369
Na^+	-161.9813348	-162.0915886
K^+	-599.5782515	-599.7643897
Rb^+	-23.9272886	-23.9320449
Cs^+	-19.9966386	-20.0041888
Be^{2+}	-13.6281011	-13.6617778
Mg^{2+}	-199.1241103	-199.2452705
Ca^{2+}	-676.7193793	-676.9154249
Sr^{2+}	-30.0651628	-30.0722600
Ba^{2+}	-24.8923080	-24.9064468

[a] Calculations are done with LANL2DZ ECP.

Table S6: Computed energies of C_7H_2 and $Si_2C_5H_2$ at different levels.

Species	Energy	ZPVE	E+ZPVE	NImag	Level
	a.u	a.u	a.u		
C_7H_2	-267.6981864	0.053703	-267.644484	0	B3LYP/6-311++G(2d,2p)
C_7H_2	-267.7143678	0.053761	-267.660606	0	B3LYP-D3BJ/6-311++G(2d,2p)
C_7H_2	-267.7309604	0.053793	-267.677167	0	TPSSh/6-311++G(2d,2p)
C_7H_2	-267.7415055	0.053829	-267.687677	0	TPSSh-D3BJ/6-311++G(2d,2p)
C_7H_2	-267.4069299	0.054893	-267.352037	0	PBE0-D3/def2-TZVP
C_7H_2	-267.7654245	0.054107	-267.711317	0	TPSSh-D3BJ/def2-TZVP
$Si_2C_5H_2$	-770.6783795	0.049725	-770.628654	0	B3LYP/6-311++G(2d,2p)
$Si_2C_5H_2$	-770.7025997	0.049832	-770.652768	0	B3LYP-D3BJ/6-311++G(2d,2p)
$Si_2C_5H_2$	-770.6883995	0.049733	-770.638667	0	TPSSh/6-311++G(2d,2p)
$Si_2C_5H_2$	-770.7042208	0.049788	-770.654433	0	TPSSh-D3BJ/6-311++G(2d,2p)
$Si_2C_5H_2$	-770.1942060	0.050514	-770.143692	0	PBE0-D3/def2-TZVP
$Si_2C_5H_2$	-770.7229473	0.049915	-770.673033	0	TPSSh-D3BJ/def2-TZVP

Table S7: Computed energies of M^+-C_7H_2 at different levels.

Species	Energy	ZPVE	E+ZPVE	NImag	Level
	a.u	a.u	a.u		
Li^+-C_7H_2	-275.0528128	0.055819	-274.996994	0	B3LYP/6-311++G(2d,2p)
Li^+-C_7H_2	-275.0727011	0.055932	-275.016769	0	B3LYP-D3BJ/6-311++G(2d,2p)
Li^+-C_7H_2	-275.0859395	0.055950	-275.029989	0	TPSSh/6-311++G(2d,2p)
Li^+-C_7H_2	-275.0988982	0.056019	-275.042879	0	TPSSh-D3BJ/6-311++G(2d,2p)
Li^+-C_7H_2	-274.7399222	0.057041	-274.682881	0	PBE0-D3/def2-TZVP
Li^+-C_7H_2	-275.1234595	0.056313	-275.067147	0	TPSSh-D3BJ/def2-TZVP
Na^+-C_7H_2	-429.8393383	0.055151	-429.784188	0	B3LYP/6-311++G(2d,2p)
Na^+-C_7H_2	-429.8595976	0.055236	-429.804362	0	B3LYP-D3BJ/6-311++G(2d,2p)
Na^+-C_7H_2	-429.8690981	0.055263	-429.813835	0	TPSSh/6-311++G(2d,2p)
Na^+-C_7H_2	-429.8822881	0.055294	-429.826994	0	TPSSh-D3BJ/6-311++G(2d,2p)
Na^+-C_7H_2	-429.4434626	0.056357	-429.387106	0	PBE0-D3/def2-TZVP
Na^+-C_7H_2	-429.9128682	0.055596	-429.857273	0	TPSSh-D3BJ/def2-TZVP
K^+-C_7H_2	-867.5006320	0.054914	-867.445718	0	B3LYP/6-311++G(2d,2p)
K^+-C_7H_2	-867.5211400	0.055016	-867.466124	0	B3LYP-D3BJ/6-311++G(2d,2p)
K^+-C_7H_2	-867.5360337	0.055020	-867.481014	0	TPSSh/6-311++G(2d,2p)
K^+-C_7H_2	-867.5494289	0.055071	-867.494358	0	TPSSh-D3BJ/6-311++G(2d,2p)
K^+-C_7H_2	-867.0293521	0.056105	-866.973247	0	PBE0-D3/def2-TZVP
K^+-C_7H_2	-867.5743104	0.055362	-867.518949	0	TPSSh-D3BJ/def2-TZVP
^{a}Rb^+-C_7H_2	-291.4387068	0.054727	-291.383980	0	B3LYP/6-311++G(2d,2p)
^{a}Rb^+-C_7H_2	-291.4590538	0.054819	-291.404235	0	B3LYP-D3BJ/6-311++G(2d,2p)
^{a}Rb^+-C_7H_2	-291.4639233	0.054833	-291.409090	0	TPSSh/6-311++G(2d,2p)
^{a}Rb^+-C_7H_2	-291.4772259	0.054885	-291.422341	0	TPSSh-D3BJ/6-311++G(2d,2p)
Rb^+-C_7H_2	-291.3745346	0.055935	-291.318599	0	PBE0-D3/def2-TZVP
Rb^+-C_7H_2	-291.7377074	0.055194	-291.682514	0	TPSSh-D3BJ/def2-TZVP
^{a}Cs^+-C_7H_2	-287.4606623	0.054639	-287.406023	0	B3LYP/6-311++G(2d,2p)
^{a}Cs^+-C_7H_2	-287.4809117	0.054733	-287.426179	0	B3LYP-D3BJ/6-311++G(2d,2p)
^{a}Cs^+-C_7H_2	-287.4934166	0.054748	-287.438669	0	TPSSh/6-311++G(2d,2p)
^{a}Cs^+-C_7H_2	-287.5066763	0.054796	-287.451880	0	TPSSh-D3BJ/6-311++G(2d,2p)
Cs^+-C_7H_2	-287.4409686	0.055830	-287.385139	0	PBE0-D3/def2-TZVP
Cs^+-C_7H_2	-287.8066632	0.055096	-287.751567	0	TPSSh-D3BJ/def2-TZVP

[a] Calculations are done with LANL2DZ ECP for the metal.

Table S8: Computed energies of M^{2+}-C_7H_2 at different levels.

Species	Energy	ZPVE	E+ZPVE	NImag	Level
	a.u	a.u	a.u		
Be^{2+}-C_7H_2	-281.7121654	0.057510	-281.654655	1	B3LYP/6-311++G(2d,2p)
Be^{2+}-C_7H_2	-281.7329559	0.057594	-281.675362	1	B3LYP-D3BJ/6-311++G(2d,2p)
Be^{2+}-C_7H_2	-281.7532073	0.057639	-281.695568	1	TPSSh/6-311++G(2d,2p)
Be^{2+}-C_7H_2	-281.7667520	0.057687	-281.709065	1	TPSSh-D3BJ/6-311++G(2d,2p)
Be^{2+}-C_7H_2	-281.3947428	0.058805	-281.335938	0	PBE0-D3/def2-TZVP
Be^{2+}-C_7H_2	-281.7890821	0.058016	-281.731066	0	TPSSh-D3BJ/def2-TZVP
Mg^{2+}-C_7H_2	-467.1548319	0.056302	-467.098530	0	B3LYP/6-311++G(2d,2p)
Mg^{2+}-C_7H_2	-467.1767142	0.056390	-467.120324	0	B3LYP-D3BJ/6-311++G(2d,2p)
Mg^{2+}-C_7H_2	-467.1907123	0.056436	-467.134277	0	TPSSh/6-311++G(2d,2p)
Mg^{2+}-C_7H_2	-467.2049451	0.056480	-467.148465	0	TPSSh-D3BJ/6-311++G(2d,2p)
Mg^{2+}-C_7H_2	-466.7487407	0.057463	-466.691278	0	PBE0-D3/def2-TZVP
Mg^{2+}-C_7H_2	-467.2300413	0.056742	-467.173299	0	TPSSh-D3BJ/def2-TZVP
Ca^{2+}-C_7H_2	-944.7647726	0.055802	-944.708971	0	B3LYP/6-311++G(2d,2p)
Ca^{2+}-C_7H_2	-944.7870706	0.055893	-944.731178	0	B3LYP-D3BJ/6-311++G(2d,2p)
Ca^{2+}-C_7H_2	-944.8076027	0.055984	-944.751619	0	TPSSh/6-311++G(2d,2p)
Ca^{2+}-C_7H_2	-944.8220842	0.056031	-944.766053	0	TPSSh-D3BJ/6-311++G(2d,2p)
Ca^{2+}-C_7H_2	-944.2908125	0.057039	-944.233773	0	PBE0-D3/def2-TZVP
Ca^{2+}-C_7H_2	-944.8486885	0.056337	-944.792352	0	TPSSh-D3BJ/def2-TZVP
$^{a}Sr^{2+}$-C_7H_2	-297.6282748	0.055672	-297.572602	0	B3LYP/6-311++G(2d,2p)
$^{a}Sr^{2+}$-C_7H_2	-297.6502728	0.055766	-297.594507	0	B3LYP-D3BJ/6-311++G(2d,2p)
$^{a}Sr^{2+}$-C_7H_2	-297.6540899	0.055842	-297.598247	0	TPSSh/6-311++G(2d,2p)
$^{a}Sr^{2+}$-C_7H_2	-297.6683802	0.055891	-297.612489	0	TPSSh-D3BJ/6-311++G(2d,2p)
Sr^{2+}-C_7H_2	-297.6128002	0.056709	-297.556091	0	PBE0-D3/def2-TZVP
Sr^{2+}-C_7H_2	-297.9803110	0.056012	-297.924299	0	TPSSh-D3BJ/def2-TZVP
$^{a}Ba^{2+}$-C_7H_2	-292.4523520	0.055477	-292.396875	0	B3LYP/6-311++G(2d,2p)
$^{a}Ba^{2+}$-C_7H_2	-292.4744870	0.055568	-292.418919	0	B3LYP-D3BJ/6-311++G(2d,2p)
$^{a}Ba^{2+}$-C_7H_2	-292.4865959	0.055658	-292.430938	0	TPSSh/6-311++G(2d,2p)
$^{a}Ba^{2+}$-C_7H_2	-292.5009711	0.055706	-292.445265	0	TPSSh-D3BJ/6-311++G(2d,2p)
Ba^{2+}-C_7H_2	-292.4223211	0.056519	-292.365802	0	PBE0-D3/def2-TZVP
Ba^{2+}-C_7H_2	-292.7967244	0.055830	-292.740895	0	TPSSh-D3BJ/def2-TZVP

[a] Calculations are done with LANL2DZ ECP for the metal.

Table S9: Computed energies of M^+-$Si_2C_5H_2$ at different levels.

Species	Energy	ZPVE	E+ZPVE	NImag	Level
	a.u	a.u	a.u		
Li^+-$Si_2C_5H_2$	-778.0089414	0.051391	-777.957550	0	B3LYP/6-311++G(2d,2p)
Li^+-$Si_2C_5H_2$	-778.0380362	0.051521	-777.986515	0	B3LYP-D3BJ/6-311++G(2d,2p)
Li^+-$Si_2C_5H_2$	-778.0204889	0.051421	-777.969068	0	TPSSh/6-311++G(2d,2p)
Li^+-$Si_2C_5H_2$	-778.0394544	0.051486	-777.987969	0	TPSSh-D3BJ/6-311++G(2d,2p)
Li^+-$Si_2C_5H_2$	-777.5018441	0.052164	-777.449680	0	PBE0-D3/def2-TZVP
Li^+-$Si_2C_5H_2$	-778.0572873	0.051571	-778.005716	0	TPSSh-D3BJ/def2-TZVP
Na^+-$Si_2C_5H_2$	-932.7918108	0.050452	-932.741359	0	B3LYP/6-311++G(2d,2p)
Na^+-$Si_2C_5H_2$	-932.8214030	0.050579	-932.770824	0	B3LYP-D3BJ/6-311++G(2d,2p)
Na^+-$Si_2C_5H_2$	-932.8005445	0.050500	-932.750044	0	TPSSh/6-311++G(2d,2p)
Na^+-$Si_2C_5H_2$	-932.8197656	0.050563	-932.769203	0	TPSSh-D3BJ/6-311++G(2d,2p)
Na^+-$Si_2C_5H_2$	-932.2026740	0.051240	-932.151434	0	PBE0-D3/def2-TZVP
Na^+-$Si_2C_5H_2$	-932.8443755	0.050664	-932.793712	0	TPSSh-D3BJ/def2-TZVP
K^+-$Si_2C_5H_2$	-1370.4539894	0.050282	-1370.403707	0	B3LYP/6-311++G(2d,2p)
K^+-$Si_2C_5H_2$	-1370.4837144	0.050422	-1370.433292	0	B3LYP-D3BJ/6-311++G(2d,2p)
K^+-$Si_2C_5H_2$	-1370.4683391	0.050314	-1370.418025	0	TPSSh/6-311++G(2d,2p)
K^+-$Si_2C_5H_2$	-1370.4876908	0.050386	-1370.437305	0	TPSSh-D3BJ/6-311++G(2d,2p)
K^+-$Si_2C_5H_2$	-1369.7898983	0.051074	-1369.738825	0	PBE0-D3/def2-TZVP
K^+-$Si_2C_5H_2$	-1370.5070248	0.050494	-1370.456531	0	TPSSh-D3BJ/def2-TZVP
[a]Rb^+-$Si_2C_5H_2$	-794.3938171	0.050176	-794.343642	0	B3LYP/6-311++G(2d,2p)
[a]Rb^+-$Si_2C_5H_2$	-794.4230479	0.050289	-794.372759	0	B3LYP-D3BJ/6-311++G(2d,2p)
[a]Rb^+-$Si_2C_5H_2$	-794.3977370	0.050220	-794.347516	0	TPSSh/6-311++G(2d,2p)
[a]Rb^+-$Si_2C_5H_2$	-794.4168082	0.050276	-794.366533	0	TPSSh-D3BJ/6-311++G(2d,2p)
Rb^+-$Si_2C_5H_2$	-794.1364761	0.050977	-794.085499	0	PBE0-D3/def2-TZVP
Rb^+-$Si_2C_5H_2$	-794.6716493	0.050394	-794.621255	0	TPSSh-D3BJ/def2-TZVP
[a]Cs^+-$Si_2C_5H_2$	-790.4174002	0.050126	-790.367275	0	B3LYP/6-311++G(2d,2p)
[a]Cs^+-$Si_2C_5H_2$	-790.4463421	0.050240	-790.396102	0	B3LYP-D3BJ/6-311++G(2d,2p)
[a]Cs^+-$Si_2C_5H_2$	-790.4286590	0.050157	-790.378502	0	TPSSh/6-311++G(2d,2p)
[a]Cs^+-$Si_2C_5H_2$	-790.4475886	0.050224	-790.397365	0	TPSSh-D3BJ/6-311++G(2d,2p)
Cs^+-$Si_2C_5H_2$	-790.2043186	0.050922	-790.153397	0	PBE0-D3/def2-TZVP
Cs^+-$Si_2C_5H_2$	-790.7418662	0.050344	-790.691522	0	TPSSh-D3BJ/def2-TZVP

[a] Calculations are done with LANL2DZ ECP for the metal.

Table S10: Computed energies of M^{2+}-$Si_2C_5H_2$ at different levels.

Species	Energy	ZPVE	E+ZPVE	NImag	Level
	a.u	a.u	a.u		
Be^{2+}-$Si_2C_5H_2$	-784.7199891	0.052803	-784.667186	0	B3LYP/6-311++G(2d,2p)
Be^{2+}-$Si_2C_5H_2$	-784.7496284	0.052950	-784.696679	0	B3LYP-D3BJ/6-311++G(2d,2p)
Be^{2+}-$Si_2C_5H_2$	-784.7371701	0.052892	-784.684278	0	TPSSh/6-311++G(2d,2p)
Be^{2+}-$Si_2C_5H_2$	-784.7565655	0.052980	-784.703585	0	TPSSh-D3BJ/6-311++G(2d,2p)
Be^{2+}-$Si_2C_5H_2$	-784.2083697	0.053634	-784.154735	0	PBE0-D3/def2-TZVP
Be^{2+}-$Si_2C_5H_2$	-784.7740145	0.053028	-784.720987	0	TPSSh-D3BJ/def2-TZVP
Mg^{2+}-$Si_2C_5H_2$	-970.1223496	0.050751	-970.071599	0	B3LYP/6-311++G(2d,2p)
Mg^{2+}-$Si_2C_5H_2$	-970.1534048	0.050879	-970.102526	0	B3LYP-D3BJ/6-311++G(2d,2p)
Mg^{2+}-$Si_2C_5H_2$	-970.1356412	0.050901	-970.084740	0	TPSSh/6-311++G(2d,2p)
Mg^{2+}-$Si_2C_5H_2$	-970.1559381	0.050975	-970.104964	0	TPSSh-D3BJ/6-311++G(2d,2p)
Mg^{2+}-$Si_2C_5H_2$	-969.5205459	0.051583	-969.468963	0	PBE0-D3/def2-TZVP
Mg^{2+}-$Si_2C_5H_2$	-970.1736987	0.051001	-970.122698	0	TPSSh-D3BJ/def2-TZVP
Ca^{2+}-$Si_2C_5H_2$	-1447.7114934	0.050586	-1447.660907	0	B3LYP/6-311++G(2d,2p)
Ca^{2+}-$Si_2C_5H_2$	-1447.7432555	0.050717	-1447.692538	0	B3LYP-D3BJ/6-311++G(2d,2p)
Ca^{2+}-$Si_2C_5H_2$	-1447.7334520	0.050659	-1447.682793	0	TPSSh/6-311++G(2d,2p)
Ca^{2+}-$Si_2C_5H_2$	-1447.7540660	0.050729	-1447.703337	0	TPSSh-D3BJ/6-311++G(2d,2p)
Ca^{2+}-$Si_2C_5H_2$	-1447.0428920	0.051392	-1446.991500	0	PBE0-D3/def2-TZVP
Ca^{2+}-$Si_2C_5H_2$	-1447.7734411	0.050808	-1447.722633	0	TPSSh-D3BJ/def2-TZVP
$^{a}Sr^{2+}$-$Si_2C_5H_2$	-800.5620237	0.050370	-800.511654	0	B3LYP/6-311++G(2d,2p)
$^{a}Sr^{2+}$-$Si_2C_5H_2$	-800.5932311	0.050497	-800.542734	0	B3LYP-D3BJ/6-311++G(2d,2p)
$^{a}Sr^{2+}$-$Si_2C_5H_2$	-800.5676506	0.050470	-800.517181	0	TPSSh/6-311++G(2d,2p)
$^{a}Sr^{2+}$-$Si_2C_5H_2$	-800.5879028	0.050538	-800.537365	0	TPSSh-D3BJ/6-311++G(2d,2p)
Sr^{2+}-$Si_2C_5H_2$	-800.3620785	0.051149	-800.310929	0	PBE0-D3/def2-TZVP
Sr^{2+}-$Si_2C_5H_2$	-800.9019560	0.050567	-800.851389	0	TPSSh-D3BJ/def2-TZVP
$^{a}Ba^{2+}$-$Si_2C_5H_2$	-795.3847069	0.050378	-795.334329	0	B3LYP/6-311++G(2d,2p)
$^{a}Ba^{2+}$-$Si_2C_5H_2$	-795.4184152	0.050586	-795.367829	0	B3LYP-D3BJ/6-311++G(2d,2p)
$^{a}Ba^{2+}$-$Si_2C_5H_2$	-795.3987371	0.050463	-795.348274	0	TPSSh/6-311++G(2d,2p)
$^{a}Ba^{2+}$-$Si_2C_5H_2$	-795.4190130	0.050494	-795.368519	0	TPSSh-D3BJ/6-311++G(2d,2p)
Ba^{2+}-$Si_2C_5H_2$	-795.1702696	0.051065	-795.119205	0	PBE0-D3/def2-TZVP
Ba^{2+}-$Si_2C_5H_2$	-795.7169907	0.050483	-795.666507	0	TPSSh-D3BJ/def2-TZVP

[a] Calculations are done with LANL2DZ ECP for the metal.

Table S11: Computed energies of $[XC_7H_2]^{-/2-}$ or $[XSi_2C_5H_2]^{-/2-}$ at different levels.

Species	Energy	ZPVE	E+ZPVE	NImag	Level
	a.u	a.u	a.u		
$(BeC_7H_2)^-$	-282.1025784	0.052329	-282.050249	2	UPBE0-D3/def2-TZVP
$(MgC_7H_2)^-$	-467.4221003	0.051910	-467.370190	2	UPBE0-D3/def2-TZVP
$(BeSi_2C_5H_2)^-$	-784.9067948	0.050131	-784.856664	3	UPBE0-D3/def2-TZVP
[a]$(MgSi_2C_5H_2)^-$					UPBE0-D3/def2-TZVP
$(BeC_7H_2)^{2-}$	-281.9626073	0.049235	-281.913372	3	PBE0-D3/def2-TZVP
$(MgC_7H_2)^{2-}$	-467.2916639	0.049054	-467.242610	3	PBE0-D3/def2-TZVP
$(BeSi_2C_5H_2)^{2-}$	-784.7973896	0.050431	-784.746958	2	PBE0-D3/def2-TZVP
[a]$(MgSi_2C_5H_2)^{2-}$					PBE0-D3/def2-TZVP

[a] Geometry did not converge in planar ppC/ptC form.

Table S12: Natural charges (q, $|e|$) on ppC atoms and Wiberg bond indices (WBI) calculated at the PBE0-D3/def2-TZVP level.

system	q	WBI_{C-M}	$\mathrm{WBI}_{C1-C/Si}$	WBI_{C1-C4}
Be^{2+}-C_7H_2	-0.4404	0.0387	1.0257	0.8487
Mg^{2+}-C_7H_2	-0.3129	0.0135	1.0429	0.8596
Be^{2+}-$Si_2C_5H_2$	-1.1092	0.1503	0.5172	1.0800
Mg^{2+}-$Si_2C_5H_2$	-0.8716	0.0827	0.5327	1.1593

Table S13: Optimized geometries of C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -267.698186				scf done: -267.714368			
C	0.000000	0.000000	0.919880	C	0.000000	0.000000	0.919342
C	-0.000000	-1.087393	-0.065416	C	-0.000000	-1.089614	-0.065468
C	0.000000	1.087393	-0.065416	C	0.000000	1.089614	-0.065468
C	0.000000	-1.475836	1.222288	C	-0.000000	-1.475015	1.222452
C	0.000000	1.475836	1.222288	C	0.000000	1.475015	1.222452
C	-0.000000	-0.685144	-1.431027	C	-0.000000	-0.685552	-1.430866
C	0.000000	0.685144	-1.431027	C	0.000000	0.685552	-1.430866
H	-0.000000	-1.344755	-2.285495	H	-0.000000	-1.344255	-2.285500
H	0.000000	1.344755	-2.285495	H	0.000000	1.344255	-2.285500
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -267.730960				scf done: -267.741505			
C	0.000000	0.000000	0.922431	C	0.000000	0.000000	0.922089
C	-0.000000	-1.085447	-0.068074	C	0.000000	-1.087246	-0.068417
C	0.000000	1.085447	-0.068074	C	0.000000	1.087246	-0.068417
C	0.000000	-1.471759	1.229450	C	0.000000	-1.471063	1.229373
C	0.000000	1.471759	1.229450	C	0.000000	1.471063	1.229373
C	-0.000000	-0.686294	-1.433993	C	-0.000000	-0.686638	-1.433697
C	0.000000	0.686294	-1.433993	C	0.000000	0.686638	-1.433697
H	-0.000000	-1.348953	-2.288309	H	-0.000000	-1.348809	-2.288015
H	0.000000	1.348953	-2.288309	H	0.000000	1.348809	-2.288015

Table S14: Optimized geometries of $Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -770.678380				scf done: -770.702600			
C	0.000000	-0.000000	0.333094	C	0.000000	-0.000000	0.332186
C	-0.000000	-1.156669	-0.570635	C	-0.000000	-1.157234	-0.571660
C	0.000000	1.156669	-0.570635	C	0.000000	1.157234	-0.571660
Si	-0.000000	-1.785540	1.063064	Si	-0.000000	-1.779004	1.063305
Si	0.000000	1.785540	1.063064	Si	0.000000	1.779004	1.063305
C	-0.000000	-0.690661	-1.909754	C	-0.000000	-0.690891	-1.909464
C	0.000000	0.690661	-1.909754	C	0.000000	0.690891	-1.909464
H	-0.000000	-1.324601	-2.784163	H	-0.000000	-1.324923	-2.783215
H	0.000000	1.324601	-2.784163	H	0.000000	1.324923	-2.783215
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -770.688400				scf done: -770.704221			
C	0.000000	-0.000000	0.337228	C	0.000000	-0.000000	0.336700
C	-0.000000	-1.158939	-0.573657	C	-0.000000	-1.159360	-0.574215
C	0.000000	1.158939	-0.573657	C	0.000000	1.159360	-0.574215
Si	-0.000000	-1.774399	1.068230	Si	-0.000000	-1.771884	1.067908
Si	0.000000	1.774399	1.068230	Si	0.000000	1.771884	1.067908
C	-0.000000	-0.691494	-1.911643	C	-0.000000	-0.691664	-1.911274
C	0.000000	0.691494	-1.911643	C	0.000000	0.691664	-1.911274
H	-0.000000	-1.327696	-2.786485	H	-0.000000	-1.327752	-2.785709
H	0.000000	1.327696	-2.786485	H	0.000000	1.327752	-2.785709

Table S15: Optimized geometries of Li^+-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -275.052813				scf done: -275.072701			
C	3.323185	-0.000000	1.000000	C	3.321530	-0.000000	1.000000
C	3.679643	0.000000	2.455257	C	3.680990	0.000000	2.453412
C	3.679643	-0.000000	-0.455257	C	3.680990	-0.000000	-0.453412
C	2.383141	0.000000	2.109673	C	2.383665	0.000000	2.112655
C	2.383141	-0.000000	-0.109673	C	2.383665	-0.000000	-0.112655
C	1.016433	-0.000000	1.686614	C	1.017663	0.000000	1.686848
C	1.016433	-0.000000	0.313386	C	1.017663	-0.000000	0.313152
H	0.158713	0.000000	2.341590	H	0.159385	0.000000	2.340532
H	0.158713	-0.000000	-0.341590	H	0.159385	-0.000000	-0.340532
Li	5.424652	0.000000	1.000000	Li	5.418758	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -275.085939				scf done: -275.098898			
C	3.323347	-0.000000	1.000000	C	3.322062	-0.000000	1.000000
C	3.685105	-0.000000	2.454264	C	3.686160	-0.000000	2.452718
C	3.685105	-0.000000	-0.454264	C	3.686160	-0.000000	-0.452718
C	2.380696	0.000000	2.108388	C	2.380924	-0.000000	2.110732
C	2.380696	-0.000000	-0.108388	C	2.380924	-0.000000	-0.110732
C	1.014225	0.000000	1.687783	C	1.015112	0.000000	1.688040
C	1.014225	-0.000000	0.312217	C	1.015112	0.000000	0.311960
H	0.156755	0.000000	2.345512	H	0.157137	0.000000	2.344724
H	0.156755	0.000000	-0.345512	H	0.157137	0.000000	-0.344724
Li	5.426789	-0.000000	1.000000	Li	5.422970	-0.000000	1.000000

Table S16: Optimized geometries of Na^+-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -429.839338				scf done: -429.859598			
C	3.290352	-0.000000	1.000000	C	3.289041	-0.000000	1.000000
C	3.632234	-0.000000	2.455639	C	3.633895	-0.000000	2.453509
C	3.632234	-0.000000	-0.455639	C	3.633895	-0.000000	-0.453509
C	2.337743	0.000000	2.103837	C	2.338461	0.000000	2.106988
C	2.337743	0.000000	-0.103837	C	2.338461	0.000000	-0.106988
C	0.970583	0.000000	1.686052	C	0.971990	0.000000	1.686340
C	0.970583	0.000000	0.313948	C	0.971990	0.000000	0.313660
H	0.113644	0.000000	2.341919	H	0.114600	0.000000	2.341105
H	0.113644	0.000000	-0.341919	H	0.114600	0.000000	-0.341105
Na	5.824936	-0.000000	1.000000	Na	5.816763	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -429.869098				scf done: -429.882288			
C	3.291344	-0.000000	1.000000	C	3.291009	-0.000000	1.000000
C	3.637053	-0.000000	2.454827	C	3.636918	-0.000000	2.454616
C	3.637053	-0.000000	-0.454827	C	3.636918	-0.000000	-0.454616
C	2.334797	0.000000	2.102140	C	2.334676	0.000000	2.103703
C	2.334797	0.000000	-0.102140	C	2.334676	0.000000	-0.103703
C	0.967812	0.000000	1.687239	C	0.968251	0.000000	1.687564
C	0.967812	0.000000	0.312761	C	0.968251	0.000000	0.312436
H	0.111344	0.000000	2.346241	H	0.111777	0.000000	2.346106
H	0.111344	0.000000	-0.346241	H	0.111777	0.000000	-0.346106
Na	5.830341	-0.000000	1.000000	Na	5.829445	-0.000000	1.000000

Table S17: Optimized geometries of K^+-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -867.500632				scf done: -867.521140			
C	3.259772	-0.000000	1.000000	C	3.258521	-0.000000	1.000000
C	3.584792	0.000000	2.461716	C	3.587671	0.000000	2.460153
C	3.584792	-0.000000	-0.461716	C	3.587671	-0.000000	-0.460153
C	2.293954	0.000000	2.098790	C	2.295873	0.000000	2.102538
C	2.293954	0.000000	-0.098790	C	2.295873	-0.000000	-0.102538
C	0.927055	0.000000	1.685628	C	0.929543	0.000000	1.685908
C	0.927055	0.000000	0.314372	C	0.929543	0.000000	0.314092
H	0.071576	0.000000	2.343416	H	0.073294	0.000000	2.342101
H	0.071576	0.000000	-0.343416	H	0.073294	0.000000	-0.342101
K	6.209171	-0.000000	1.000000	K	6.192413	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -867.536034				scf done: -867.549429			
C	3.262701	-0.000000	1.000000	C	3.261299	-0.000000	1.000000
C	3.591481	0.000000	2.459809	C	3.593246	0.000000	2.459217
C	3.591481	-0.000000	-0.459809	C	3.593246	-0.000000	-0.459217
C	2.292448	0.000000	2.097049	C	2.293564	0.000000	2.099882
C	2.292448	-0.000000	-0.097049	C	2.293564	-0.000000	-0.099882
C	0.926082	0.000000	1.686904	C	0.927412	0.000000	1.687067
C	0.926082	-0.000000	0.313096	C	0.927412	0.000000	0.312933
H	0.070945	0.000000	2.347556	H	0.071755	0.000000	2.346705
H	0.070945	-0.000000	-0.347556	H	0.071755	0.000000	-0.346705
K	6.199084	-0.000000	1.000000	K	6.190444	-0.000000	1.000000

Table S18: Optimized geometries of Rb^+-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -291.438707				scf done: -291.459054			
C	3.232931	0.000000	1.000000	C	3.232268	0.000000	1.000000
C	3.552393	0.000000	2.463005	C	3.555941	0.000000	2.461386
C	3.552393	-0.000000	-0.463005	C	3.555941	-0.000000	-0.461386
C	2.262323	0.000000	2.096358	C	2.264921	0.000000	2.100094
C	2.262323	0.000000	-0.096358	C	2.264921	0.000000	-0.100094
C	0.895351	0.000000	1.685483	C	0.898520	0.000000	1.685721
C	0.895351	0.000000	0.314517	C	0.898520	0.000000	0.314279
H	0.040171	0.000000	2.343651	H	0.042616	0.000000	2.342353
H	0.040171	0.000000	-0.343651	H	0.042616	0.000000	-0.342353
Rb	6.490291	-0.000000	1.000000	Rb	6.467431	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -291.463923				scf done: -291.477226			
C	3.236388	0.000000	1.000000	C	3.235222	0.000000	1.000000
C	3.559546	0.000000	2.460974	C	3.561565	0.000000	2.460042
C	3.559546	-0.000000	-0.460974	C	3.561565	-0.000000	-0.460042
C	2.261116	0.000000	2.094553	C	2.262451	0.000000	2.097398
C	2.261116	0.000000	-0.094553	C	2.262451	0.000000	-0.097398
C	0.894574	0.000000	1.686740	C	0.896256	0.000000	1.686893
C	0.894574	0.000000	0.313260	C	0.896256	0.000000	0.313107
H	0.039792	0.000000	2.347931	H	0.040955	0.000000	2.347021
H	0.039792	0.000000	-0.347931	H	0.040955	0.000000	-0.347021
Rb	6.477253	-0.000000	1.000000	Rb	6.466018	-0.000000	1.000000

Table S19: Optimized geometries of Cs^+-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -287.460662				scf done: -287.480912			
C	3.211018	0.000000	1.000000	C	3.210757	0.000000	1.000000
C	3.525558	0.000000	2.465296	C	3.529854	0.000000	2.463490
C	3.525558	-0.000000	-0.465296	C	3.529854	-0.000000	-0.463490
C	2.236642	0.000000	2.094602	C	2.239774	0.000000	2.098628
C	2.236642	0.000000	-0.094602	C	2.239774	0.000000	-0.098628
C	0.869707	0.000000	1.685335	C	0.873423	0.000000	1.685610
C	0.869707	0.000000	0.314665	C	0.873423	0.000000	0.314390
H	0.014989	0.000000	2.344071	H	0.017831	0.000000	2.342648
H	0.014989	0.000000	-0.344071	H	0.017831	0.000000	-0.342648
Cs	6.718886	-0.000000	1.000000	Cs	6.691176	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -287.493417				scf done: -287.506676			
C	3.215373	0.000000	1.000000	C	3.214242	0.000000	1.000000
C	3.533824	0.000000	2.462817	C	3.536230	0.000000	2.461754
C	3.533824	-0.000000	-0.462817	C	3.536230	-0.000000	-0.461754
C	2.236317	0.000000	2.092843	C	2.237862	0.000000	2.095916
C	2.236317	0.000000	-0.092843	C	2.237862	0.000000	-0.095916
C	0.869806	0.000000	1.686587	C	0.871697	0.000000	1.686782
C	0.869806	0.000000	0.313413	C	0.871697	0.000000	0.313218
H	0.015542	0.000000	2.348425	H	0.016726	0.000000	2.347355
H	0.015542	0.000000	-0.348425	H	0.016726	0.000000	-0.347355
Cs	6.697346	-0.000000	1.000000	Cs	6.684423	-0.000000	1.000000

Table S20: Optimized geometries of Be^{2+}-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -281.712165				scf done: -281.732956			
C	3.284832	-0.000000	1.000000	C	3.284481	-0.000000	1.000000
C	3.774937	-0.000000	2.384892	C	3.774452	-0.000000	2.384559
C	3.774937	-0.000000	-0.384892	C	3.774452	-0.000000	-0.384559
C	2.440263	0.000000	2.161750	C	2.440165	0.000000	2.162450
C	2.440263	-0.000000	-0.161750	C	2.440165	-0.000000	-0.162450
C	1.071866	0.000000	1.696408	C	1.072583	0.000000	1.696429
C	1.071866	0.000000	0.303592	C	1.072583	0.000000	0.303571
H	0.200637	0.000000	2.340550	H	0.201606	0.000000	2.340235
H	0.200637	0.000000	-0.340550	H	0.201606	0.000000	-0.340235
Be	4.963459	-0.000000	1.000000	Be	4.961606	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -281.753207				scf done: -281.766752			
C	3.281071	-0.000000	1.000000	C	3.280724	-0.000000	1.000000
C	3.780557	-0.000000	2.386466	C	3.780293	-0.000000	2.386415
C	3.780557	-0.000000	-0.386466	C	3.780293	-0.000000	-0.386415
C	2.438857	-0.000000	2.161668	C	2.438943	-0.000000	2.162213
C	2.438857	0.000000	-0.161668	C	2.438943	0.000000	-0.162213
C	1.070406	0.000000	1.697757	C	1.070817	0.000000	1.697785
C	1.070406	0.000000	0.302243	C	1.070817	0.000000	0.302215
H	0.198822	0.000000	2.343609	H	0.199352	0.000000	2.343324
H	0.198822	0.000000	-0.343609	H	0.199352	0.000000	-0.343324
Be	4.965343	-0.000000	1.000000	Be	4.964161	-0.000000	1.000000

Table S21: Optimized geometries of Mg^{2+}-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -467.154832				scf done: -467.176714			
C	3.275919	-0.000000	1.000000	C	3.275039	-0.000000	1.000000
C	3.701796	0.000000	2.397331	C	3.701839	-0.000000	2.396746
C	3.701796	-0.000000	-0.397331	C	3.701839	-0.000000	-0.396746
C	2.381488	0.000000	2.137705	C	2.381837	0.000000	2.139334
C	2.381488	-0.000000	-0.137705	C	2.381837	0.000000	-0.139334
C	1.012310	0.000000	1.691607	C	1.013388	0.000000	1.691649
C	1.012310	0.000000	0.308393	C	1.013388	0.000000	0.308351
H	0.147072	0.000000	2.340791	H	0.148033	0.000000	2.340259
H	0.147072	0.000000	-0.340791	H	0.148033	0.000000	-0.340259
Mg	5.462444	-0.000000	1.000000	Mg	5.458464	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -467.190712				scf done: -467.204945			
C	3.276051	-0.000000	1.000000	C	3.275726	-0.000000	1.000000
C	3.706220	-0.000000	2.403349	C	3.705993	-0.000000	2.403317
C	3.706220	-0.000000	-0.403349	C	3.705993	-0.000000	-0.403317
C	2.380885	0.000000	2.136161	C	2.380876	0.000000	2.137004
C	2.380885	0.000000	-0.136161	C	2.380876	0.000000	-0.137004
C	1.011693	0.000000	1.692710	C	1.012111	0.000000	1.692842
C	1.011693	0.000000	0.307290	C	1.012111	0.000000	0.307158
H	0.146391	0.000000	2.344195	H	0.146986	0.000000	2.344128
H	0.146391	0.000000	-0.344195	H	0.146986	0.000000	-0.344128
Mg	5.457264	-0.000000	1.000000	Mg	5.456038	-0.000000	1.000000

Table S22: Optimized geometries of Ca^{2+}-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -944.764773				scf done: -944.787071			
C	3.289990	-0.000000	1.000000	C	3.288706	-0.000000	1.000000
C	3.649334	0.000000	2.440782	C	3.649777	0.000000	2.439716
C	3.649334	-0.000000	-0.440782	C	3.649777	-0.000000	-0.439716
C	2.348919	0.000000	2.122440	C	2.349094	0.000000	2.125191
C	2.348919	-0.000000	-0.122440	C	2.349094	-0.000000	-0.125191
C	0.983414	-0.000000	1.689018	C	0.984385	0.000000	1.689257
C	0.983414	-0.000000	0.310982	C	0.984385	0.000000	0.310743
H	0.122902	0.000000	2.343639	H	0.124209	0.000000	2.343654
H	0.122902	-0.000000	-0.343639	H	0.124209	0.000000	-0.343654
Ca	5.724568	0.000000	1.000000	Ca	5.720062	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -944.807603				scf done: -944.822084			
C	3.291063	-0.000000	1.000000	C	3.290734	-0.000000	1.000000
C	3.656368	0.000000	2.440753	C	3.656235	0.000000	2.440925
C	3.656368	-0.000000	-0.440753	C	3.656235	-0.000000	-0.440925
C	2.348853	0.000000	2.121047	C	2.348970	0.000000	2.122620
C	2.348853	-0.000000	-0.121047	C	2.348970	-0.000000	-0.122620
C	0.983205	0.000000	1.690289	C	0.983811	0.000000	1.690559
C	0.983205	0.000000	0.309711	C	0.983811	0.000000	0.309441
H	0.123821	0.000000	2.348644	H	0.124350	0.000000	2.348340
H	0.123821	-0.000000	-0.348644	H	0.124350	0.000000	-0.348340
Ca	5.708137	-0.000000	1.000000	Ca	5.706229	-0.000000	1.000000

Table S23: Optimized geometries of Sr^{2+}-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -297.628275				scf done: -297.650273			
C	3.257052	0.000000	1.000000	C	3.256297	0.000000	1.000000
C	3.614102	0.000000	2.434739	C	3.614952	0.000000	2.433792
C	3.614102	-0.000000	-0.434739	C	3.614952	-0.000000	-0.433792
C	2.312985	0.000000	2.115061	C	2.313664	0.000000	2.117768
C	2.312985	0.000000	-0.115061	C	2.313664	0.000000	-0.117768
C	0.945265	0.000000	1.687730	C	0.946782	0.000000	1.688043
C	0.945265	0.000000	0.312270	C	0.946782	0.000000	0.311957
H	0.086313	0.000000	2.343168	H	0.087563	0.000000	2.342469
H	0.086313	0.000000	-0.343168	H	0.087563	0.000000	-0.342469
Sr	6.049314	-0.000000	1.000000	Sr	6.041476	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -297.654090				scf done: -297.668380			
C	3.259121	0.000000	1.000000	C	3.258828	0.000000	1.000000
C	3.620879	0.000000	2.435713	C	3.621053	0.000000	2.435804
C	3.620879	-0.000000	-0.435713	C	3.621053	-0.000000	-0.435804
C	2.312963	0.000000	2.113636	C	2.313360	0.000000	2.115417
C	2.312963	-0.000000	-0.113636	C	2.313360	-0.000000	-0.115417
C	0.945503	0.000000	1.689086	C	0.946320	0.000000	1.689250
C	0.945503	0.000000	0.310914	C	0.946320	0.000000	0.310750
H	0.086928	0.000000	2.347274	H	0.087553	0.000000	2.346746
H	0.086928	0.000000	-0.347274	H	0.087553	0.000000	-0.346746
Sr	6.032030	-0.000000	1.000000	Sr	6.028296	-0.000000	1.000000

Table S24: Optimized geometries of Ba^{2+}-C_7H_2 in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -292.452352				scf done: -292.474487			
C	3.246176	0.000000	1.000000	C	3.244995	0.000000	1.000000
C	3.587193	0.000000	2.444226	C	3.588425	0.000000	2.442933
C	3.587193	-0.000000	-0.444226	C	3.588425	-0.000000	-0.442933
C	2.290871	0.000000	2.110033	C	2.291634	0.000000	2.112969
C	2.290871	0.000000	-0.110033	C	2.291634	0.000000	-0.112969
C	0.923531	0.000000	1.687038	C	0.925052	0.000000	1.687408
C	0.923531	0.000000	0.312962	C	0.925052	0.000000	0.312592
H	0.065829	0.000000	2.343631	H	0.067286	0.000000	2.343258
H	0.065829	0.000000	-0.343631	H	0.067286	0.000000	-0.343258
Ba	6.242674	-0.000000	1.000000	Ba	6.233909	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -292.486596				scf done: -292.500971			
C	3.249486	0.000000	1.000000	C	3.248627	0.000000	1.000000
C	3.595067	0.000000	2.444338	C	3.595622	0.000000	2.443918
C	3.595067	-0.000000	-0.444338	C	3.595622	-0.000000	-0.443918
C	2.291696	0.000000	2.108388	C	2.292030	0.000000	2.110574
C	2.291696	0.000000	-0.108388	C	2.292030	0.000000	-0.110574
C	0.924488	0.000000	1.688374	C	0.925277	0.000000	1.688623
C	0.924488	0.000000	0.311626	C	0.925277	0.000000	0.311377
H	0.067441	0.000000	2.348126	H	0.068030	0.000000	2.347676
H	0.067441	0.000000	-0.348126	H	0.068030	0.000000	-0.347676
Ba	6.216827	-0.000000	1.000000	Ba	6.213152	-0.000000	1.000000

Table S25: Optimized geometries of Li^+-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -778.008941				scf done: -778.038036			
C	3.225131	-0.000000	1.000000	C	3.223466	-0.000000	1.000000
Si	3.785200	0.000000	2.948383	Si	3.787378	0.000000	2.940408
Si	3.785200	-0.000000	-0.948383	Si	3.787378	-0.000000	-0.940408
C	2.264923	0.000000	2.130268	C	2.264225	0.000000	2.131981
C	2.264923	-0.000000	-0.130268	C	2.264225	-0.000000	-0.131981
C	0.923677	-0.000000	1.687775	C	0.924147	-0.000000	1.688072
C	0.923677	-0.000000	0.312225	C	0.924147	-0.000000	0.311928
H	0.060854	0.000000	2.334790	H	0.061649	0.000000	2.334804
H	0.060854	-0.000000	-0.334790	H	0.061649	-0.000000	-0.334804
Li	5.461544	0.000000	1.000000	Li	5.457722	0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -778.020489				scf done: -778.039454			
C	3.223356	-0.000000	1.000000	C	3.222640	-0.000000	1.000000
Si	3.795519	0.000000	2.922400	Si	3.795689	0.000000	2.920157
Si	3.795519	-0.000000	-0.922400	Si	3.795689	-0.000000	-0.920157
C	2.257218	0.000000	2.131310	C	2.257038	0.000000	2.132472
C	2.257218	-0.000000	-0.131310	C	2.257038	-0.000000	-0.132472
C	0.916534	-0.000000	1.688968	C	0.916951	-0.000000	1.689170
C	0.916534	-0.000000	0.311032	C	0.916951	-0.000000	0.310830
H	0.053973	0.000000	2.338789	H	0.054740	0.000000	2.338882
H	0.053973	-0.000000	-0.338789	H	0.054740	-0.000000	-0.338882
Li	5.486142	0.000000	1.000000	Li	5.484510	0.000000	1.000000

Table S26: Optimized geometries of Na^+-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -932.791811				scf done: -932.821403			
C	3.232611	-0.000000	1.000000	C	3.232362	-0.000000	1.000000
Si	3.852793	-0.000000	2.882265	Si	3.854908	-0.000000	2.875221
Si	3.852793	-0.000000	-0.882265	Si	3.854908	-0.000000	-0.875221
C	2.293818	0.000000	2.137763	C	2.294362	0.000000	2.138949
C	2.293818	0.000000	-0.137763	C	2.294362	0.000000	-0.138949
C	0.951737	0.000000	1.688468	C	0.953367	0.000000	1.688726
C	0.951737	0.000000	0.311532	C	0.953367	0.000000	0.311274
H	0.085379	0.000000	2.331003	H	0.087483	0.000000	2.331158
H	0.085379	0.000000	-0.331003	H	0.087483	0.000000	-0.331158
Na	6.155922	-0.000000	1.000000	Na	6.143384	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -932.800545				scf done: -932.819766			
C	3.229358	-0.000000	1.000000	C	3.229563	-0.000000	1.000000
Si	3.860919	-0.000000	2.858062	Si	3.861213	-0.000000	2.855978
Si	3.860919	-0.000000	-0.858062	Si	3.861213	-0.000000	-0.855978
C	2.285377	0.000000	2.140156	C	2.285696	0.000000	2.140936
C	2.285377	0.000000	-0.140156	C	2.285696	0.000000	-0.140936
C	0.944509	0.000000	1.689774	C	0.945392	0.000000	1.689890
C	0.944509	0.000000	0.310226	C	0.945392	0.000000	0.310110
H	0.077653	0.000000	2.334195	H	0.079039	0.000000	2.334468
H	0.077653	0.000000	-0.334195	H	0.079039	0.000000	-0.334468
Na	6.189711	-0.000000	1.000000	Na	6.183742	-0.000000	1.000000

Table S27: Optimized geometries of K^+-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -1370.453989				scf done: -1370.483714			
C	3.154172	-0.000000	1.000000	C	3.159094	-0.000000	1.000000
Si	3.810299	0.000000	2.840511	Si	3.814680	0.000000	2.836856
Si	3.810299	-0.000000	-0.840511	Si	3.814680	-0.000000	-0.836856
C	2.225053	0.000000	2.143915	C	2.229813	0.000000	2.144614
C	2.225053	0.000000	-0.143915	C	2.229813	0.000000	-0.144614
C	0.884148	0.000000	1.689147	C	0.889923	0.000000	1.689305
C	0.884148	0.000000	0.310853	C	0.889923	0.000000	0.310695
H	0.015416	0.000000	2.328777	H	0.021734	0.000000	2.328941
H	0.015416	0.000000	-0.328777	H	0.021734	0.000000	-0.328941
K	6.731984	-0.000000	1.000000	K	6.684592	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -1370.468339				scf done: -1370.487691			
C	3.158817	-0.000000	1.000000	C	3.161946	0.000000	1.000000
Si	3.819071	0.000000	2.825460	Si	3.820854	0.000000	2.825013
Si	3.819071	-0.000000	-0.825460	Si	3.820854	-0.000000	-0.825013
C	2.222978	0.000000	2.145738	C	2.225703	0.000000	2.146176
C	2.222978	-0.000000	-0.145738	C	2.225703	0.000000	-0.146176
C	0.883191	0.000000	1.690220	C	0.886406	0.000000	1.690302
C	0.883191	0.000000	0.309780	C	0.886406	0.000000	0.309698
H	0.014237	0.000000	2.332077	H	0.017943	0.000000	2.332352
H	0.014237	0.000000	-0.332077	H	0.017943	0.000000	-0.332352
K	6.718214	-0.000000	1.000000	K	6.692229	-0.000000	1.000000

Table S28: Optimized geometries of Rb^+-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -794.393817				scf done: -794.423048			
C	2.843190	0.000000	1.000000	C	2.849841	0.000000	1.000000
Si	3.520752	0.000000	2.819040	Si	3.527136	0.000000	2.815001
Si	3.520752	-0.000000	-0.819040	Si	3.527136	-0.000000	-0.815001
C	1.921384	0.000000	2.147538	C	1.928057	0.000000	2.148169
C	1.921384	0.000000	-0.147538	C	1.928057	0.000000	-0.148169
C	0.580847	0.000000	1.689523	C	0.588529	0.000000	1.689677
C	0.580847	0.000000	0.310477	C	0.588529	0.000000	0.310323
H	-0.289456	0.000000	2.327274	H	-0.281228	0.000000	2.327396
H	-0.289456	0.000000	-0.327274	H	-0.281228	0.000000	-0.327396
Rb	6.917681	-0.000000	1.000000	Rb	6.853096	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -794.397737				scf done: -794.416808			
C	2.850655	0.000000	1.000000	C	2.853442	0.000000	1.000000
Si	3.530571	0.000000	2.805905	Si	3.533232	0.000000	2.804521
Si	3.530571	-0.000000	-0.805905	Si	3.533232	-0.000000	-0.804521
C	1.921708	0.000000	2.149437	C	1.924678	0.000000	2.150015
C	1.921708	0.000000	-0.149437	C	1.924678	0.000000	-0.150015
C	0.582426	0.000000	1.690550	C	0.585896	0.000000	1.690667
C	0.582426	0.000000	0.309450	C	0.585896	0.000000	0.309333
H	-0.288077	0.000000	2.330559	H	-0.284351	0.000000	2.330574
H	-0.288077	0.000000	-0.330559	H	-0.284351	0.000000	-0.330574
Rb	6.884016	-0.000000	1.000000	Rb	6.855573	-0.000000	1.000000

Table S29: Optimized geometries of Cs^{+}-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -790.417400				scf done: -790.446342			
C	2.807408	0.000000	1.000000	C	2.815158	0.000000	1.000000
Si	3.491181	0.000000	2.813310	Si	3.499823	0.000000	2.808899
Si	3.491181	-0.000000	-0.813310	Si	3.499823	-0.000000	-0.808899
C	1.887243	0.000000	2.148799	C	1.895744	0.000000	2.149574
C	1.887243	0.000000	-0.148799	C	1.895744	0.000000	-0.149574
C	0.547028	0.000000	1.689615	C	0.556403	0.000000	1.689783
C	0.547028	0.000000	0.310385	C	0.556403	0.000000	0.310217
H	-0.323735	0.000000	2.326874	H	-0.313972	0.000000	2.326848
H	-0.323735	0.000000	-0.326874	H	-0.313972	0.000000	-0.326848
Cs	7.217084	-0.000000	1.000000	Cs	7.136772	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -790.428659				scf done: -790.447589			
C	2.818233	0.000000	1.000000	C	2.821962	0.000000	1.000000
Si	3.503340	0.000000	2.801178	Si	3.507397	0.000000	2.798989
Si	3.503340	-0.000000	-0.801178	Si	3.507397	-0.000000	-0.798989
C	1.890731	0.000000	2.150583	C	1.894773	0.000000	2.151329
C	1.890731	0.000000	-0.150583	C	1.894773	0.000000	-0.151329
C	0.551733	0.000000	1.690615	C	0.556359	0.000000	1.690749
C	0.551733	0.000000	0.309385	C	0.556359	0.000000	0.309251
H	-0.319220	0.000000	2.330150	H	-0.314291	0.000000	2.330207
H	-0.319220	0.000000	-0.330150	H	-0.314291	0.000000	-0.330207
Cs	7.156524	-0.000000	1.000000	Cs	7.117489	-0.000000	1.000000

Table S30: Optimized geometries of Be^{2+}-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -784.719989				scf done: -784.749628			
C	3.379638	-0.000000	1.000000	C	3.377945	-0.000000	1.000000
Si	3.939672	0.000000	3.003370	Si	3.941053	0.000000	2.995762
Si	3.939672	-0.000000	-1.003370	Si	3.941053	-0.000000	-0.995762
C	2.420260	0.000000	2.134192	C	2.419455	0.000000	2.135647
C	2.420260	-0.000000	-0.134192	C	2.419455	-0.000000	-0.135647
C	1.089754	0.000000	1.697224	C	1.090025	0.000000	1.697549
C	1.089754	-0.000000	0.302776	C	1.090025	-0.000000	0.302451
H	0.221984	0.000000	2.340580	H	0.222737	0.000000	2.340813
H	0.221984	-0.000000	-0.340580	H	0.222737	-0.000000	-0.340813
Be	5.033008	-0.000000	1.000000	Be	5.031502	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -784.737170				scf done: -784.756565			
C	3.375844	-0.000000	1.000000	C	3.373937	-0.000000	1.000000
Si	3.952940	0.000000	2.977329	Si	3.953268	0.000000	2.974157
Si	3.952940	-0.000000	-0.977329	Si	3.953268	-0.000000	-0.974157
C	2.415897	0.000000	2.133683	C	2.415796	0.000000	2.135706
C	2.415897	-0.000000	-0.133683	C	2.415796	-0.000000	-0.135706
C	1.082611	0.000000	1.698049	C	1.083695	0.000000	1.698289
C	1.082611	-0.000000	0.301951	C	1.083695	-0.000000	0.301711
H	0.216242	0.000000	2.345794	H	0.216435	0.000000	2.344064
H	0.216242	-0.000000	-0.345794	H	0.216435	-0.000000	-0.344064
Be	5.044765	-0.000000	1.000000	Be	5.043660	-0.000000	1.000000

Table S31: Optimized geometries of Mg^{2+}-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -970.122350				scf done: -970.153405			
C	3.347459	-0.000000	1.000000	C	3.345594	-0.000000	1.000000
Si	3.835803	-0.000000	3.087603	Si	3.839514	-0.000000	3.076347
Si	3.835803	-0.000000	-1.087603	Si	3.839514	-0.000000	-1.076347
C	2.395168	0.000000	2.124913	C	2.393564	0.000000	2.126554
C	2.395168	0.000000	-0.124913	C	2.393564	0.000000	-0.126554
C	1.049861	0.000000	1.689097	C	1.049452	0.000000	1.689572
C	1.049861	0.000000	0.310903	C	1.049452	0.000000	0.310428
H	0.187782	0.000000	2.338332	H	0.187468	0.000000	2.338236
H	0.187782	0.000000	-0.338332	H	0.187468	0.000000	-0.338236
Mg	5.514358	-0.000000	1.000000	Mg	5.513455	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -970.135641				scf done: -970.155938			
C	3.347073	-0.000000	1.000000	C	3.344816	-0.000000	1.000000
Si	3.857958	-0.000000	3.032638	Si	3.859712	-0.000000	3.028877
Si	3.857958	-0.000000	-1.032638	Si	3.859712	-0.000000	-1.028877
C	2.382010	0.000000	2.123904	C	2.381865	0.000000	2.125669
C	2.382010	0.000000	-0.123904	C	2.381865	0.000000	-0.125669
C	1.038111	0.000000	1.690995	C	1.038226	0.000000	1.691148
C	1.038111	0.000000	0.309005	C	1.038226	0.000000	0.308852
H	0.176686	0.000000	2.343530	H	0.176681	0.000000	2.343052
H	0.176686	0.000000	-0.343530	H	0.176681	0.000000	-0.343052
Mg	5.542443	-0.000000	1.000000	Mg	5.541262	-0.000000	1.000000

Table S32: Optimized geometries of Ca^{2+}-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -1447.711493				scf done: -1447.743255			
C	3.317730	-0.000000	1.000000	C	3.315942	-0.000000	1.000000
Si	3.813754	0.000000	2.988236	Si	3.816036	0.000000	2.980823
Si	3.813754	-0.000000	-0.988236	Si	3.816036	-0.000000	-0.980823
C	2.327029	0.000000	2.123475	C	2.326409	0.000000	2.125720
C	2.327029	0.000000	-0.123475	C	2.326409	0.000000	-0.125720
C	0.987991	0.000000	1.689254	C	0.988426	0.000000	1.689625
C	0.987991	0.000000	0.310746	C	0.988426	0.000000	0.310375
H	0.126475	0.000000	2.339081	H	0.127217	0.000000	2.339246
H	0.126475	0.000000	-0.339081	H	0.127217	0.000000	-0.339246
Ca	5.927757	-0.000000	1.000000	Ca	5.923869	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -1447.733452				scf done: -1447.754066			
C	3.320738	-0.000000	1.000000	C	3.319400	-0.000000	1.000000
Si	3.826895	-0.000000	2.960285	Si	3.827678	0.000000	2.958445
Si	3.826895	-0.000000	-0.960285	Si	3.827678	-0.000000	-0.958445
C	2.320953	0.000000	2.123089	C	2.321061	0.000000	2.124941
C	2.320953	0.000000	-0.123089	C	2.321061	0.000000	-0.124941
C	0.981995	0.000000	1.690599	C	0.982593	0.000000	1.690835
C	0.981995	0.000000	0.309401	C	0.982593	0.000000	0.309165
H	0.121614	0.000000	2.344398	H	0.122235	0.000000	2.344151
H	0.121614	0.000000	-0.344398	H	0.122235	0.000000	-0.344151
Ca	5.932336	-0.000000	1.000000	Ca	5.929450	-0.000000	1.000000

Table S33: Optimized geometries of Sr^{2+}-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -800.562024				scf done: -800.593231			
C	3.220355	0.000000	1.000000	C	3.220152	0.000000	1.000000
Si	3.760249	0.000000	2.941881	Si	3.761989	0.000000	2.936518
Si	3.760249	-0.000000	-0.941881	Si	3.761989	-0.000000	-0.936518
C	2.250953	0.000000	2.124899	C	2.251651	0.000000	2.126581
C	2.250953	0.000000	-0.124899	C	2.251651	0.000000	-0.126581
C	0.907580	0.000000	1.687939	C	0.909277	0.000000	1.688243
C	0.907580	0.000000	0.312061	C	0.909277	0.000000	0.311757
H	0.045352	0.000000	2.336320	H	0.047406	0.000000	2.336272
H	0.045352	0.000000	-0.336320	H	0.047406	0.000000	-0.336272
Sr	6.329187	-0.000000	1.000000	Sr	6.317013	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -800.567651				scf done: -800.587903			
C	2.998177	0.000000	1.000000	C	2.997957	0.000000	1.000000
Si	3.548088	0.000000	2.915029	Si	3.548761	0.000000	2.913415
Si	3.548088	-0.000000	-0.915029	Si	3.548761	-0.000000	-0.913415
C	2.020210	0.000000	2.126081	C	2.020737	0.000000	2.127407
C	2.020210	0.000000	-0.126081	C	2.020737	0.000000	-0.127407
C	0.678062	0.000000	1.689438	C	0.679026	0.000000	1.689611
C	0.678062	0.000000	0.310562	C	0.679026	0.000000	0.310389
H	-0.183900	0.000000	2.340563	H	-0.182659	0.000000	2.340613
H	-0.183900	0.000000	-0.340563	H	-0.182659	0.000000	-0.340613
Sr	6.104828	-0.000000	1.000000	Sr	6.098239	-0.000000	1.000000

Table S34: Optimized geometries of Ba^{2+}-$Si_2C_5H_2$ in Cartesian coordinates (in Å) and their total energies (in a.u) obtained at different levels.

B3LYP/6-311++G(2d,2p)				B3LYP-D3BJ/6-311++G(2d,2p)			
scf done: -795.384707				scf done: -795.418415			
C	3.175415	0.000000	1.000000	C	3.119910	0.000000	1.000000
Si	3.745223	0.000000	2.905458	Si	3.734151	0.000000	2.864339
Si	3.745223	-0.000000	-0.905458	Si	3.734151	-0.000000	-0.864339
C	2.212929	0.000000	2.129626	C	2.176687	0.000000	2.136639
C	2.212929	0.000000	-0.129626	C	2.176687	0.000000	-0.136639
C	0.870960	0.000000	1.688323	C	0.834980	0.000000	1.689244
C	0.870960	0.000000	0.311677	C	0.834980	0.000000	0.310756
H	0.006880	0.000000	2.334212	H	-0.030968	0.000000	2.331813
H	0.006880	0.000000	-0.334212	H	-0.030968	0.000000	-0.331813
Ba	6.630412	-0.000000	1.000000	Ba	6.928201	-0.000000	1.000000
TPSSh/6-311++G(2d,2p)				TPSSh-D3BJ/6-311++G(2d,2p)			
scf done: -795.398737				scf done: -795.419013			
C	2.956965	-0.000000	1.000000	C	2.956602	0.000000	1.000000
Si	3.532191	0.000000	2.886116	Si	3.531722	0.000000	2.885567
Si	3.532191	-0.000000	-0.886116	Si	3.531722	-0.000000	-0.885567
C	1.986169	0.000000	2.130784	C	1.986190	0.000000	2.131615
C	1.986169	-0.000000	-0.130784	C	1.986190	-0.000000	-0.131615
C	0.644745	-0.000000	1.689500	C	0.645206	0.000000	1.689674
C	0.644745	-0.000000	0.310500	C	0.645206	0.000000	0.310326
H	-0.218623	-0.000000	2.338729	H	-0.217810	0.000000	2.338858
H	-0.218623	-0.000000	-0.338729	H	-0.217810	0.000000	-0.338858
Ba	6.381999	-0.000000	1.000000	Ba	6.380708	-0.000000	1.000000

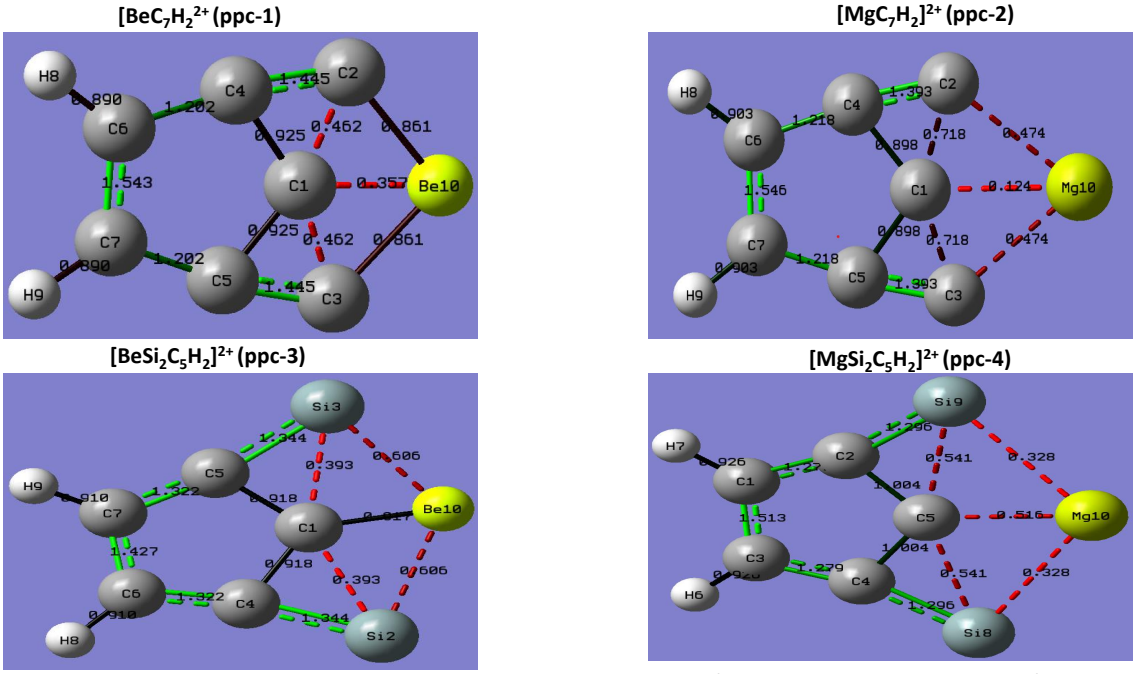

Figure S11: Mayer bonding analysis of $[BeC_7H_2]^{2+}$(**ppC-1**), $[MgC_7H_2]^{2+}$(**ppC-2**), $[BeSi_2C_5H_2]^{2+}$(**ppC-3**), and $[MgSi_2C_5H_2]^{2+}$(**ppC-4**) obtained at PBE0-D3/def2-TZVP level of theory.

Mayer bonding analysis of $[BeC_7H_2]^{2+}$(ppC-1) obtained at PBE0-D3/def2-TZVP level of theory.

********** Bond order matrix **********

	1	2	3	4	5
1	3.16688594	0.46204262	0.46204262	0.92463322	0.92463322
2	0.46204262	3.00540197	0.07688240	1.44488333	0.08353146
3	0.46204262	0.07688240	3.00540197	0.08353146	1.44488333
4	0.92463322	1.44488333	0.08353146	3.89080095	0.11247450
5	0.92463322	0.08353146	1.44488333	0.11247450	3.89080095
6	0.01069814	0.00249285	0.06788831	1.20246225	0.07556516
7	0.01069814	0.06788831	0.00249285	0.07556516	1.20246225
8	0.00755248	0.00170940	0.00544960	0.00608027	0.00689007
9	0.00755248	0.00544960	0.00170940	0.00689007	0.00608027

10	0.35703303	0.86052199	0.86052199	0.03428070	0.03428070
	6	7	8	9	10
1	0.01069814	0.01069814	0.00755248	0.00755248	0.35703303
2	0.00249285	0.06788831	0.00170940	0.00544960	0.86052199
3	0.06788831	0.00249285	0.00544960	0.00170940	0.86052199
4	1.20246225	0.07556516	0.00608027	0.00689007	0.03428070
5	0.07556516	1.20246225	0.00689007	0.00608027	0.03428070
6	3.82957828	1.54330107	0.89044970	0.00635882	0.03036197
7	1.54330107	3.82957828	0.00635882	0.89044970	0.03036197
8	0.89044970	0.00635882	0.92695717	0.00008321	0.00238362
9	0.00635882	0.89044970	0.00008321	0.92695717	0.00238362
10	0.03036197	0.03036197	0.00238362	0.00238362	2.21212959

Mayer bonding analysis of $[MgC_7H_2]^{2+}$(ppC-2) obtained at PBE0-D3/def2-TZVP level of theory.

********** Bond order matrix **********

	1	2	3	4	5
1	3.38050804	0.71820452	0.71820452	0.89834732	0.89834732
2	0.71820452	2.78924586	-0.00969728	1.39293559	0.13975659
3	0.71820452	-0.00969728	2.78924586	0.13975659	1.39293559
4	0.89834732	1.39293559	0.13975659	3.89966332	0.13318124
5	0.89834732	0.13975659	1.39293559	0.13318124	3.89966332
6	0.00260321	-0.00896838	0.07793997	1.21745082	0.07157265
7	0.00260321	0.07793997	-0.00896838	0.07157265	1.21745082
8	0.00920584	0.00028619	0.00453476	0.00227781	0.00667231
9	0.00920584	0.00453476	0.00028619	0.00667231	0.00227781

10	0.12378626	0.47425391	0.47425391	0.03746898	0.03746898
	6	7	8	9	10
1	0.00260321	0.00260321	0.00920584	0.00920584	0.12378626
2	-0.00896838	0.07793997	0.00028619	0.00453476	0.47425391
3	0.07793997	-0.00896838	0.00453476	0.00028619	0.47425391
4	1.21745082	0.07157265	0.00227781	0.00667231	0.03746898
5	0.07157265	1.21745082	0.00667231	0.00227781	0.03746898
6	3.82956663	1.54631783	0.90286758	0.00723846	0.01254449
7	1.54631783	3.82956663	0.00723846	0.90286758	0.01254449
8	0.90286758	0.00723846	0.93412216	0.00012824	0.00091097
9	0.00723846	0.90286758	0.00012824	0.93412216	0.00091097
10	0.01254449	0.01254449	0.00091097	0.00091097	1.17414297

Mayer bonding analysis of $[BeSi_2C_5H_2]^{2+}$(ppC-3) obtained at PBE0-D3/def2-TZVP level of theory.

********** Bond order matrix **********

	1	2	3	4	5
1	3.57173052	0.39339784	0.39339784	0.91851268	0.91851268
2	0.39339784	2.64409973	0.04202707	1.34429970	0.13344378
3	0.39339784	0.04202707	2.64409973	0.13344378	1.34429970
4	0.91851268	1.34429970	0.13344378	3.96445348	0.08115450
5	0.91851268	0.13344378	1.34429970	0.08115450	3.96445348
6	0.00777873	0.03939484	0.07903784	1.32175459	0.04108361
7	0.00777873	0.07903784	0.03939484	0.04108361	1.32175459
8	0.00771722	0.00089789	0.00557681	0.00638836	0.00676996
9	0.00771722	0.00557681	0.00089789	0.00676996	0.00638836
10	0.91691758	0.60602395	0.60602395	0.11104629	0.11104629

	6	7	8	9	10
1	0.00777873	0.00777873	0.00771722	0.00771722	0.91691758
2	0.03939484	0.07903784	0.00089789	0.00557681	0.60602395
3	0.07903784	0.03939484	0.00557681	0.00089789	0.60602395
4	1.32175459	0.04108361	0.00638836	0.00676996	0.11104629
5	0.04108361	1.32175459	0.00676996	0.00638836	0.11104629
6	3.88503957	1.42723205	0.91024830	0.00609071	0.05241889
7	1.42723205	3.88503957	0.00609071	0.91024830	0.05241889
8	0.91024830	0.00609071	0.94575212	0.00028175	0.00178113
9	0.00609071	0.91024830	0.00028175	0.94575212	0.00178113
10	0.05241889	0.05241889	0.00178113	0.00178113	2.45945810

Mayer bonding analysis of $[MgSi_2C_5H_2]^{2+}$(ppC-4)obtained at PBE0-D3/def2-TZVP level of theory.

********** Bond order matrix **********

	1	2	3	4	5
1	3.91250604	1.27882094	1.51329477	0.02840045	0.00594909
2	1.27882094	3.93135480	0.02840065	0.09830460	1.00449672
3	1.51329477	0.02840065	3.91250622	1.27882143	0.00594928
4	0.02840045	0.09830460	1.27882143	3.93136320	1.00449711
5	0.00594909	1.00449672	0.00594928	1.00449711	3.63528611
6	0.00337266	0.00741677	0.92624777	-0.00063351	0.00806198
7	0.92624777	-0.00063349	0.00337262	0.00741678	0.00806196
8	0.08589365	0.13613148	0.03779789	1.29576216	0.54129686
9	0.03779787	1.29575530	0.08589318	0.13613091	0.54130048
10	0.03272883	0.08266184	0.03272863	0.08266328	0.51567261

	6	7	8	9	10
1	0.00337266	0.92624777	0.08589365	0.03779787	0.03272883
2	0.00741677	-0.00063349	0.13613148	1.29575530	0.08266184
3	0.92624777	0.00337262	0.03779789	0.08589318	0.03272863
4	-0.00063351	0.00741678	1.29576216	0.13613091	0.08266328
5	0.00806198	0.00806196	0.54129686	0.54130048	0.51567261
6	0.95066652	-0.00008414	0.00048021	0.00516038	0.00064440
7	-0.00008414	0.95066650	0.00516037	0.00048021	0.00064441
8	0.00048021	0.00516037	2.46776875	0.03694669	0.32829943
9	0.00516038	0.00048021	0.03694669	2.46775428	0.32828926
10	0.00064440	0.00064441	0.32829943	0.32828926	1.40433270