Synthesis and Properties of 9-Anthryldiphosphene

Takahiro Sasamori,[1] Akihiro Tsurusaki,[1] Noriyoshi Nagahora,[1,2] Kazunari Matsuda,[1] Yoshihiko Kanemitsu,[1]
Yasuaki Watanabe,[3] Yukio Furukawa,[3] and Norihiro Tokitoh*[1]
[1]*Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011*
[2]*Institute of Sustainability Science, Kyoto University, Gokasho, Uji, Kyoto 611-0011*
[3]*Department of Chemistry, School of Science and Engineering, Waseda University,*
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555

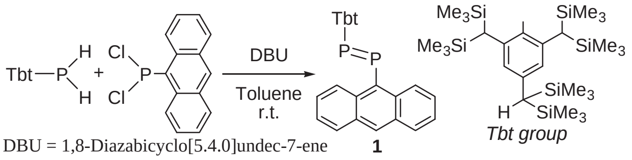
(Received September 13, 2006; CL-061054; E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp)

The first stable 9-anthryldiphosphene, TbtP=P(9-Anth) (**1**: Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, 9-Anth = 9-anthryl), was synthesized and its properties were revealed by spectroscopic and X-ray crystallographic analyses. The weak fluorescence of **1** was observed in hexane solution.

The chemistry of low-coordinated compounds of heavier group 15 elements has been one of the most attractive areas in main group element chemistry.[1,2] Recently, much attention has been focused on the unique properties of phosphaalkenes and diphosphenes from the viewpoints of material science, e.g., they are known to be more easily reduced than olefins or *azo*-compounds.[3] To date, unique properties of phosphaalkenes and diphosphenes bearing an electrochemically reactive unit such as amine,[4] *p*-phenylene,[5] ferrocene,[6] another diphosphene,[5–7] and thiophene[8] units have been reported. Particularly, Protasiewicz et al. reported the synthesis and photochemical properties of the "*phospha*-PPVs," poly(*p*-phenylenephosphaalkene)s, which exhibit unique fluorescence due to the π-conjugated P=C units.[5b–5d] However, they reported π-conjugated polymer containing P=P (instead of P=C) and *p*-phenylene units does not exhibit appreciable photoluminescence.[5d] Since a P=P double bond should possess apparently smaller HOMO–LUMO energy gap compared with those of a P=C double bond, fundamental studies on the properties of a π-electron extended system of a diphosphene should also be interesting and important for opening new chemistry of material science.

We have already reported the synthesis of kinetically stabilized diphosphenes, TbtP=PTbt (**2**) and BbtP=PBbt,[9] and revealed their chemical and physical properties together with the systematic elucidation of redox behavior of the dipnictenes (BbtE=EBbt, E = P, Sb, Bi).[10] Under these circumstances, we have designed a 9-anthryldiphosphene derivative as a candidate of a novel π-conjugated diphosphene system, since an anthryl group should be an extended π-electron system itself and possess unique fluorescent properties. We report here the synthesis and properties of the first stable 9-anthryldiphosphene, TbtP=P(9-Anth), which has a diphosphene unit tethered with a Tbt group for steric protection and a 9-anthryl group for electronic communications between the P=P π-electrons.

Condensation reaction of $TbtPH_2$ with $(9\text{-Anth})PCl_2$ in the presence of DBU as a base in toluene at rt afforded diphosphene **1** as stable red crystals in 71% yield (Scheme 1).[11] It should be noted that **1** is quite stable under inert gas conditions even in solution (C_6D_6, 80 °C for 26 h) reflecting the superior steric protecting ability of the Tbt group for preventing from oligomerization. The ^{31}P NMR of **1** showed characteristic AB quartet at δ 526 and δ 584 with $^1J_{PP} = 581$ Hz, supporting the P=P double bond character similar to those of previously reported unsymmetrically substituted diaryldiphosphenes.[1] X-ray crystallographic analysis of **1** revealed its molecular structure (Figure 1),[11] where the intermolecular π–π interaction (ca. 3.55 Å) between the anthryl moieties of **1** can be seen in the packing structure. The P=P bond length and P–P–C angles are 2.0352(16) Å, 101.86(14)° (P2–P1–C1), and 100.79(13)° (P1–P2–C15), respectively, which are within the range of the previously reported structural parameters of diaryldiphosphenes. It should be noted that the anthryl group is nearly perpendicular (81.7°) to the P=P axis probably due to the steric reason, indicating the less effective π-electron conjugation between the P=P and anthryl moieties in the solid state. In addition, optimized structure of the model compound, DmpP=P(9-Anth) (**3**, Dmp = 2,6-dimethylphenyl), shows the geometries similar to those observed for **1**. The observed vibrational frequency of the P=P bond of **1** (619 cm^{-1}) in the Raman spectrum is in good agreement with the calculated value ($\nu_{PP} = 612$ cm^{-1}).[12] The similarity between the molecular geometry observed for **1** in the solid state and that optimized for **3** in the gas phase should be supported.



DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene **1**

Scheme 1.

Electrochemical data of **1** were determined by cyclic voltammetry, showing two reversible one-electron redox couples at $E_{1/2} = -1.73$ and -2.32 V (vs Ag/Ag^+) (Figure 2a).[11]

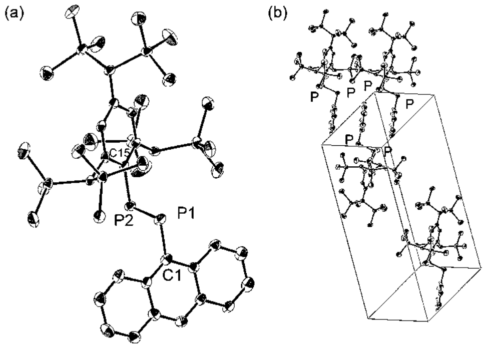


Figure 1. (a) ORTEP drawing of **1** (50% probability). Hydrogen atoms were omitted for clarity. (b) Packing structure of **1**.

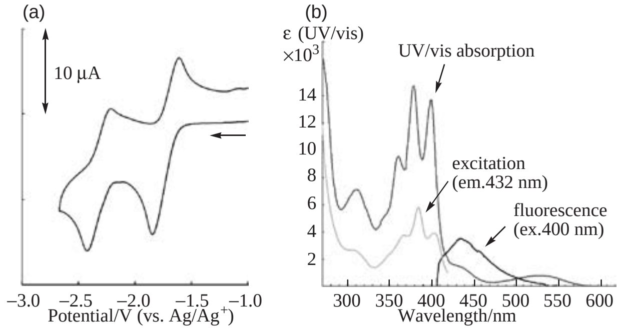


Figure 2. (a) Cyclic voltammogram of **1** (0.1 M Bu_4NBF_4 in THF, $E_{1/2}$ (Cp_2Fe/Cp_2Fe^+) $= +0.20$ V vs Ag/Ag^+). (b) UV–vis, excitation (em. 432 nm), and fluorescence (ex. 400 nm) spectra of **1** in hexane solution.

It should be worthy of note that the first reduction potential of **1** ($E_{1/2} = -1.73$) at less negative region than those of TbtP=PTbt (**2**, $E_{1/2} = -1.93$ vs Ag/Ag^+) and anthracene ($E_{1/2} = -2.42$ vs Ag/Ag^+) demonstrates the stability of the anion radical species of **1** due to the delocalization of the unpaired electron on the P=P and the anthryl moieties in solution. In addition, theoretical calculations for electron affinity (EA) of the model compounds of DmpP=P(9-Anth) (**3**) and DmpP=PDmp (**4**) show that the one-electron reduction of **3** should be more exothermic (1.27 eV) than that of **4** (1.06 eV), supporting the experimental results.[12] Whereas the optimized structure of the anion radical species of **4** shows geometry similar to that of **4** with the aryl-rings of the Dmp group perpendicularly oriented to the P=P π-orbitals, the optimized geometry of the anion radical species of **3** exhibits considerable coplanarity between the π-electron planes of the anthryl and P=P moieties in contrast to the geometry of **3**, indicating the extension of π-orbitals in [$3^{\bullet-}$].

In the UV–vis spectrum of **1** in hexane solution, the complicated pattern due to π–π^* electron transitions of the anthryl and P=P moieties was observed in the longer wavelength region than those of anthracene, indicating somewhat extended π-electron conjugation in solution (Figure 2b). The weak absorptions observed at longer wavelengths (530 and 438 nm) can be attributable to the symmetry forbidden π(9-Anth)–π^*(P=P) and n–π^*(P=P) transitions, respectively, based on the TDDFT calculations for **3**.[13] Interestingly, 9-anthryldiphosphene **1** shows weak, but apparent, fluorescence emissions ($\Phi = 1.2 \times 10^{-3}$)[14] in the range of ca. 400–500 nm ($\lambda_{max} = 432$ nm),[15] though TbtP=PTbt (**2**) exhibits no appreciable luminescence under the same conditions. The emission can be conceivable to be due to $S_n - S_0$ ($n \neq 1$) transitions, since the HOMO–LUMO and HOMO−1–LUMO transitions should be symmetry forbidden. The observed lifetime of the photoluminescence of **1** is ca. 8–10 ns,[11] which is slightly longer than that of anthracene, indicating the luminescence of **1** should be not phosphorescence but fluorescence. In addition, the quantum yield of fluorescence of **1** increases (ca. 1.3 times) at −100 °C as compared with that at room temperature. The weakness of the fluorescence of **1** should be due to quenching by the phosphorus lone pair[16] or the deformation of the structure in the excited state.

In summary, the first stable 9-anthryldiphosphene (**1**) was synthesized and its structure and physical properties were revealed. The cyclic voltammetry and UV–vis spectrum of **1** indicate the effective π-electron communication between the P=P and anthryl moieties in solution. In addition, **1** showed weak fluorescence. These results on the fundamental studies of **1** should be important for the molecular design of novel materials utilizing the characteristic properties of a P=P π-bond. Further investigations on the chemical and physical properties of **1** are currently in progress.

This work was supported by Grants-in-Aid for Scientific Research (Nos. 17GS0207 and 18750030) and the 21st Century COE on Kyoto University Alliance for Chemistry from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 For reviews, see: a) L. Weber, *Chem. Rev.* **1992**, *92*, 1839. b) P. P. Power, *Chem. Rev.* **1999**, *99*, 3463. c) N. Tokitoh, *J. Organomet. Chem.* **2000**, *611*, 217.

2 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587.

3 a) S. Shah, S. C. Burdette, S. Swavey, F. L. Urbach, J. D. Protasiewicz, *Organometallics* **1997**, *16*, 3395. b) T. L. Allen, A. C. Scheiner, H. F. Schaefer, III, *J. Phys. Chem.* **1990**, *94*, 7780. c) H. Binder, B. Riegel, G. Heckmann, M. Moscherosch, W. Kaim, H.-G. von Schnering, W. Hönle, H.-J. Flad, A. Savin, *Inorg. Chem.* **1996**, *35*, 2119. d) J. Geier, J. Harmer, H. Grützmacher, *Angew. Chem., Int. Ed.* **2004**, *43*, 4093.

4 a) K. Tsuji, S. Sasaki, M. Yoshifuji, *Tetrahedron Lett.* **1999**, *40*, 3203. b) S. Sasaki, H. Aoki, K. Sutoh, S. Hakiri, K. Tsuji, M. Yoshifuji, *Helv. Chim. Acta* **2002**, *85*, 3842.

5 a) V. A. Wright, D. P. Gates, *Angew. Chem., Int. Ed.* **2002**, *41*, 2389. b) R. C. Smith, X. Chen, J. D. Protasiewicz, *Inorg. Chem.* **2003**, *42*, 5468. c) R. C. Smith, J. D. Protasiewicz, *Eur. J. Inorg. Chem.* **2004**, 998. d) R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2004**, *126*, 2268. e) S. Shah, T. Concolino, A. L. Rheingold, J. D. Protasiewicz, *Inorg. Chem.* **2000**, *39*, 3860. f) C. Dutan, S. Shah, R. C. Smith, S. Choua, T. Berclaz, M. Geoffroy, J. D. Protasiewicz, *Inorg. Chem.* **2003**, *42*, 6241.

6 a) S. Shah, J. D. Protasiewicz, *Chem. Commun.* **1998**, 1585. b) R. Pietschnig, E. Niecke, *Organometallics* **1996**, *15*, 891. c) N. Nagahora, T. Sasamori, N. Takeda, N. Tokitoh, *Chem. Eur. J.* **2004**, *10*, 6146. d) N. Nagahora, T. Sasamori, N. Takeda, N. Tokitoh, *Organometallics* **2005**, *24*, 3074. e) N. Nagahora, T. Sasamori, N. Tokitoh, *Chem. Lett.* **2006**, *35*, 220. f) C. Moser, M. Nieger, R. Pietschnig, *Organometallics* **2006**, *25*, 2667.

7 M. Yoshifuji, N. Shinohara, K. Toyota, *Tetrahedron Lett.* **1996**, *37*, 7815.

8 a) A. Jouaiti, A. Al Badri, M. Geoffroy, G. Bernardinelli, *J. Organomet. Chem.* **1997**, *529*, 143. b) S. Shah, J. D. Protasiewicz, *Coord. Chem. Rev.* **2000**, *210*, 181. c) F. Murakami, S. Sasaki, M. Yoshifuji, *J. Am. Chem. Soc.* **2005**, *127*, 8926.

9 Bbt denotes 2,6-[$CH(SiMe_3)_2$]-4-[$C(SiMe_3)_3$]-C_6H_2: T. Sasamori, N. Takeda, N. Tokitoh, *J. Phys. Org. Chem.* **2003**, *16*, 450.

10 a) T. Sasamori, E. Mieda, N. Nagahora, N. Takeda, N. Takagi, S. Nagase, N. Tokitoh, *Chem. Lett.* **2005**, *34*, 166. b) T. Sasamori, E. Mieda, N. Nagahora, K. Sato, D. Shiomi, T. Takui, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase, N. Tokitoh, *J. Am. Chem. Soc.* **2006**, *128*, 12582.

11 Experimental procedures, compound data, lifetime of the photoluminescence, and crystal data (CCDC 619888) of **1** are described in Supporting Information.

12 B3LYP/6-31G(d) for C,H, 6-311+G(2d) for P level.

13 TD-B3LYP/6-31+G(2d,p)//opt (Ref. 12) level.

14 The quantum yield of **1** was estimated by the comparison with that of anthracene as a standard under the same conditions, see: W. H. Melhuish, *J. Phys. Chem.* **1961**, *65*, 229.

15 No fluorescence was observed by using $\lambda = 530$ nm excitation.

16 It has been reported that Ph_2(9-Anth)P and (9-Anth)$_3$P show no fluorescence, whereas the corresponding phosphine oxide exhibits intense fluorescence. a) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Organomet. Chem.* **2002**, *652*, 3. b) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Organomet. Chem.* **2002**, *646*, 277, references cited therein.

Published on the web (Advance View) November 11, 2006; doi:10.1246/cl.2006.1382