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Phosphatetrasilatricyclo[2.1.0.0^{2,5}]pentane

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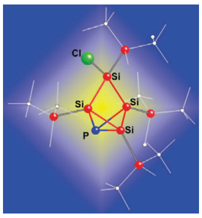
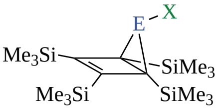
The phosphatetrasilatricyclo[2.1.0.0^{2,5}]pentane cage compound was synthesized by the reaction of the tetrasilacyclobutadiene dianion dipotassium salt precursor with PCl_3. The structure, bonding nature, and mechanism of formation of the title compound were studied both experimentally (NMR, X-ray) and computationally (DFT).



Keywords: DFT calculations, housene, phosphorus, silicon, tricyclo[2.1.0.0^{2,5}]pentane, X-ray diffraction.

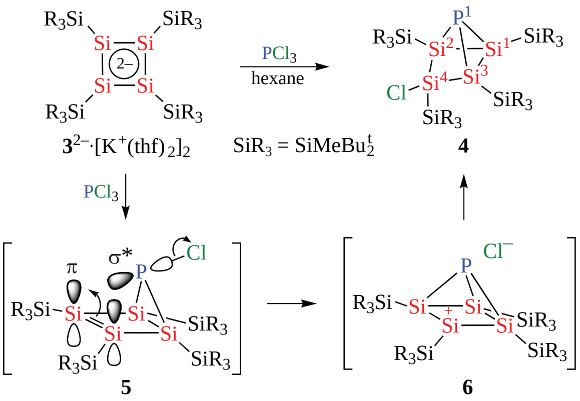
Highly strained bicyclo[2.1.0]pentenes (otherwise known as *housenes*) are among very attractive synthetic challenges in both organic and Main Group element chemistry.[1–3] Recently, employing readily available cyclobutadiene dianion derivatives, we prepared a series of hybrid housenes of the group 14/group 15 elements. Thus, by the reaction of the cyclobutadiene dianion $[(Me_3Si)_4C_4][Li^+(thf)]_2$[4] with either PCl_3 or SbF_3 we synthesized (chlorophospha)-housene $(Cl–P)[C_4(SiMe_3)_4]$ **1**[5] and (fluorostiba)housene $(F–Sb)[C_4(SiMe_3)_4]$ **2**[6] (Scheme 1). Inspired by these results, we challenged a preparation of the silicon analogue of **1**, namely, (chlorophospha)tetrasilahousene $(Cl–P)[Si_4(SiMeBu^t_2)_4]$. However, the outcome of our attempted synthesis was surprisingly different.



1 E = P, X = Cl
2 E = Sb, X = F

Thus, the reaction of the dipotassium salt of the tetrasilacyclobutadiene dianion derivative $\mathbf{3}^{2-}{\cdot}[K^+(thf)_2]_2$[7] with PCl_3 in hexane formed as a major product 1-phospha-2,3,4,5-tetrasilatricyclo[2.1.0.0^{2,5}]pentane cage **4**, representing a first example of the hybrid heavier group 14/group 15 elements tricyclopentane (Scheme 1).§ The presence of the highly strained tricyclic $[Si_4P]$-skeleton in **4** was clearly manifested in the characteristic high-field signals of its bridgehead atom [Si^1: –198.2 ppm (d, $^1J(^{29}Si–^{31}P)$ 59.6 Hz), P^1: –380.0 ppm] and bridging atoms [Si^2 and Si^3: –93.1 ppm (d, $^1J(^{29}Si–^{31}P)$ 60.6 Hz)].

The crystal structure of **4** was determined by X-ray diffraction analysis (Figure 1).§,¶ The cyclic Si(2)–Si(4) and Si(3)–Si(4) bonds of 2.343(3) and 2.349(3) Å are quite normal for the Si–Si single bonds, whereas Si(1)–Si(2) and Si(1)–Si(3) bonds are



Scheme 1

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[§] For the experimental (synthetic procedure for **4** and its spectral and crystallographic data) and computational (optimized geometries, total energies) details, see Online Supplementary Materials.

[¶] *Crystal data for* **4**. $C_{36}H_{84}ClPSi_8$ (M = 808.17), monoclinic, space group $P2_1/c$ at 150 K, a = 15.624(3), b = 17.873(3) and c = 17.796(3) Å, β = 93.931(2)°, V = 4975.8(15) Å^3, Z = 4, d_{calc} = 1.083 g cm^{-3}, μ(MoKα) = 0.326 mm^{-1}, F(000) = 1776. A total of 68725 reflections were collected [7020 independent reflections with $I > 2\sigma(I)$, R_{int} = 0.0717], GOF = 1.196, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0848 and wR_2 = 0.2342, R indices (all data): R_1 = 0.0883 and wR_2 = 0.2360, 527 refined parameters. X-ray diffraction data were collected on a Bruker AXS APEX II diffractometer with a CCD area detector with λ(MoKα) = 0.71073 Å at 150 K. The structure was solved by the direct method with the SHELXS-97 program[8,9] and refined by the full-matrix least-squares method with the SHELXL-2014 program.[10] All nonhydrogen atoms were refined anisotropically, whereas all hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The crystallographic program CrystalMaker 8.6 (version 8.6.3)

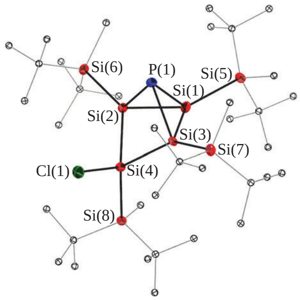
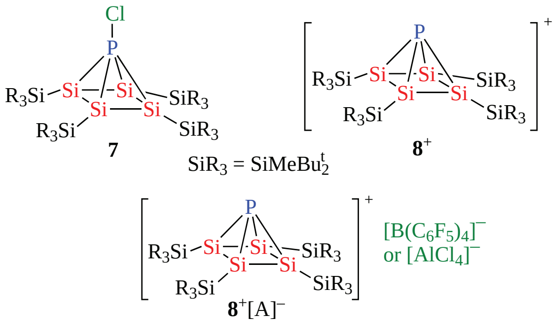


Figure 1 ORTEP view of **4** [thermal ellipsoids are given at 40% probability level, H atoms are not shown. The $\mathrm{Bu^t_2}$Me[Si(6)]-substituent at the Si(2)-skeletal atom is orientationally disordered, and only major orientation (75%) is shown].

slightly shorter, 2.297(3) and 2.301(3) Å, respectively. The optimized geometry of **4** well matches its X-ray structure (Figure S2). Calculations were performed at the TPSSh/Def2TZVP level of theory using GAUSSIAN16 suite of computational programs (see Online Supplementary Materials for details).[11]

Due to its incorporation into the highly strained and rigidly fixed tricyclopentane skeleton, P atom features highly distorted trigonal-pyramidal configuration with the sum of the bond angles around it totaling only 200.2°. This forces phosphorus to form very high *p*-character bonds to its silicon neighbors (90, 86 and 87% *p*-orbital contribution for Si(1), Si(2) and Si(3), respectively), and accordingly the lone pair at the P center is rich in *s*-character (69%).[11] Accordingly, the bridgehead P(1)–Si(1) bond in **4** is notably stretched [2.313(3) Å], thus being longer than the sum of the P and Si atoms covalent single bond radii of 2.27 Å[12] (although tricyclo[2.1.0.0^{2,5}]pentanes typically exhibit quite short bridgehead C–C bonds[13]), and longer than the P(1)–Si(2) and P(1)–Si(3) bonds of 2.274(3) and 2.286(3) Å, respectively. The interatomic distance P(1)···Si(4) (3.380 Å) is beyond the range of covalent interactions, thus excluding bonding between P(1) and Si(4).

For the mechanism of the unexpected formation of **4** upon the reaction of **3**$^{2-}\cdot$[K$^+$(thf)$_2$]$_2$ with PCl$_3$, initial generation of the (phosphatetrasila)bicyclo[2.1.0]pentene (‘housene’) **5** can be reasonably imagined as the first step of the reaction (see Scheme 1).[5,6] The subsequent isomerization of **5** to **4** is apparently driven by the $\pi_{Si=Si}$–σ^*_{P-Cl} orbital interaction, whose importance for housenes’ stabilization has been previously acknowledged.[3,6] This results in the generation of the key intermediate **6** featuring cationic silicon center, which finally scavenges chloride ion to form the final product **4**. Overall, transformation of the transient housene **5** into the stable tricyclopentane **4** is triggered by important thermodynamic stabilization gained in this process: according to our calculations, **5** (as energy minimum) is destabilized compared to **4** by 44 kcal mol^{-1}.[11] In a sharp contrast, previously reported (chlorophospha)housene **1** was quite stable and did not rearrange into the corresponding tricyclic cage.[5] Such a distinction between the C$_4$-based housene **1** and hypothetical Si$_4$-based housene **5** most likely results from the intrinsic instability of the latter caused by the presence of highly reactive endocyclic Si=Si double bond. Indeed, the preference of the (tetrasila)bicyclo[1.1.0]butane system over the isomeric cyclotetrasilene was previously documented by us.[14]



7

SiR$_3$ = SiMeBu$^t_2$

8$^+$

8$^+$[A]$^-$

[A]$^-$ = [B(C$_6$F$_5$)$_4$]$^-$ or [AlCl$_4$]$^-$

On the other hand, a hypothetical (chlorophospha)pyramidane **7** which is isomeric to tricyclopentane **4**, was also not formed. According to our calculations,[11] if **4** is the stable energy minimum, **7** is only a second-order saddle point remarkably destabilized by 53 kcal mol^{-1} towards **4**. This was further substantiated by the natural population analysis charge calculations of the corresponding free phosphapyramidane cation **8**$^+$ (energy minimum): –0.33 (P), +0.05 (skeletal Si), +1.50 (substituent Si). As can be seen, the phosphorus apex in **8**$^+$ is negatively polarized thus being reluctant towards attachment of the chloride ion, and accordingly (chlorophospha)pyramidane **7** is not formed. By contrast, when very bulky and exceptionally low-nucleophilic anion, such as borate [B(C$_6$F$_5$)$_4$]$^-$ (and even aluminate [AlCl$_4$]$^-$), is applied in our calculations instead of chloride ion, then the cationic phosphapyramidane derivatives **8**$^+\cdot$[A]$^-$ ([A]$^-$ = [B(C$_6$F$_5$)$_4$]$^-$ or [AlCl$_4$]$^-$) are quite stable being found as energy minimum structures.[15]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.009.

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was used for visualization crystal structure and preparation of the illustrations for publication.

CCDC 2094603 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.