J|A|C|S
COMMUNICATIONS

π-Conjugated Phosphasilenes Stabilized by Fused-Ring Bulky Groups

Baolin Li,[†] Tsukasa Matsuo,*[,†] Daisuke Hashizume,[‡] Hiroyuki Fueno,[§] Kazuyoshi Tanaka,[§] and Kohei Tamao*[,†]

Functional Elemento-Organic Chemistry Unit and Advanced Technology Support Division, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan, and Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

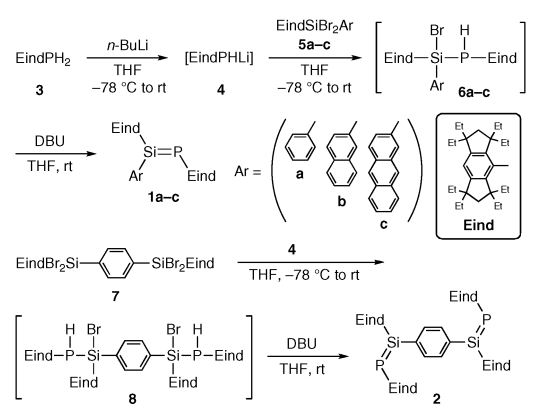
Received June 22, 2009; E-mail: matsuo@riken.jp; tamao@riken.jp

Organic π-conjugated architectures featuring multiple bonds of the heavier main group elements[1] have attracted much attention because of their potentially useful properties and unique functions.[2] For example, a number of oligomers and polymers encapsulating P=E (E = C, P)[3] and Si=Si[4] bonds have been investigated, which would open the way to new elemento−organic hybrid materials. Recently, we[5] and the Scheschkewitz group[6] independently reported the synthesis of disilene analogues of oligo(*p*-phenylenevinylene)s (Si-OPVs). In our case, the fused-ring bulky Eind groups (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl) effectively protected the reactive Si=Si fragments, thus producing the highly coplanar arrangement of the Si-OPV framework. Notably, our 1,4-bis(disilenyl)benzene derivative shows a unique fluorescence at room temperature based on the efficient π-delocalization over the skeleton.

Although various phosphasilenes have been reported by taking advantage of the steric protection with appropriate bulky substituents, their electronic properties have rarely been explored;[7,8] weak absorptions probably due to the n−π* transition have been reported only in rare cases.[8c,g] We now report the synthesis and characterization of a series of π-conjugated phosphasilenes **1a**−**c** and **2** stabilized by the Eind groups. In our case, strong π−π* absorptions have been observed due to the highly coplanar framework incorporating the Si=P unit and the aromatic ring on the silicon atom.

Phosphasilenes **1a**−**c** and **2** were synthesized starting from the bulky phosphine **3** (Scheme 1). The coupling reaction between lithium phosphide **4** and dibromosilanes **5a**−**c** and subsequent removal of HBr from phosphasilanes **6a**−**c** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), afforded phosphasilenes **1a**−**c**, as yellow to yellow-orange crystals in 25−65% yields. We have also isolated the orange crystals of 1,4-bis(phosphasilenyl)benzene **2** using 1,4-bis(dibromosilyl)benzene **7** in 29% yield, in which two Si=P bonds are connected by a phenylene linker. The formation of the Si=P bond was clearly confirmed by the ^{29}Si and ^{31}P NMR spectra. In the ^{29}Si NMR spectra of **1a**−**c**, one signal was observed at 161.7−162.1 ppm as a doublet with a $^{1}J_{\mathrm{SiP}}$ coupling constant of 171−174 Hz. The characteristic ^{31}P NMR signal was observed at 89.2−89.7 ppm. Solid-state NMR experiments have been utilized for characterization of **2**, due to its poor solubility in organic solvents. The NMR data indicated a highly symmetrical structure for **2** in the solid state, which is in agreement with the crystal structure (vide infra). The resulting phosphasilenes were found to be stable in air for months in the solid state and for a week as a dilute solution, demonstrating the efficient protection ability of the Eind groups. Each compound has high thermal stability; **1a**−**c** have melting points of >250 °C under argon atmosphere in a sealed tube.

Scheme 1



The crystal structures of **1a**−**c** and **2** were revealed by X-ray analysis, as represented by **1c** and **2** shown in Figure 1. The aryl and the arylene groups are entirely coplanar with the Si=P bond(s), having a P−Si−C−C torsion angle of 3.04(13)° (**1a**), 1.1(4)° (**1b**), 2.0(2)° (**1c**), and 0.8(2)° (**2**), respectively, which is well suited for the 2p$_\pi$−3p$_\pi$ conjugation. This coplanarity is apparently attained by the two rigid Eind groups, oriented *trans* and perpendicular with respect to the Si=P bond, as observed in the disilene case.[5] For **1b** and **1c**, the arrangement between the Si=P bond and the polycyclic aromatic substituents about the intervening Si−C bond is described as an s-*cis* conformational geometry in the crystals.[9] The Si=P bond lengths (ca. 2.09−2.10 Å) are in the range of those for typical phosphasilenes.[7,8]

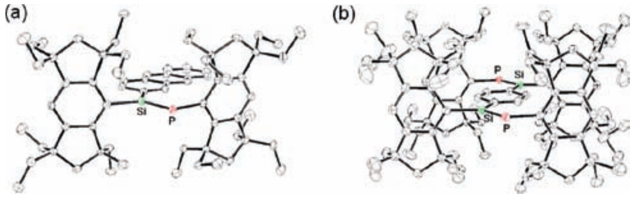


Figure 1. Molecular structures of **1c** (a) and **2** (b) (50% probability level). Hydrogen atoms are omitted for clarity.

Some photophysical and electrochemical properties are summarized as follows. (1) The UV−vis spectrum of **1a** shows an absorption peak at 385 nm ($\epsilon = 1.2 \times 10^4$), which is bathochromically shifted about 50 nm and 2-orders stronger relative to the longest wavelength absorption of the previously reported phosphasilenes.[8c,g] The introduction of the 2-naphthyl (**1b**) and the 2-anthryl (**1c**) groups to the silicon atom causes further red-shifts to 405 nm ($\epsilon = 1.1 \times 10^4$) and 430 nm (sh, $\epsilon = 1.3 \times 10^4$), respectively.

[†] RIKEN, Functional Elemento-Organic Chemistry Unit.
[‡] RIKEN, Advanced Technology Support Division.
[§] Kyoto University.

10.1021/ja9051153 CCC: \$40.75 © 2009 American Chemical Society

Moreover, the absorption maximum of **2** is observed at 449 nm ($\epsilon = 2.2 \times 10^4$), which is 64 nm red-shifted from **1a**, indicating the extension of π-conjugation over the 1,4-bis(phosphasilenyl)benzene skeleton. (2) The extended **2** shows a weak, but distinct emission in the solid state. The emission maximum of **2** is observed at 592 nm. The large Stokes shift may be attributed to the structural change from the coplanar structure in the ground state to the twisted structure in the excited state.[10] (3) The irreversible oxidation waves at +0.94 V (**1a**) and +0.97 V (**2**) as well as the quasi-reversible and the irreversible reduction waves at −2.55 V (**1a**) and −2.12 V (**2**) were observed by cyclic voltammetry, respectively, as the first experimental electrochemical studies of the phosphasilenes.

To delineate the nature of the bonding in the phosphasilenes, DFT computations at the B3LYP/6-31G** level were carried out for **1a** and **2** using the Gaussian 03 program package.[11] The optimized structures reproduced well the X-ray crystal structures. Three pertinent MOs of **1a** are shown in Figure 2. While the HOMO of **1a** is primarily represented by the $3p_\pi$(Si−P) orbital, the LUMO involves the substantial contribution of the $3p_\pi$*(Si−P)−$2p_\pi$*(phenyl) conjugation. The lower-lying HOMO-1 involves the 3n−$2p_\pi$ conjugation due to the lone pair on the phosphorus atom and the π-orbital on the Eind benzene ring; the maximum orbital interaction of these two orbitals is attained by the perpendicularly-fixed Eind group. Calculations for the π-extended **2** have demonstrated that the LUMO level is lowered [−1.552 (**1a**) and −2.108 (**2**) eV], thus keeping the HOMO levels nearly constant [−5.141 (**1a**) and −5.137 (**2**) eV], in agreement with the orbital shapes for **1a** and the electrochemical experimental results mentioned above.

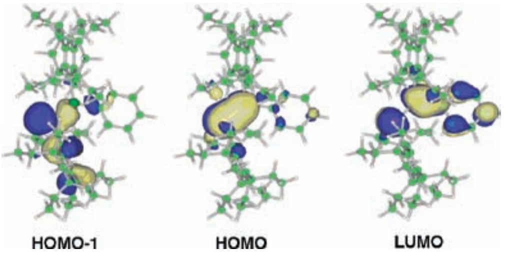


Figure 2. Selected molecular orbitals of **1a** (top view).

The wavelengths were calculated to be 364 (**1a**) and 456 (**2**) nm based on TD-DFT calculations, comparable to the observed values. The absorption at 364 nm of **1a** is assignable to the mixed version of the HOMO→LUMO (π−π*) and HOMO-1→LUMO ((n + π of Eind benzene)−π*) transitions with almost equal weighting. In contrast, the absorption at 456 nm of **2** is mainly assigned to the HOMO→LUMO (π−π*) transition.

In conclusion, we have established for the first time that the Si═P bond can conjugate with the carbon π-electron system by introduction of a variety of aryl substituents on the silicon atom and the use of the Eind groups as protecting groups. Further work to clarify the promising coordination abilities of these phosphasilenes is currently underway.

Acknowledgment. We thank the Ministry of Education, Culture, Sports, Science, and Technology of Japan for the Grant-in-Aid for Specially Promoted Research (No. 19002008). We also thank Dr. Yayoi Hongo and Mr. Takashi Nakamura (RIKEN) for their kind help with mass spectrometry and solid-state NMR spectroscopy. Numerical calculations were partly performed at the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

Supporting Information Available: Experimental details, crystallographic data of **1a**−**c** and **2** (CIF), details for calculations of **1a** and **2**, and full listing for ref 11. This material is available free of charge via Internet at http://pubs.acs.org.

References

(1) For reviews, see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (c) Lee, V. Y.; Sekiguchi, A. *Organometallics* **2004**, *23*, 2822. (d) Kira, M.; Iwamoto, T. *Adv. Organomet. Chem.* **2006**, *54*, 73. (e) Escudié, J.; Ranaivojatovo, H. *Organometallics* **2007**, *26*, 1542.

(2) For reviews, see: (a) Gates, D. P. *Top. Curr. Chem.* **2005**, *250*, 107. (b) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681.

(3) (a) Shah, S.; Concolino, T.; Rheingold, A. L.; Protasiewicz, J. D. *Inorg. Chem.* **2000**, *39*, 3860. (b) Wright, V. A.; Gates, D. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2389. (c) Smith, R. C.; Chen, X.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468. (d) Smith, R. C.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2004**, 998. (e) Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 2268. (f) Toyota, K.; Ujita, J.; Kawasaki, S.; Abe, K.; Yamada, N; Yoshifuji, M. *Tetrahedron Lett.* **2004**, 7609. (g) Nagahora, N.; Sasamori, T.; Tokitoh, N. *Chem. Lett.* **2006**, *35*, 220. (h) Wright, V. A.; Patrick, B. O.; Schneider, C.; Gates, D. P. *J. Am. Chem. Soc.* **2006**, *128*, 8836. (i) Moser, C.; Nieger, M.; Pietschnig, R. *Organometallics* **2006**, *25*, 2667. (j) Nagahora, N.; Sasamori, T.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1884.

(4) (a) Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. *Angew, Chem., Int. Ed. Engl.* **1997**, *36*, 2503. (b) Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Science* **2000**, *290*, 504. (c) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. *Nature* **2003**, *421*, 725. (d) Ichinohe, M.; Sanuki, K.; Inoue, S.; Sekiguchi, A. *Organometallics* **2004**, *23*, 3088. (e) Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumitomo, M; Nagase, S. *J. Am. Chem. Soc.* **2007**, *129*, 7766. (f) Uchiyama, K.; Nagendran, S.; Ishida, S.; Iwamoto, T.; Kira, M. *J. Am. Chem. Soc.* **2007**, *129*, 10638. (g) Sasamori, T.; Yuasa, A.; Hosoi, Y.; Furukawa, Y; Tokitoh, N. *Organometallics* **2008**, *27*, 3325. (h) Iwamoto, T.; Kobayashi, M.; Uchiyama, K.; Sasaki, S.; Nagendran, S.; Isobe, H.; Kira, M. *J. Am. Chem. Soc.* **2009**, *131*, 3156. (i) Yasuda, H.; Lee, V. Ya.; Sekiguchi, A. *J. Am. Chem. Soc.* **2009**, *131*, 6352.

(5) Fukazawa, A.; Li, Y.; Yamaguchi, S.; Tsuji, H.; Tamao, K. *J. Am. Chem. Soc.* **2007**, *129*, 14164.

(6) Bejan, I.; Scheschkewitz, D. *Angew, Chem., Int. Ed.* **2007**, *46*, 5783.

(7) For reviews, see: (a) Driess, M. *Coord. Chem. Rev.* **1995**, *145*, 1. (b) Driess, M. *Adv. Organomet. Chem.* **1996**, *39*, 193.

(8) For examples, see: (a) Smit, C. N.; Lock, F. M.; Bickelhaupt, F. *Tetrahedoron Lett.* **1984**, *25*, 3011. (b) Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156. (c) Winkel, Y. van den; Bastiaans, H. M. M.; Bickelhaupt, F. *J. Organomet. Chem.* **1991**, *405*, 183. (d) Driess, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1022. (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.; Rell, S.; Pritzkow, H.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1326. (i) Lange, D.; Klein, E.; Bender, H.; Niecke, E.; Nieger, M.; Pietschnig, R.; Schoeller, W. W.; Ranaivonjatovo, H. *Organometallics* **1998**, *17*, 2425. (j) Driess, M.; Block, S.; Brym, M.; Gamer, M. T. *Angew. Chem., Int. Ed.* **2006**, *45*, 2293. (k) Yao, S.; Block, S.; Brym, M.; Driess, M. *Chem. Commun.* **2007**, 3844. (l) Lee, V. Ya.; Kawai, M.; Sekiguchi, A.; Ranaivonjatovo, H.; Escudié, J. *Organometallics* **2009**, *28*, 4262.

(9) Rotational isomers of arylethenes, see: Mazzucato, U.; Momicchioli, F. *Chem. Rev.* **1991**, *91*, 1679.

(10) See Supporting Information for details of calculations including the excited structures of **1a** and **2**.

(11) Frisch, M. J.; et al. *Gaussian 03*, revision E.01; Gaussian Inc.: Wallingford, CT, 2004.

JA9051153