A Theoretical Study of the Cyclization Processes of Energized CCCSi and CCCP

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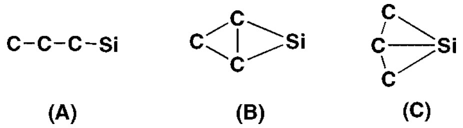
Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory have shown that cyclization of both the ground state triplet and the corresponding singlet state of CCCSi may rearrange to give cyclic isomers which upon ring opening may reform linear C_3Si isomers in which the carbon atoms are scrambled. The cyclization processes are energetically favorable with barriers to the transition states from 13 to 16 kcal mol^{-1}. This should be contrasted with the analogous process of triplet CCCC to triplet rhombic C_4, which requires an excess energy of 25.8 kcal mol^{-1}. A similar cyclization of doublet CCCP requires 50.4 kcal mol^{-1} of excess energy; this should be contrasted with the same process for CCCN, which requires 54.7 kcal mol^{-1} to effect cyclization.

Introduction

The cumulenes CCCC[1] and CCCN[2,3] have been tentatively identified in interstellar dust clouds, while CCCO and CCCS are known to be abundant in such interstellar regions.[4−9] All four cumulenes have been shown to be stable species, but, when energized, they may undergo interesting reactions. Energized singlet CCCC undergoes cyclization to planar rhombic C_4 in an exothermic reaction (−10 kcal mol^{-1}) over a barrier of 29.5 kcal mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G(d) level of theory. The corresponding reaction of ground state triplet CCCC is endothermic by 17.2 kcal mol^{-1} with a barrier of 25.8 kcal mol^{-1}. Loss of C (in a reaction endothermic by 122 kcal mol^{-1} for triplet CCCC) occurs such that the C is scrambled within an equilibrating CCCC/rhombic C_4 system.[10] In contrast, energized CCCO decomposes to yield CC and CO (endothermicity +79.8 kcal mol^{-1}) without any scrambling of the skeleton,[11] while CCCS fragments to CCC and S. The calculated barrier for the conversion of CCCS to a "rhomboid" C_3S is 80.3 kcal mol^{-1}, which makes this process energetically unfavorable.[11] Finally, the loss of C from doublet CCCN occurs following partial scrambling from an equilibrating CCCN/CCNC system through planar "rhombic" C_3N.[12] The barrier to this process [59.9 kcal mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory] is significantly higher than that required for the CCCC/rhombic C_4 process.[10,12]

To complete this particular series of cumulenes (groups 6, 7, and 8 of the second and third periods of the Mendeleev periodic classification) the rearrangements of CCCSi and CCCP need to be studied. In the studies of CCCX systems outlined above, we produced the appropriate heterocumulene by charge-stripping (in the collision cell of a mass spectrometer) an anion of known bond connectivity.[10−12] Preparation of $[CCCSi]^{-\bullet}$ and $[CCCP]^{-}$ by unequivocal syntheses of this type is not possible. As a consequence, we have studied rearrangements of these two systems theoretically. The C_3Si radical potential surface has been studied extensively,[13−31] and is of particular interest because there is experimental evidence to show that there are three stable isomers: a linear triplet **A** and two cyclic rings **B** and **C** (Scheme 1).[20,22] Rhomboid **B** has been identified in the evolved carbon star system IRC+10216,[18,20] but linear CCCSi has not been identified to date, even though the higher homologue, linear CCCCSi, has.[16,18] C_3Si isomeric structures have been studied by photoelectron spectroscopy,[20] and by FT microwave spectroscopy.[21−23] A number of theoretical studies have been reported for the C_3Si system.[24−32] The relative energies of the linear structure **A** and the two cyclic structures **B** and **C** are dependent on the level of theory and the basis set used, with recent work using MRPTZ theory suggesting that singlet **B** is

SCHEME 1



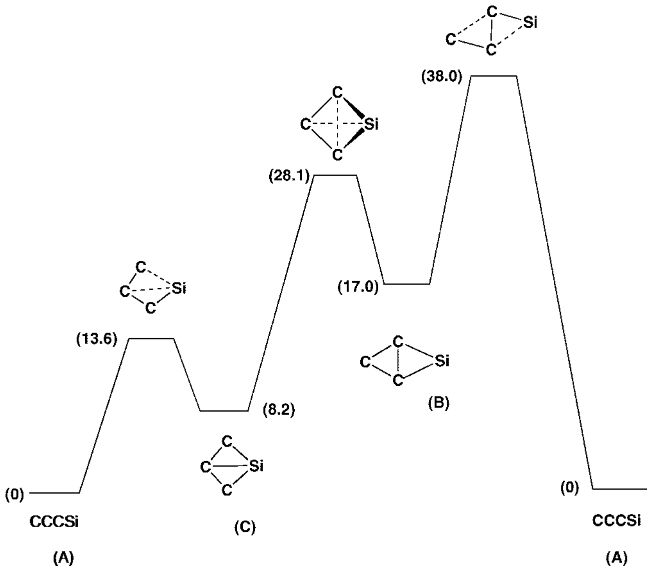


Figure 1. Rearrangement of triplet CCCSi. Geometries were determined at the B3LYP/6-31+G(d) level of theory and energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Relative energies are quoted in kcal mol^{-1}. For full details of geometries and energies of all species shown in Figure 1 see Table 1.

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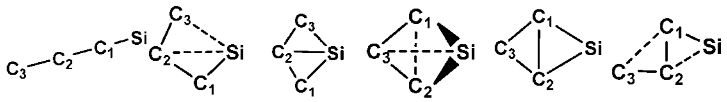
10.1021/jp807403s CCC: $40.75

TABLE 1: Structures Shown in Figure 1



	^{3}A	TS ^{3}A/^{3}C	^{3}C	TS ^{3}C/^{3}B	^{3}B	TS ^{3}B/^{3}A
State	^{3}SG	^{3}A”	^{3}B$_1$	^{3}A	^{3}A”	^{3}A”
Symmetry	C_{*V}	C_S	C_{2V}	C_1	C_S	C_S
Energy (Hartrees)	-402.78612	-402.76438	-402.77305	-402.74133	-402.75895	-402.72555
Energy Relative to A^3	0	+13.6	+8.2	+28.1	+17.0	+38.0
Dipole Moment (Debye)	4.484	3.115	1.751	1.668	0.417	3.270
Bond Lengths (Å)						
SiC$_1$	1.736	1.795	1.960	2.093	1.943	1.804
C$_1$C$_2$	1.293	1.346	1.345	2.239	1.508	1.430
C$_2$C$_3$	1.312	1.323	1.345	1.410	1.362	1.320
SiC$_2$	-	2.090	1.974	1.848	1.942	2.01
SiC$_3$	-	2.669	1.960	2.268	-	-
C$_1$C$_3$	-	-	-	1.319	1.362	1.905
Bond Angles (°)						
SiC$_1$C$_2$	180.0	82.1	70.5	50.4	67.2	75.9
C$_1$C$_2$C$_3$	180.0	158.8	138.9	33.6	56.4	87.6
C$_1$SiC$_2$	-	39.6	40.0	68.9	45.7	43.6
C$_3$C$_2$Si	-	100.5	69.5	87.2	123.5	148.1
C$_1$C$_2$Si	-	58.3	69.5	60.7	67.1	60.5
C$_3$SiC$_1$	-	68.7	80.0	34.9	-	-
C$_2$C$_3$C$_1$	-	-	-	110.2	67.2	48.6
C$_3$C$_1$Si	-	-	-	79.8	123.6	119.7
C$_3$C$_1$C$_2$	-	-	-	36.2	56.4	43.8
Dihedral Angle (°)						
SiC$_1$C$_2$C$_3$	0.0	0.0	0.0	138.0	180.0	180.0
C$_3$C$_2$SiC$_1$	-	180.0	180.0	-21.7	0.0	0.0

more stable than triplet **A** and singlet **C** by 2.2 and 4.7 kcal mol^{-1}, respectively.[31] C_3Si anions have also been studied.[25,26,33]

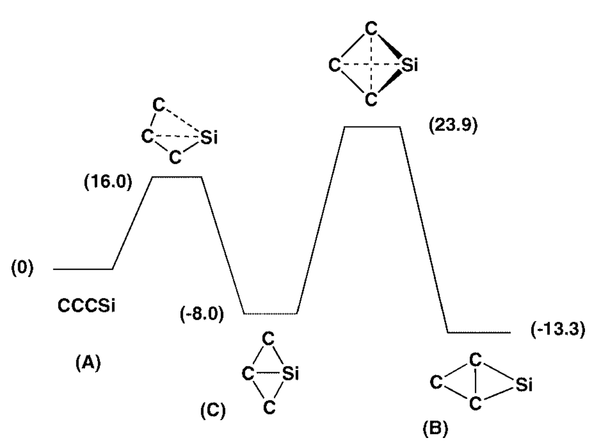


Figure 2. Rearrangement of singlet CCCSi. Geometries were determined at the B3LYP/6-31+G(d) level of theory and energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Relative energies are quoted in kcal mol^{-1}. For full details of geometries and energies of all species shown in Figure 2 see Table 2.

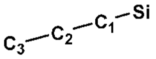
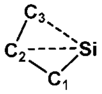
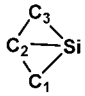
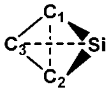
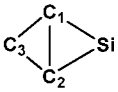
Much less is known about the chemistry of cumulenes containing P. Although there are several interstellar molecules containing P,[34] namely CP[35] and NP,[36,37] CCP and CCCP have, to this time, not been detected. Theoretical studies of linear CCP[38] and CCCP[39,40] have been reported; CCCP is reported to have a linear 2π electronic state at the MP2/6-31G* level of theory.[39] C_3P cations[40−42] and anions[43−45] have also been studied.

The aims of the present study were to see whether the behavior of energized CCCSi and CCCP follow those of CCCC and CCCN. In particular, to determine whether the carbons of CCCSi and CCCP may scramble via rearrangement through cyclic intermediates like **B**.

Experimental Section

Geometry optimizations were carried out with the Becke 3LYP method,[47,48] using the 6-31+G(d) basis set[49] within the GAUSSIAN 03 suite of programs.[50] Stationary points were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by

TABLE 2: Structures Shown in Figure 2

					
	^{1}**A**	**TS ^{1}A/^{1}C**	^{1}**C**	**TS ^{1}C/^{1}B**	^{1}**B**
State	-	$^1A'$	$^1A'$	^1A	$^1A'$
Symmetry	$C_{\infty v}$	C_S	C_S	C_1	C_S
Energy (Hartrees)	-402.77329	-402.74785	-402.78604	-402.73528	-402.79445
Energy Relative to A^1	0	+16.0	-8.0	+23.9	-13.3
Dipole Moment (Debye)	4.309	5.749	2.276	2.024	4.193
Bond Lengths (Å)					
SiC_1	1.744	1.767	2.056	2.137	1.851
C_1C_2	1.296	1.344	1.343	1.987	1.474
C_2C_3	1.310	1.321	1.343	1.322	1.437
SiC_2	-	2.415	1.909	1.820	1.852
SiC_3	-	3.454	2.056	2.046	-
C_1C_3	-	-	-	1.404	1.437
Bond Angles (°)					
SiC_1C_2	180.0	101.0	64.4	52.2	66.5
$C_1C_2C_3$	180.0	178.9	152.4	44.9	59.1
C_1SiC_2	-	33.1	39.4	59.6	46.9
C_3C_2Si	-	133.0	76.2	98.7	125.6
C_1C_2Si	-	45.9	76.2	68.2	66.6
C_3SiC_1	-	30.8	78.8	35.4	-
$C_2C_3C_1$	-	-	-	93.5	61.7
C_3C_1Si	-	-	-	82.8	125.7
$C_3C_1C_2$	-	-	-	41.6	59.2
Dihedral Angle (°)					
$SiC_1C_2C_3$	0.0	0.0	0.0	129.4	180.0
$C_3C_2SiC_1$	-	180.0	180.0	-35.5	0.0

intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies which were then scaled by 0.9804[51] and used as a zero-point correction for electronic energies. We have reported the success of this method in predicting geometries of unsaturated chain structures, and that this method produces optimized structures, at low computational cost, that compare favorably with higher level calculations.[52] More accurate energies for the B3LYP geometries were determined by using the CCSD(T)/aug-cc-pVDZ level of theory including zero-point energy correction (calculated by vibrational frequencies at the B3LYP/6-31+G(d) level of theory). All calculations were carried out at the South Australian Partnership for Advanced Computing (SAPAC) facility.

Results and Discussion

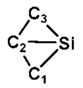
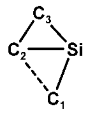
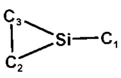
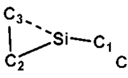
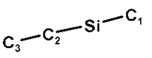
Geometries were determined at the B3LYP/6-31+G(d) level of theory and energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Relative energies are quoted in kcal mol^{-1}.

1. Rearrangements of Linear Singlet and Triplet CCCSi. Three important isomers of C_3Si considered in this study are linear **A** and the two cyclic structures **B** and **C**. With use of the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) protocol, triplet **A** is more stable than singlet **A** by 8.1 kcal mol^{-1}, while the singlet forms of **B** and **C** are more stable than the triplet states by 22.3 and 8.2 kcal mol^{-1}, respectively. The relative energies of singlet **B**, triplet **A**, and singlet **C** are +5.2 (+2.2), 0, and +5.3 (+4.7) kcal mol^{-1} [values in parentheses are those calculated at the MRPT2 theory[31] and listed for comparison]. Can linear CCCSi (**A**) ring close to **B** and/or **C**? If so, and if these processes are equilibria, they will result in atom scrambling of linear CCCSi by processes analogous to those described for linear CCCC.[10] The reaction coordinates of such rearrangements have been explored: results are summarized in Figures 1−3, with full details of geometries of minima and transition states listed in Tables 1−3. Intersystem crossing between singlet/triplet potential surfaces has not been explored.

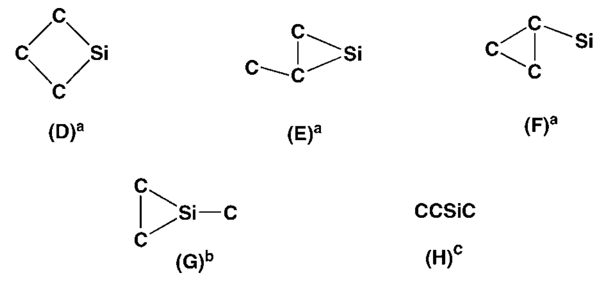
The C_3Si potential surface is different from the analogous C_4 surface because a number of the C_3Si analogues of the stable intermediates of C_4 are not stable. Relevant C_3Si isomers are shown in Scheme 2. Structure **G** is the only cyclic isomer shown in Scheme 2 where both singlet and triplet are stable, while only the singlet of linear CCSiC is stable.

Because the ground state triplet and singlet CCCSi are separated by only 8.1 kcal mol^{-1}, we have considered both the

TABLE 3: Structures Shown in Figure 3

	 ^{1}C	 TS ^{1}C/^{1}G	 ^{1}G	 TS ^{1}G/^{1}H	 ^{1}H
State	^{1}A'	^{1}A	^{1}A'	^{1}A	-
Symmetry	C_S	C_1	C_S	C_1	C_S
Energy (Hartrees)	-402.78604	-402.64411	-402.65526	-402.63936	-402.64707
Energy Relative to A^1 (0 kcal mol^{-1})	-8.0	+81.1	+74.1	+84.0	+79.2
Dipole Moment (Debye)	2.276	2.705	0.365	1.633	1.710
Bond Lengths (Å)					
SiC_1	2.056	1.831	1.826	1.820	1.813
C_1C_2	1.343	2.807	-	-	-
C_2C_3	1.343	1.313	1.298	1.294	1.287
SiC_2	1.909	2.008	1.838	1.706	1.694
SiC_3	2.056	1.793	1.838	2.533	-
Bond Angles (°)					
$C_1C_2C_3$	152.4	100.2	-	-	-
C_1SiC_2	39.4	93.9	159.3	173.9	180.0
C_3C_2Si	76.2	61.2	69.3	114.5	180.0
C_1C_2Si	76.2	40.6	-	-	-
C_3SiC_1	78.8	131.4	-	158.4	-
SiC_3C_2	64.4	78.9	69.3	37.8	-
C_2SiC_3	39.4	39.9	41.3	27.7	-
Dihedral Angle (°)					
$SiC_1C_2C_3$	0.0	15.8	-	-	-
$C_3C_2SiC_1$	180.0	-162.1	180.0	-180.0	0.0

SCHEME 2



^{a} Both singlet and triplet are unstable. ^{b} Both singlet and triplet are stable. ^{c} Singlet stable, triplet unstable.

singlet and triplet potential surfaces of this system. The rearrangements of triplet **A** to **B** and **C** are summarized in Figure 1, while full data concerning geometries and energies of minima and transition states shown in Figure 1 are listed in Table 1. Stepwise processes of the type proposed for rearrangement of triplet CCCC do not occur, because the required intermediate triplet **E** is not stable at the level of theory used for this study.

Figure 1 shows the conversion of triplet **A** to **B** and **A** to **C** respectively. The cyclization of triplet **A** to **B** is endothermic (+17.0 kcal mol^{-1}) with a barrier to the transition state of 38.0 kcal mol^{-1}. The alternate process, triplet **A** to triplet **C**, is more facile. It is endothermic (+8.2 kcal mol^{-1}) with a barrier of only 13.6 kcal mol^{-1}. The conversion of triplet **A** to **C** has a lower barrier (+13.6 kcal mol^{-1}) than the ring closure of triplet

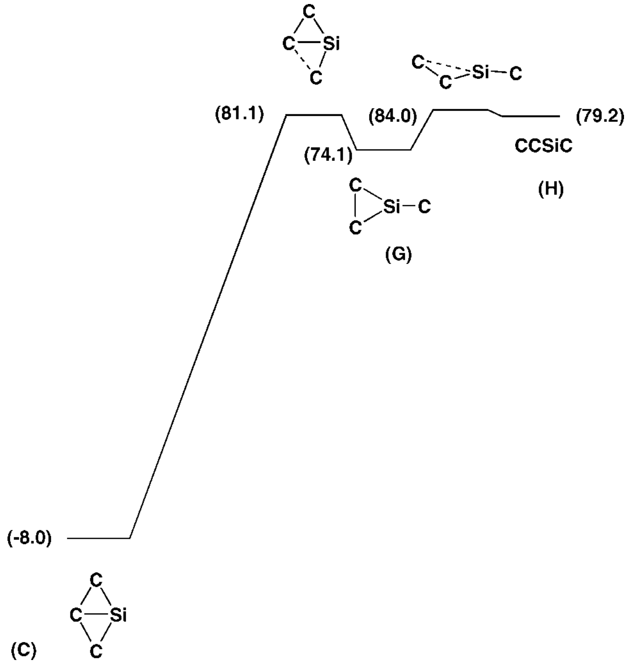
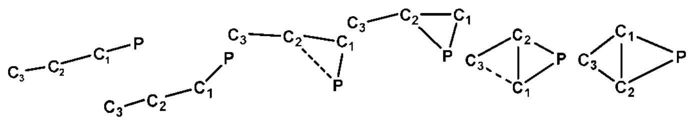


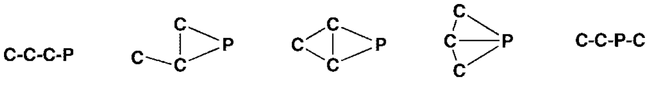
Figure 3. Rearrangement of singlet B to CCSiC. Geometries were determined at the B3LYP/6-31+G(d) level of theory and energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Relative energies are quoted in kcal mol^{-1}. For full details of geometries and energies of all species shown in Figure 3 see Table 3.

TABLE 4: Structures Shown in Figure 4



	^{2}I	^{2}I	TS ^{2}I/^{2}J	^{2}J	TS ^{2}J/^{2}K	^{2}K
State	-	^4A	^2A	$^2A''$	$^2A'$	$^2A''$
Symmetry	$C_{\infty V}$	C_1	C_1	C_S	C_S	C_S
Energy (Hartrees)	-454.65473	-454.59405	-454.57439	-454.60878	-454.59533	-454.63011
Energy Relative to I	0	+38.1	+50.4	+13.4	+37.3	+15.4
Dipole Moment (Debye)	3.797	3.536	4.372	2.284	3.344	3.655
Bond Lengths (Å)						
PC_1	1.600	1.742	1.664	1.783	1.788	1.783
C_1C_2	1.314	1.287	1.384	1.403	1.515	1.479
C_2C_3	1.297	1.333	1.309	1.321	1.321	1.434
PC_2	-	-	2.261	1.839	1.731	1.783
C_3C_1	-	-	-	-	2.306	1.434
Bond Angles (°)						
PC_1C_2	180.0	142.0	95.3	69.3	62.6	65.5
$C_1C_2C_3$	180.0	174.2	179.2	164.0	108.6	59.0
C_1PC_2	-	-	37.5	45.5	51.0	49.0
C_3C_2P	-	-	133.6	98.9	175.0	124.5
$C_2C_3C_1$	-	-	-	-	38.5	65.1
$C_3C_1C_2$	-	-	-	-	32.9	59.0
C_3C_1P	-	-	-	-	95.5	124.5
Dihedral Angle (°)						
$PC_1C_2C_3$	0.0	-179.9	178.3	0.0	180.0	180.0
$C_3C_2PC_1$	-	-	-180.0	180.0	0.0	0.0
$PC_1C_3C_2$	-	-	-	-	0.0	0.0

SCHEME 3: Doublet Structures



(I)[a] (J)[a] (K)[a] (L)[b] (M)[b]

[a] Stable. [b] Triplet unstable.

CCCC (+25.8 kcal mol^{-1}), with the CCCC and CCCSi processes both endothermic (17.2 and 8.2 kcal mol^{-1}, respectively). Cyclic forms **B** and **C** are interconvertible: the barrier is only 11.1 kcal mol^{-1} from **B** to **C**. Thus energized triplet CCCSi should cyclize readily producing cyclic isomers **B** and **C** which on ring opening may reform CCCSi but with the carbon atoms rearranged. The linear species CCSiC cannot be a product in this system since triplet CCSiC is not stable at the level of theory used in this study.

The singlet C_3Si reaction coordinate is shown in Figure 2, with details of energies and geometries of minima and transition states (shown in Figure 2) recorded in Table 2. Singlet CCCSi (**A**) interconverts in a concerted process to singlet **C**, but we can find no concerted pathway of singlet **A** to singlet **B**, the more stable of the two cyclized singlet isomers. There is also no stepwise rearrangement forming singlet **B**, since the required key intermediate, singlet **E**, is unstable at the level of theory used in this study. However, singlet **B** is convertible synchronously to singlet **C** over a barrier of 37.2 kcal mol^{-1}. The cyclization of singlet **A** to singlet **C** is exothermic (−8.0 kcal mol^{-1}) with the barrier to the transition state being 16.0 kcal mol^{-1}. This should be compared with the conversion of singlet CCCC to rhombic singlet C_4: barrier, 29.5 kcal mol^{-1}; exothermicity, −10.0 kcal mol^{-1}. So both triplet and singlet **A** should (i) form cyclic isomers which when ring opened may partially scramble the C atoms throughout the backbone of the linear molecule and (ii) the rearrangement of CCCSi should be more facile than CCCC.

There is, however, a significant difference between the triplet and singlet C_3Si potential surfaces in that singlet CCSiC is stable, whereas triplet CCSiC is not. Singlet CCSiC lies 79.2 kcal mol^{-1} above CCCSi and so any processes forming this species from **A**, **B**, or **C** will require significant excess energy. We have explored one such process, which is shown in Figure 3 (see also Table 3). Ring opening of **C** to the only stable isomer containing one three-membered ring (**G**) has a barrier of 81.1 kcal mol^{-1}, and once formed, this species should ring open to CCSiC. This rearrangement is energetically unfavorable compared with other such processes shown in Figures 1 and 2.

2. Rearrangement of Linear Doublet CCCP. The key isomers of the doublet C_3P potential surface are linear CCCP (**I**), the half-cyclized isomer **J**, and fully cyclized **K** (Scheme 3). In this case, **L** [cf. the Si isomer (**C**) above] is not a stable entity at the level of theory used in this study. Interestingly, linear CCPC is also not a stable species, so even if **I** can

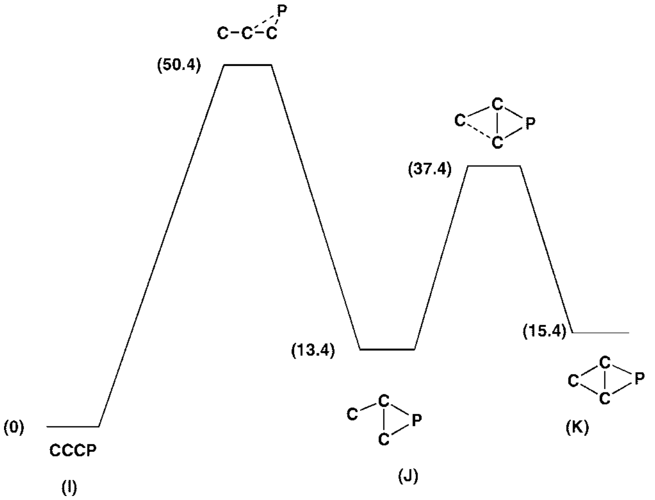


Figure 4. Rearrangement of doublet CCCP. Geometries were determined at the B3LYP/6-31+G(d) level of theory and energies at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory. Relative energies are quoted in kcal mol^{-1}. For full details of geometries and energies of all species shown in Figure 4 see Table 4.

transform to **K**, the only linear species to which **K** can ring open is CCCP (**I**). Calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory (Table 4) show that doublet CCCP is linear with essentially CC and CP double bonds. The quartet structure of **I** (see Table 4) lies 38.1 kcal mol^{-1} above doublet **I** and we have not considered the quartet potential surface further.

The rearrangement of **I** through **J** to **K** is shown in Figure 4 with full details of energies and geometries of species shown in Figure 4 recorded in Table 4. The reaction profile shown in Figure 4 is similar to that obtained for the ring closure of doublet CCCN at the same level of theory. The CCCP process is the more energetically favorable with a maximum barrier of +50.4 kcal mol^{-1} at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory (Figure 4) (cf. + 54.7 kcal mol^{-1} for CCCN) and an overall endothermicity of +15.4 kcal mol^{-1} (+41.6 kcal mol^{-1} for CCCN). Since we have already shown experimentally that there is partial C scrambling of energized CCCN,[12] it is probable that (at least) partial C scrambling should also be observed for energized CCCP.

In conclusion, the linear systems CCCSi and CCCP when energized may undergo cyclization to planar "rhomboid" systems, which when ring opened to reform CCCSi and CCCP may cause scrambling of the carbons. The cyclization of linear CCCSi to rhomboid C_3Si is more energetically favorable than cyclization of CCCC to rhombic C_4. As a consequence, it is likely that linear CCCSi (**A**) should be detectable together with the known rhombic C_3Si (**B**) in interstellar molecular clouds. Rearrangement of linear CCCP to a cyclic system is more energetically favorable than the analogous cyclization of the interstellar analogue CCCN.[54]

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Supporting Information Available: Table 1, a summary of rearrangements and dissociation of CCCX systems (X = C, Si, N, P, O, and S); Table 2, the 298 K enthalpies of formation of C_3Si and C_3P isomers; and Table 3, dissociation energies for the processes CCCX → CC + CX. This material is available free of charge via the Internet at http://pubs.acs.org.

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(54) A reviewer has requested that (i) a table be constructed summarizing all the important parameters resulting from our studies of the rearrangements of all C_3X systems, (ii) the 298 K enthalpies of formation of the main C_3Si and C_3P isomers, and (iii) the CCCX → CC + CX dissociation energies. These data are summarized in Tables 1−3 in the Supporting Information.

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