Supporting Information:

Planar Pentacoordinate Carbon in CAl_5^+: A Global Minimum

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Part I. Isomer structures and their relative energies: CAl_5^+, CSi_5^{2-}, CBe_5, CP_5^{3+}, and CB_5.

Part II. PpC contained local minimum structures CSi_4P^- and CSi_3P_2 (Ref. 27b).

Part III. Figure S1: Calculated IR spectrum for the 2D ppC structure of CAl_5^+ and vibration frequencies.

Part IV. Complete reference 47.

Part V. Movie S1: A movie of quantum molecular dynamics trajectory (10 ps simulation) of the ppC CAl_5^+ at 300 K.

Part VI. Movie S2: Movies of the two lowest-frequency vibration modes for the ppC CAl_5^+.

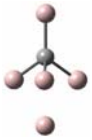
Part I. Isomer structures and their relative energies: CAl_5^+, CSi_5^{2-}, CBe_5, CP_5^{3+}, and CB_5. The planar pentacoordinate carbon structures are highlighted in red.

Top 10 isomer structures and relative energies (kcal/mol, at 0 K) of **CAl_5^+**. (The B3LYP/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ relative energies are in black and red, respectively，in unit of kcal/mol).

D_{5h}, $^1A_1$'

(0.00)

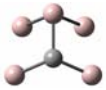
(0.00)



C_{3v}, $^1A_1$'

(3.96)

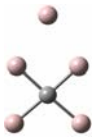
(5.00)



C_s, ^1A'

(10.15)

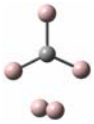
(10.04)



C_{2v}, $^3A_1$

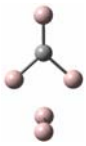
(11.78)

(17.41)



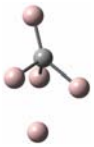
C_{2v}, $^1A_1$

(16.11)



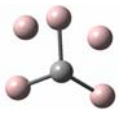
C_{2v}, $^3A_1$

(20.06)



C_1, ^3A

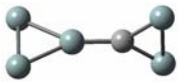
(21.22)



C_1, ^3A

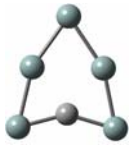
(25.51)

Top 8 isomer structures and relative energies (kcal/mol, at 0 K) of **CSi_5^{2-}**. (B3LYP/aug-cc-pVTZ energies).



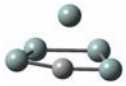
0.00

C_2, ^1A



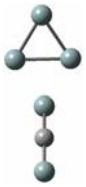
1.31

C_{2v}, $^1A_1$



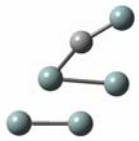
1.77

C_1, ^1A



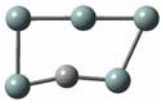
5.75

C_s, $^1A'$



8.93

C_1, ^1A



14.12

C_s, $^1A'$

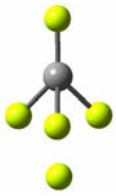
14.57

D_{5h}, $^1A_1'$

15.27

C_s, $^1A'$

Top 10 isomer structures and relative energies (kcal/mol, at 0 K) of **CBe_5.** (B3LYP/aug-cc-pVTZ energies).

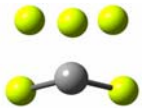


C_s, $^3A'$

0.00

C_s, $^1A'$

4.16

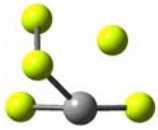


C_s, $^1A'$

5.75

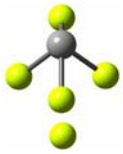
C_s, $^3A'$

6.56



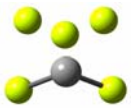
C_1, ^1A

7.14



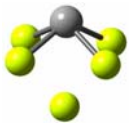
C_s, $^1A'$

7.81



C_s, $^1A'$

7.94

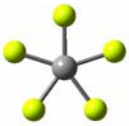


C_{2v}, $^3A_1$

9.81

C_s, $^1A'$

11.1



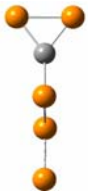
D5h, $^1A_1'$

18.50

Top 8 isomer structures and relative energies (kcal/mol, at 0 K) of **CP_5^{3+}**. (B3LYP/aug-cc-pVTZ energies).

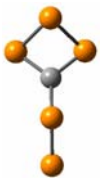
C_2, ^1A

0.00



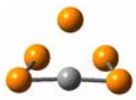
C_s, $^1A'$

17.22



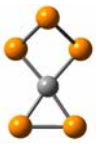
C_s, $^1A'$

32.11



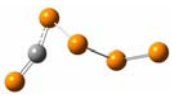
C_s, $^1A'$

34.71



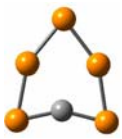
C_s, $^1A'$

35.50



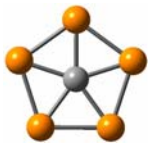
C_1, ^1A

38.00



C_{2v}, $^1A_1$

41.08



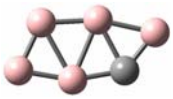
D5h, $^1A_1'$

63.86

Top 8 isomer structures and relative energies (kcal/mol, at 0 K) of **CB_5**. (B3LYP/aug-cc-pVTZ energies).

C_{2v}, $^2A_1$

0.00



C_s, $^2A'$

7.06

C_s, $^2A'$

28.93

C_s, $^2A'$

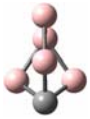
37.45

C_s, $^2A'$

38.79

C_s, $^2A'$

43.13



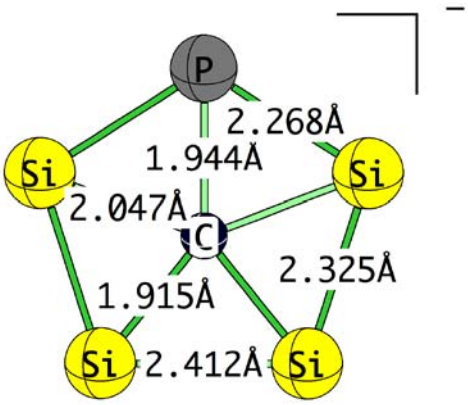
C_s, $^2A'$

44.48

C_{2v}, $^2A_1$

44.59

Part II. PpC contained local minimum structures CSi_4P^- and CSi_3P_2 (Ref. 27b).



CSi_4P^- C_{2v}

$E_{Tot.}$ = –1537.54345 a.u.

ZPE = 6.10 kcal/mol

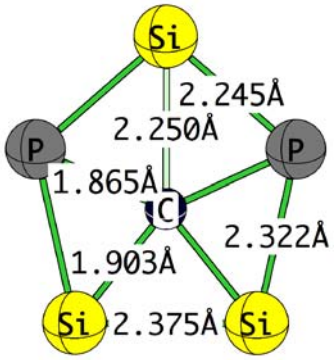
HOMO-LUMO Gap = 2.54 eV

NImag = 0

$\nu_{Min.}$ = 132.6 cm^{-1}

Cartesian Coordinate (Å)

C	-0.10265	0.00000	0.00000
P	1.84154	0.00000	0.00000
Si	0.62500	1.91367	0.00000
Si	0.62500	-1.91367	0.00000
Si	-1.58954	1.20610	0.00000
Si	-1.58954	-1.20610	0.00000



CSi_3P_2 C_{2v}

$E_{Tot.}$ = –1589.34615 a.u.

ZPE = 6.36 kcal/mol

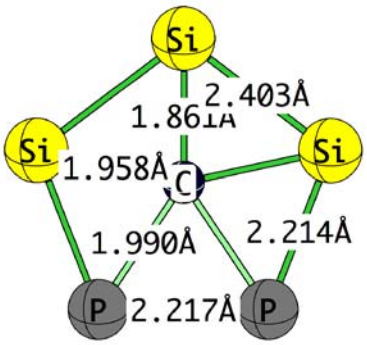
HOMO-LUMO Gap = 3.11 eV

NImag = 0

$\nu_{Min.}$ = 122.1 cm^{-1}

Cartesian Coordinate (Å)

C	-0.16908	0.00000	0.00000
P	0.60892	-1.69489	0.00000
P	0.60892	1.69489	0.00000
Si	2.08106	0.00000	0.00000
Si	-1.65671	-1.18735	0.00000
Si	-1.65671	1.18735	0.00000



CSi_3P_2 C_{2v}

$E_{Tot.}$ = –1589.33894 a.u.

ZPE = 6.36 kcal/mol

HOMO-LUMO Gap = 3.47 eV

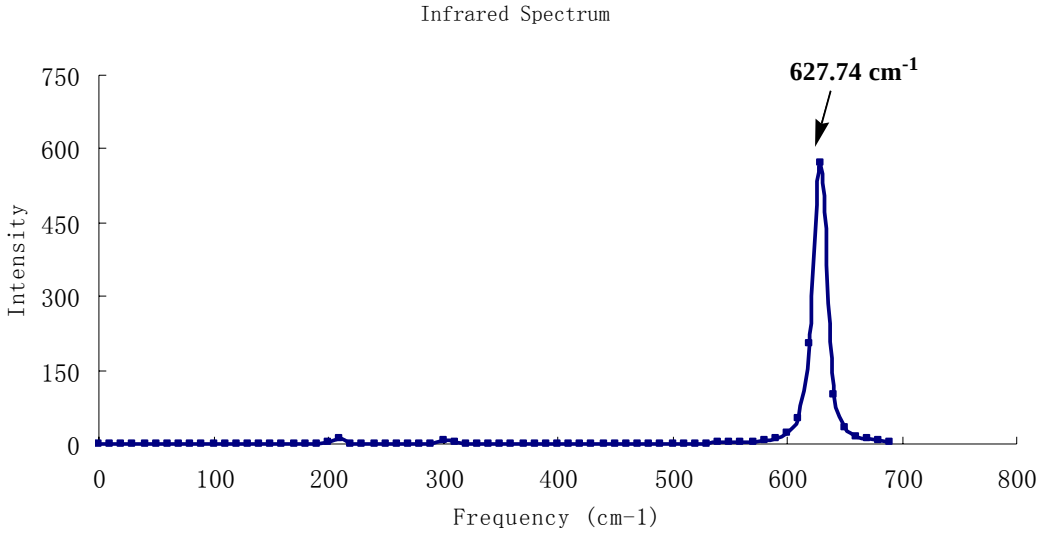
NImag = 0

$\nu_{Min.}$ = 126.6 cm^{-1}

Cartesian Coordinate (Å)

C	0.15440	0.00000	0.00000
Si	0.56414	-1.91457	0.00000
Si	0.56414	1.91457	0.00000
Si	2.01550	0.00000	0.00000
P	-1.49798	-1.10839	0.00000
P	-1.49798	1.10839	0.00000

Part III. *Figure S1*. Calculated IR spectrum for the 2D ppC structure of CAl_5^+ and vibration frequencies.



$v_1(e_2'')$	**69.4 cm^{-1}**
$v_2(e_2'')$	**69.4 cm^{-1}**
$v_3(e_1'')$	**79.1 cm^{-1}**
$v_4(e_1'')$	**79.1 cm^{-1}**
$v_5(a_2'')$	**208.6 cm^{-1}**
$v_6(e_1')$	**300.8 cm^{-1}**
$v_7(e_1')$	**300.8 cm^{-1}**
$v_8(a_1')$	**370.4 cm^{-1}**
$v_9(e_2')$	**406.8 cm^{-1}**
$v_{10}(e_2')$	**406.8 cm^{-1}**
$v_{11}(e_1')$	**627.7 cm^{-1}**
$v_{12}(e_1')$	**627.7 cm^{-1}**

Reference 47

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, 2004.