

An Ylide-like Phoshasilene and Striking Formation of a 4 π -Electron, Resonance-Stabilized 2,4-Disila-1,3-diphosphacyclobutadiene

Shigeyoshi Inoue,* Wenyuan, Wang, Carsten Präsang, Matthew Asay, Elisabeth Irran, and Matthias Driess*

Institute of Chemistry: Metalorganics and Inorganic Materials, Technische Universität Berlin, Strasse des 17, Juni 135, Sekr. C2, D-10623 Berlin, Germany

Supporting Information

ABSTRACT: The first N-donor-stabilized phoshasilene $\text{LSi}(\text{SiMe}_3)=\text{PSiMe}_3$ ($\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$) has been synthesized in 87% yield through 1,2-silyl migration of the $(\text{Me}_3\text{Si})_2\text{P}$ -substituted, N-heterocyclic silylene $[\text{LSi}-\text{P}(\text{SiMe}_3)_2]$. Remarkably, the latter reacts with dichlorotriphenylphosphorane Ph_3PCl_2 to give the unprecedented 4 π -electron Si_2P_2 -cycloheterobutadiene $[(\text{LSi})_2\text{P}_2]$ with two-coordinate phosphorus atoms. The striking molecular structures as well as the ^{29}Si and ^{31}P NMR spectroscopic features of both products indicate the presence of zwitterionic $\text{Si}=\text{P}$ bonds which is also in accordance with results by DFT calculations.

Compounds with a heteroleptic multiple bond between heavier main-group elements, in particular those between group 14 and 15 elements, have attracted considerable attention because of their unique reactivity and electronic properties, which can be attributed to the pronounced polarity of the $E_{14}-E_{15}$ multiple bonds.¹ Since the first isolable phoshasilene with a three-coordinate Si and a two-coordinate P atom reported by Bickelhaupt and co-workers in 1984,² several derivatives could be synthesized and structurally characterized containing localized and delocalized $\text{Si}=\text{P}$ bonds.³ Their rich chemistry opened new doorways to functional $\text{Si}-\text{P}$ compounds. The availability of elusive phoshasilyne species, that is, compounds with a silicon-phosphorus triple bond, would be a highly desired progression in that field with respect to the synthesis of polyfunctional silicon-phosphorus containing materials. However, the chances of success for the preparation of stable phoshasilynes seem to be much more difficult due to the high tendency of highly polarized $\text{Si}-\text{P}$ multiple bonds to undergo dimerization or even oligomerization. In fact, to the best of our knowledge, an isolable phoshasilyne is hitherto unknown.⁴ Beside the spatial protection of a $\text{Si}-\text{P}$ multiple bond by steric congestion with suitable substituents, the oligomerization of highly polarized $\text{P}-\text{Si}$ multiple bonds could be prevented additionally by taking advantage of the donor-acceptor stabilization of a $\text{Si}-\text{P}$ multiple bond.^{3d} Herein, we report the facile synthesis of the first N-heterocyclic zwitterionic phoshasilene $[\text{LSi}(\text{SiMe}_3)=\text{PSiMe}_3]$ **1** with four-coordinate silicon and of the unique 2,4-disila-1,3-diphosphacyclobuta-1,3-diene $[(\text{LSi})_2\text{P}_2]$ **3**, starting from the new N-heterocyclic bis(trimethylsilyl)phosphino silylene precursor **2**.

The starting material, bis(trimethylsilyl)phosphino silylene **2**, is facily accessible in 83% yield by phosphanylation of

Scheme 1. Synthesis of Phoshasilene **1** from N-Heterocyclic Phosphino Silylene **2**

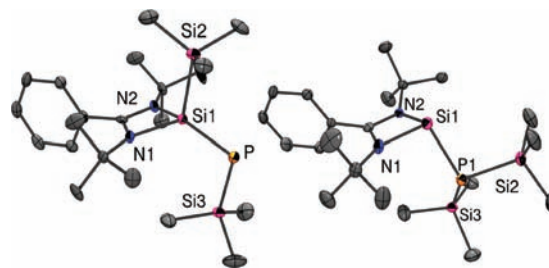
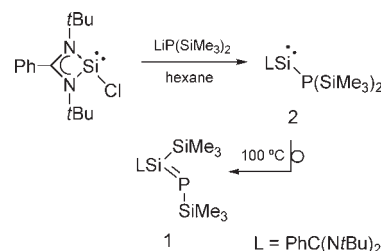


Figure 1. Molecular structures of **1** (left) and **2** (right). Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

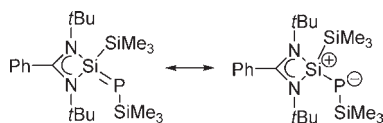
N-heterocyclic chlorosilylene LSiCl^5 with the corresponding lithium phosphide $\text{LiP}(\text{SiMe}_3)_2$ at room temperature (Scheme 1). The molecular structure of **2** has been elucidated by NMR spectroscopy and single-crystal X-ray diffraction analysis (Figure 1). The $\text{Si1}-\text{P1}$ distance of **2** (2.2838(12) Å) is slightly shorter than that of the previously reported $\text{LSiP}(\text{SiMe}_3)_2$ derivative (2.307(8) Å),⁶ and the elongated $\text{P1}-\text{Si2}$ and $\text{P1}-\text{Si3}$ single bonds in **2** [2.2264(13) and 2.2321(12) Å] reflect steric congestion within the $\text{P}(\text{SiMe}_3)_2$ subunit.

The relatively long $\text{Si}-\text{P}$ bonds of the $\text{P}(\text{SiMe}_3)_2$ subunit in close vicinity to the unsaturated ring $\text{Si}(\text{II})$ atom could enable a silyl group shift similar to the situation reported for the isomerization of silylenes into silenes via 1,2-silyl migration.⁷ For instance, Kira and co-workers have reported the formation of a cyclosilene from a cyclic dialkylsilylene via a 1,2-shift of a Me_3Si group.⁸ The latter result encouraged us to probe whether 1,2-silyl migration in **2** leads to the formation of the corresponding

Received: January 17, 2011

Published: February 15, 2011

Scheme 2. Resonance Structures of 1



phosphasilene **1**. In fact, heating solutions of **2** in toluene at 100 °C furnishes the desired phosphasilene **1** quantitatively (NMR spectroscopy), which could be isolated as air-sensitive pale yellow crystals in 87% yield (Scheme 1).

The composition of **1** has been confirmed by X-ray crystallography (Figure 1, left). The four-coordinate Si1 atom is bonded to the phosphorus atom (P1), the amidinato chelate ligand L, and the Si2 atom of the trimethylsilyl group. Compound **1** exhibits an *E*-configuration with a Si2–Si1–P–Si3 torsion angle of 177.5°. Although the Si1 atom is four-coordinate, the Si1–P1 distance of 2.095(3) Å, which is 8.4% shorter than the corresponding Si–P single bond of **2**, represents a Si=P bond; similar values were reported for phosphasilenes with three-coordinate silicon.³ However, as shown previously for related donor-stabilized Si=X compounds containing four-coordinate silicon,⁹ the additionally dative N→Si bond favors an ylide-like character of the Si1=P1 subunit of **1** (see Scheme 2 and discussion below). The Si1–N1 [1.862(2) Å] and Si1–N2 [1.849(2) Å] bond lengths of **1** are slightly shorter than those of **2** [1.877(3) and 1.882(2) Å], owing to a higher formal oxidation state of the ring Si atom in **1**.

The ²⁹Si NMR spectrum of **1** exhibits three doublet signals at $\delta = -17.5$ (Me₃Si–Si1, ²J_{SiP} = 36.3 Hz), 3.0 (Me₃Si–P1, ¹J_{SiP} = 70.5 Hz), and 40.5 ppm (Si=P, ¹J_{SiP} = 191.4 Hz), respectively. Theoretical calculations of the NMR chemical shifts [GIAO/B3LYP/6-311(d) (H, C, N, P), 6-311+G(3d) (Si)//B3LYP/6-31G(d)] of **1** (–15.3, 7.9, and 45.5) confirmed the assignment, and the calculated values agree well with the experimental data.¹⁰ Owing to the higher coordination of the ring Si atom, its δ value is shifted significantly upfield in comparison to those of phosphasilenes with three-coordinate silicon ($\delta > 200$ ppm).³ Correspondingly, the ³¹P NMR signal of $\delta = -252.9$ ppm is shifted drastically to higher field in comparison to related *P*-silyl substituted phosphasilenes with three-coordinate silicon ($\delta > -40$ ppm).³ Clearly, the drastic changes of the NMR data can only be rationalized by the N→Si donor coordination in **1** which favors a stronger polarization of the Si^{δ+}=P^{δ-} π bond and thus leads to a significant contribution of betaine (ylide-like) structures to its electronic ground state (Scheme 2). The UV–vis spectrum of **1** in hexane reveals an absorption maximum at 333 nm, due to the π–π* transition of the Si=P bond, a value that is similar to those observed for other polarized phosphasilenes (331–343 nm).³⁸ In other words, both NMR and UV–vis spectroscopic data support the ylide-like resonance structures of **1**.

The successful access to phosphino silylene **2** with its potentially reactive Me₃Si (leaving) groups at phosphorus also led us to investigate its suitability as a precursor for a phosphasilene with a Si–P triple bond.¹¹ Because of the labile nature of the P–SiMe₃ bonds in **2**, the compound was exposed to dichlorotriphenylphosphorane, Cl₂PPh₃, as a promising smooth oxidation reagent for desilylation with the intention to produce the desired phosphasilene along with Me₃SiCl and PPh₃. To our surprise, the reaction of **2** with 1 molar equiv of Cl₂PPh₃ in toluene at room temperature leads to the formation of the unique compound **3**

Scheme 3. Synthesis of 3

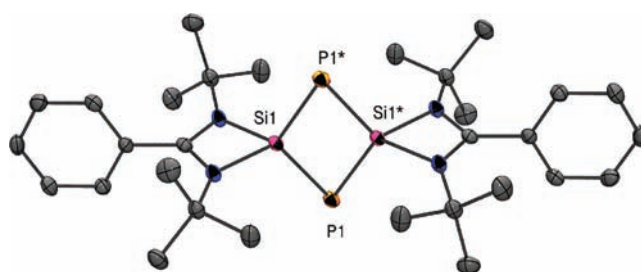
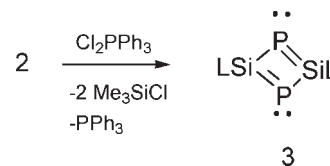


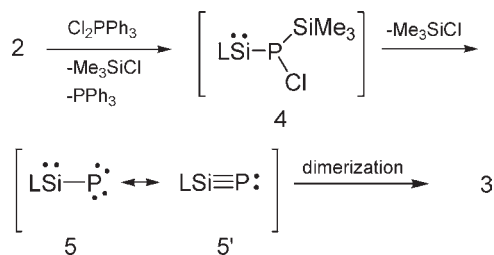
Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

which could be isolated as yellow crystals in 72% yield (Scheme 3). Compound **3** represents a head-to-tail dimer of the desired phosphasilene and was fully characterized by multinuclear NMR spectroscopy (see Supporting Information) and a single-crystal X-ray analysis. The ²⁹Si NMR spectrum of **3** shows a triplet resonance at $\delta = 26.5$ ppm (¹J_{SiP} = 99.8 Hz) which indicates the presence of two P atoms bonded to silicon. The ³¹P NMR spectrum exhibits a singlet at $\delta = -164.9$ ppm which is more deshielded (ca. 90 ppm) than that in **2** and reflects the four-membered ring structure of **3** with two polarized Si–P π bonds.

An X-ray crystal structure analysis confirmed that **3** is a 2,4-disila-1,3-diphosphacyclobuta-1,3-diene (Figure 2). The Si₂P₂ core in **3** is planar and diamond-shaped and possesses two-coordinate P atoms and four-coordinate Si atoms each with a dative N→Si bond. The Si–P bond lengths in **3** are with 2.1701(12) and 2.1717(11) Å practically equal and represent intermediate values between the Si=P bond length of **1** (2.095(3) Å) and the ring Si–P single bond length of **2** (2.2838(12) Å). The equal Si–P distances in **3** already indicate σ- and π-electron resonance stabilization within the Si₂P₂ cycle which has been confirmed by theoretical calculations (see below). Of particular interest seem the trans-annular Si···Si (2.5626(16) Å), and P···P (3.505 Å) separations in **3**: Interestingly, the Si···Si separation is shorter than the Si–Si distance of disilacyclopropene [(Ad)(*t*Bu₃Si)₂]Si₂C [2.5797(8) and 2.5991(9) Å]¹² (Ad = adamantyl) and hexa-*tert*-butyldisilane, *t*Bu₃Si–Si(*t*Bu)₃ (2.697(9) Å).¹³ The P···P distance in **3** is much larger than that for P–P bonds observed in tetrahedral P₄ (2.21 Å).¹⁴ Evidently, the peculiarly short Si···Si distance is caused by the geometric constraints of the Si1–P–Si1* and endocyclic P1–Si1–P1* angles of 72.34(4)° and 107.66(4)°, respectively, and not driven by attractive Si–Si interaction.

Although the mechanism is still unknown, we propose that **3** is formed in a multistep process as portrayed in Scheme 4. At first, we assume that one of the Si–P bonds of the P(SiMe₃)₂ subunit is cleaved by Ph₃PCl₂ to form the corresponding chloro-(silyl)phosphino silylene intermediate **4**, LSiP(Cl)(SiMe₃). Subsequent liberation of ClSiMe₃ from **4** affords a reactive

Scheme 4. Proposed Mechanism for the Formation of 3



Scheme 5. Resonance Structures of 3

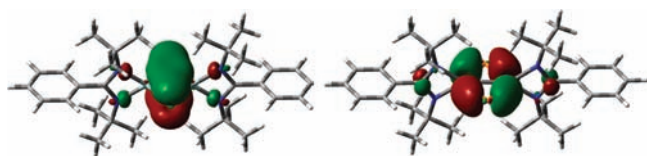
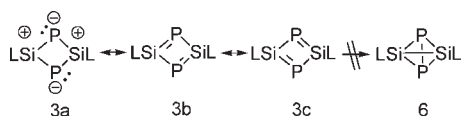


Figure 3. Molecular orbitals of **3** representing the presence of σ - and π -electron delocalization within the Si_2P_2 cycle: HOMO-2 (left) and HOMO-5 (right).

intermediate, which could represent either a silylene-phosphinidene **5** [$\text{L}(\text{Si})-\text{P}:$] or a phosphasilylene $\text{5}'$, $\text{LSi}\equiv\text{P}$. Dimerization of the latter intermediate produces the observed product **3**. A similar dimerization process has been proposed by Wiberg et al. for disilynes ($\text{Si}-\text{Si}$ triple bonds) as reactive intermediates to produce tetrasilatetrahedranes.¹⁵ This raised the question why is **3** preferred over its hypothetical Si_2P_2 -tetrahedrane isomer **6** (Scheme 5)? To answer this question we performed DFT calculations of **3** and of disiladiphosphatetrahedrane **6**. It turned out **6** is far less stable than compound **3** by $46.2 \text{ kcal mol}^{-1}$, which agrees with the experimental result. The planar structure of **3** is most likely stabilized from the dative $\text{N}\rightarrow\text{Si}$ coordination of the bulky amidinato ligands. The $\text{N}\rightarrow\text{Si}$ donor stabilization of **3** further suggests that the compound has an ylide-like electronic structure (Scheme 5) akin to the situation in **1**.

In order to clarify the electronic nature of **3**, we carried out DFT calculations at the B3LYP/6-31G(d) level using the parameters obtained by X-ray crystallographic analysis as the initial structure.¹⁰ The optimized structure closely matched the experimental data (for complete details see Supporting Information). According to the NPA charges, each Si atom in the Si_2P_2 ring bears a large positive net charge ($+1.204$), while the P atoms in the ring have somewhat smaller negative charges (-0.765) as expected. Furthermore, the HOMO-2 of **3** represents mainly the delocalized two π bonding orbitals (Figure 3, left), whereas HOMO-5 depicts a set of $\text{Si}-\text{P}$ σ bonding orbitals (Figure 3, right). Accordingly, an NBO analysis of **3** leads to a Lewis structure of the Si_2P_2 core with four occupied σ bond orbitals for the $\text{Si}-\text{P}$ bonds (1.917e for $\text{Si1}-\text{P1}$, 1.916e for $\text{Si1}-\text{P1}^*$, 1.916e for $\text{Si1}^*-\text{P1}$, and 1.918e for $\text{Si1}^*-\text{P1}^*$) as well as two

filled $\text{Si}-\text{P}$ π bond orbitals, with 1.770e and 1.770e for the $\text{Si1}-\text{P1}$ and $\text{Si1}^*-\text{P1}^*$ π bonding interaction, respectively.

The latter canonical π bond orbitals are strongly polarized toward the P atoms (87.53% at the P and 12.47% at the Si). Likewise, the WBI (Wiberg Bond Index) values of the $\text{Si}-\text{P}$ bonds (1.142 and 1.140) are higher than that of the phosphino silylene **2** (0.920) and lower than that of phosphasilylene **1** (1.552). Owing to the aforementioned betaine (ylide)-like resonance stabilization, **3** is distinctly different from cyclobuta-1,3-diene derivatives. This is supported by calculations of the nucleus independent chemical shift (NICS)¹⁶ of **3** which revealed negative values [$\text{NICS}(1) = -2.57$ and $\text{NICS}(0) = -6.01$ ppm], indicating that **3** has a somewhat aromatic character, in contrast to cyclobuta-1,3-dienes which are antiaromatic.¹⁷ Altogether, the theoretical analysis is consistent with the picture that **3** is best described by the ylide-like resonance structure **3a** with some contribution of the resonance forms **3b** and **3c** (Scheme 5). As a result, the endocyclic angle at phosphorus is smaller than that at silicon due to repulsion between the negatively charged P atoms.

In summary, we have reported the synthesis and isomerization of bis(trimethylsilyl)phosphino silylene **2** into the unprecedented zwitterionic phosphasilylene **1** via 1,2-silyl migration. Unexpectedly, precursor silylene **2** reacts with Ph_3PCl_2 to form the first 2,4-disila-1,3-diphosphacyclobuta-1,3-diene **3** via dimerization of the corresponding phosphasilylene as a reactive intermediate. Skillful modification of the latter synthetic protocol could be useful for the synthesis of elusive phosphasilylene derivatives with a $\text{Si}\equiv\text{P}$ bond. This and the investigation of the reactivity of **3** toward metals are currently in progress.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details including spectroscopic data, CIF files, and DFT computational details for compounds **1**–**3** and **6**; complete ref 10. This material is available free of charge via Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

matthias.driess@tu-berlin.de;
shigeyoshi.inoue@mailbox.tu-berlin.de

■ ACKNOWLEDGMENT

This work was financially supported by the Deutsche Forschungsgemeinschaft (DR 226/17-1). We thank the Alexander von Humboldt Foundation (S.I. and M.A.) for financial support. This work is dedicated to Prof. Siegfried Blechert on the occasion of his 65th birthday.

■ REFERENCES

- (1) For reviews, see: (a) Schoeller, W. W. In *Multiple bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; John Wiley & Sons: New York, 1990; p 5. (b) Driess, M. *Coord. Chem. Rev.* **1995**, *14*, 1287. (c) Lee, V. Ya.; Sekiguchi, A.; Escudé, J.; Ranaivonjatovo, H. *Chem. Lett.* **2010**, *39*, 312.
- (2) Smit, C. N.; Lock, F. M.; Bickelhaupt, F. *Tetrahedron. Lett.* **1984**, *25*, 3011.
- (3) Phosphasilylene: (a) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156. (b) Niecke, E.; Klein, E.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 751. (c) Driess, M. *Angew. Chem., Int. Ed. Engl.* **1991**,

30, 1022. (d) Corriu, R.; Lanneau, G.; Priou, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1130. (e) Bender, H. R. G.; Niecke, E.; Nieger, M. *J. Am. Chem. Soc.* **1993**, *115*, 3314. (f) Driess, M.; Rell, S.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1995**, 253. (g) Driess, M.; Pritzkow, H.; Rell, S.; Winkler, U. *Organometallics* **1996**, *15*, 1845. (h) Driess, M.; Block, S.; Brym, M.; Gamer, M. T. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 2293. (i) Yao, S.; Block, S.; Brym, M.; Driess, M. *Chem. Commun.* **2007**, 3844. (j) Lee, V. Ya.; Kawai, M.; Sekiguchi, A.; Ranaivonjatovo, H.; Escudié, J. *Organometallics* **2009**, *28*, 6625. (k) Li, B.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. *J. Am. Chem. Soc.* **2009**, *131*, 13222.

(4) Theoretical calculations of phosphasilyne: (a) Lai, C.-H.; Su, M.-D.; Chu, S.-Y. *Inorg. Chem.* **2002**, *41*, 1320. (b) Pietschnig, R.; Orthaber, A. *Eur. J. Inorg. Chem.* **2006**, 4570. (c) Chen, C.-H.; Su, M.-D. *Eur. J. Inorg. Chem.* **2008**, 1241. (d) Lattanzi, V.; Thorwirth, S.; Halfen, D. T.; Mück, L. A.; Ziurys, L. M.; Thaddeus, P.; Gauss, J.; McCarthy, M. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 5661.

(5) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948.

(6) So, C.-W.; Roesky, H. W.; Gurubasavaraj, P. M.; Oswald, R. B.; Gamer, M. T.; Jones, P. G.; Blaurock, S. *J. Am. Chem. Soc.* **2007**, *129*, 12049.

(7) For reviews, see: (a) Schaefer, H. F., III. *Acc. Chem. Res.* **1982**, *15*, 283. (b) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, U.K., 1989; Vol. 1, p 59. (c) Gaspar, P. P.; West, R., In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z. Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, U.K., 1998; Vol. 2, p 2463.

(8) (a) Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.* **1999**, *121*, 9722. (b) Ishida, S.; Iwamoto, T.; Kira, M. *Organometallics* **2009**, *28*, 919.

(9) Epping, J.-D.; Yao, S.; Karni, M.; Apeloig, Y.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 5443.

(10) All calculations have been done using the Gaussian 03, revision E.01.; Gaussian, Inc.; Wallingford, CT, 2004.

(11) (a) Appel, R.; Paulen, W. A. *Angew. Chem., Int. Ed.* **1981**, *20*, 869. (b) Cappello, V.; Baumgartner, J.; Dransfeld, A.; Hassler, K. *Eur. J. Inorg. Chem.* **2006**, 4589.

(12) Igarashi, M.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2007**, *129*, 12660.

(13) Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem., Int. Ed.* **1986**, *25*, 79.

(14) Cotton, F. A.; Wilkinson, G.; Murillo, C.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.

(15) (a) Wiberg, N.; Finger, C. M. M.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1054. (b) Ichinohe, M.; Toyoshima, M.; Kinjo, R.; Sekiguchi, A. *J. Am. Chem. Soc.* **2003**, *125*, 13328.

(16) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(17) (a) Longuet-Higgins, H. C.; Orgel, L. E. *J. Chem. Soc.* **1956**, 1969. (b) Fallah-Bagher-Shaidai, H.; Wannere, C.-S.; Corminboeuf, C.; Putcha, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863. (c) Stanger, A. *J. Org. Chem.* **2006**, *71*, 883. (d) Karadakov, P. B. *J. Phys. Chem. A* **2008**, *112*, 7303. (e) Athanassios, C. T. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8244.