Synthesis and Redox Properties of Bis{4-[bis(4-methoxyphenyl)amino]-2,6-bis(2,4,6-triisopropylphenyl)phenyl}diphosphene

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Dedicated to Professor Dr. *Dieter Seebach* on the occasion of his 65th birthday

Bis{4-[bis(4-methoxyphenyl)amino]-2,6-bis(2,4,6-triisopropylphenyl)phenyl}diphosphene (**1**), possessing two bis(4-methoxyphenyl)amino groups as redox sites as well as electron-donating sources, was synthesized and isolated as a red solid. The cyclic voltammogram of **1** at $-78°$ consisted of three reversible redox waves corresponding to two-step oxidation of the triarylamine moieties and reduction of the diphosphene moiety. Introduction of the two amino groups also contributed to a red shift of the absorption maximum in the UV/VIS spectrum, which was responsible for the intense red color of **1**.

Introduction. – Sterically protected diaryldiphosphenes [1] generally have an intense orange color and are reduced to the corresponding radical anion at a moderate potential [2]. Recently, we have been interested in molecules that have a P=P bond as a redox center as well as chromophore, and prepared the model compound, {2,6-dimesityl-4[bis(4-methoxyphenyl)amino]phenyl}[2,4,6-tri(*tert*-butyl)phenyl]diphosphene (**2**), which has the bis(4-methoxyphenyl)amino group as a reversible redox center [3]. Diphosphene **2** was revealed to be a two-step reversible redox system at low temperature due to oxidation to the aminium radical cation and reduction to the diphosphene radical anion. In addition, a red shift of the electronic spectra was observed as compared with typical diphosphenes. However, oxidation to the aminium radical cation became irreversible at room temperature, and the 2,6-dimesityl-4-[bis(4-methoxyphenyl)amino]phenyl group did not allow isolation of a symmetrical diphosphene. To further stabilize the redox system as well as the P=P bond, we employed the 4-[bis(4-methoxyphenyl)amino]-2,6-bis(2,4,6-triisopropylphenyl)phenyl group, since the 2,6-bis(2,4,6-triisopropylphenyl)aryl group has been utilized as a sterically protecting group for diphosphenes [4] and is expected to be more sterically demanding than 2,6-dimesitylaryl groups. Herein, we report the synthesis, redox properties, and electronic spectra of bis{4-[bis(4-methoxyphenyl)amino]-2,6-bis(2,4,6-triisopropylphenyl)phenyl}diphosphene (**1**).

Results and Discussion. – The novel sterically protecting group, the 4-[bis(4-methoxyphenyl)amino]-2,6-bis(2,4,6-triisopropylphenyl)phenyl group, was synthesized as a corresponding iodobenzene derivative **5** in an analogous manner to the preparation of 2,6-dimesityl-4-[bis(4-methoxyphenyl)amino]iodobenzene [3] (*Scheme 1*). Bromoiodobenzene **3** was prepared by the reaction of 2,4,6-triisopropyl-

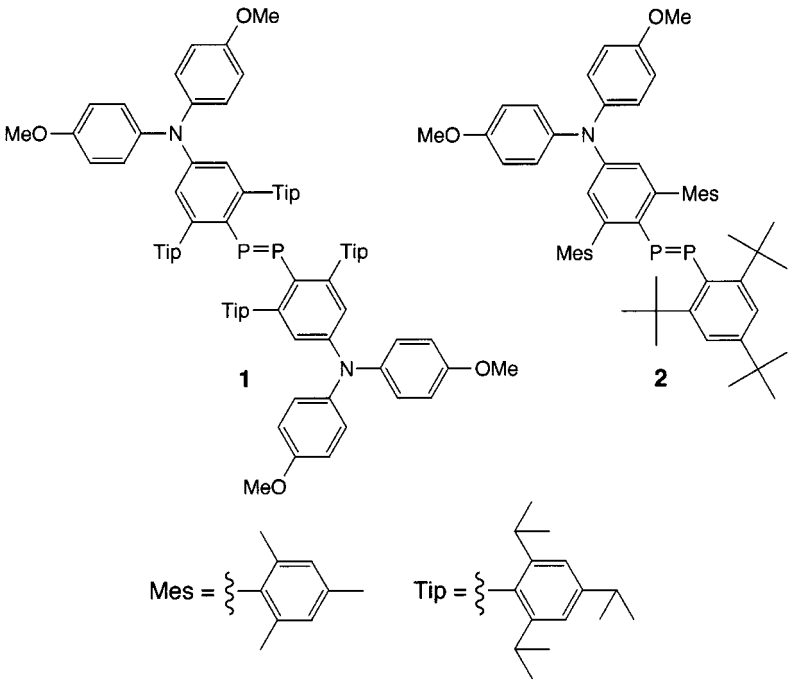
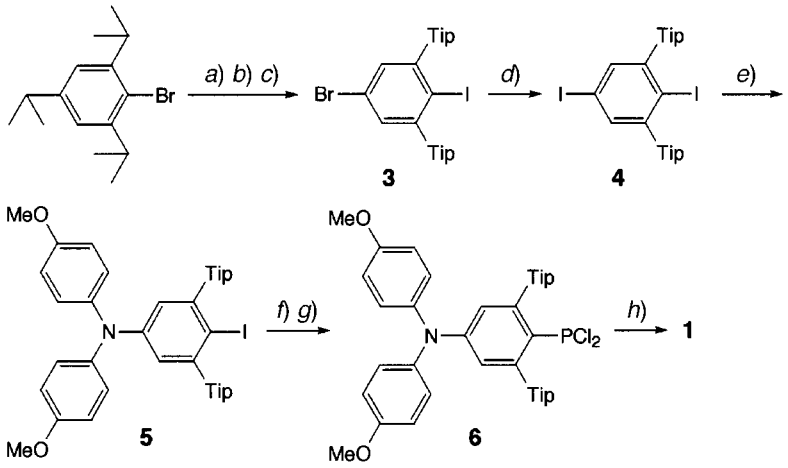


Fig. 1. *Diphosphenes possessing multiple redox sites*

phenylmagnesium bromide with 2,4,6-tribromoiodobenzene followed by quenching with I_2 [5]. Employment of the 2,4,6-triisopropylphenyl group suppressed formation of by-products, and **3** was obtained in a better yield by an easier purification process as compared with the mesityl derivative. The Br-substituent of **3** was replaced by the I-substituent [6], and the amino group was introduced by *Ullmann* coupling [7]. Synthetic intermediates **3** and **4** are expected to be useful compounds for the preparation of the sterically protecting groups carrying various functional groups. Iodobenzene **5** was lithiated with ^{t}BuLi and allowed to react with phosphorus trichloride to afford dichlorophosphine **6**. Reductive coupling of **6** by ^{t}BuLi afforded diphosphene **1** as a mixture with by-products mainly arising from over-reduction. Diphosphene **1** was obtained as red glassy solid after column chromatography (silica gel) and further purification by gel-permeation chromatography.

Electronic Spectra and Cyclic Voltammetry. Electronic properties of diphosphene **1** were studied by the UV/VIS spectrum (*Fig. 2*) and cyclic voltammetry (*Fig. 3*). Diphosphene **1** displayed an intense red color in solutions as well as in the solid state. US/VIS spectra of **1** (*Fig. 2*) exhibited a more-intense absorption at a longer wavelength ($\lambda_{max}(\log \varepsilon)$ 530 (3.83) nm) than the typical diphosphenes such as bis[2,4,6-tri(*tert*-butyl)phenyl]diphosphene (^{t}Bu$_3$C$_6$H$_2$–P=P–C$_6$H$_2$^{t}Bu$_3$; **7**) and the unsymmetrical diphosphene **2** carrying one 4-aminoaryl group. Although the 2,6-bis(2,4,6-triisopropylphenyl)aryl groups are reported to have a considerable effect on the electronic spectra of dipnictenes and to generally afford absorption maxima at

Scheme 1. *Synthesis of Diphosphene* **1**



a) Mg, THF. *b*) 2,4,6-Tribromoiodobenzene. *c*) I_2. *d*) KI, CuI, DMF. *e*) Bis(4-methoxyphenyl)amine, Cu, K_2CO_3, [18]crown-6, 1,2,4-trichlorobenzene. *f*) ^{t}BuLi, THF. *g*) PCl_3. *h*) ^{t}BuLi, THF.

longer wavelength than bis(2,6-dimesitylaryl)dipnictenes [4], the much more intense absorption of **1** at longer wavelength than bis [2,6-bis(2,4,6-triisopropylphenyl)phenyl]diphosphene (λ_{max}(log ε) 502 (2.76) nm) implies a significant effect of the 4-amino group on the electronic spectra of diaryldiphosphenes.

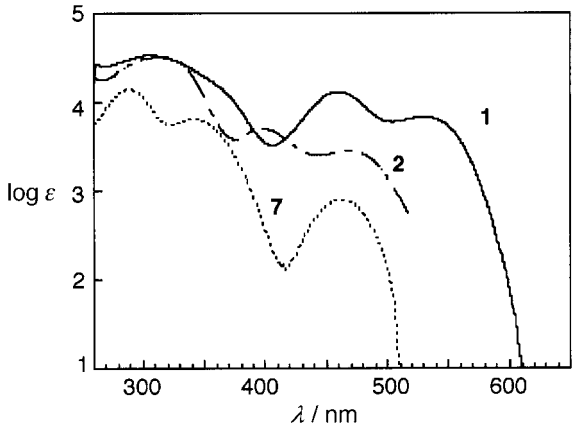


Fig. 2. *UV/VIS Spectra of* **1**, **2**, *and bis[2,4,6-tri(*tert-*butyl)phenyl]diphosphene* (**7**). Solvent: CH_2Cl_2 (**1**) or hexanes (**2** and **7**).

The cyclic voltammogram of **1** at $-78°$ consisted of three reversible redox waves corresponding to oxidation of the amino groups at $E_{1/2} = 0.46$, 0.60 V *vs.* Ag/Ag^+ and reduction of the diphosphene moitey at $E_{1/2} = -1.99$ V, respectively. Therefore, the diphosphene **1** is regarded to be a three-step reversible redox cycle from the dication diradical to the anion radical (*Scheme 2*). Interestingly, oxidation of the amino group

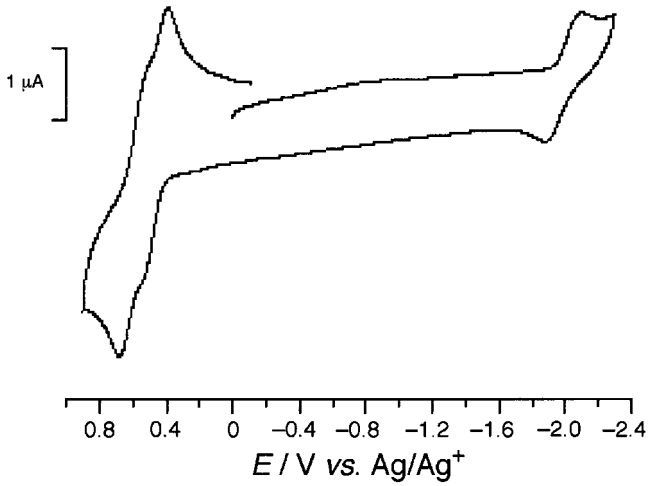
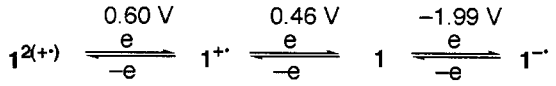


Fig. 3. *Cyclic voltammogram of* **1** *at 195 K*. Solvent, THF with 0.1M $(Bu_4N)ClO_4$ as supporting electrolyte; working electrode, glassy carbon; counter electrode; Pt wire; reference electrode, Ag/0.01M $AgNO_3$ in MeCN with 0.1M $(Bu_4N)ClO_4$ (ferrocene/ferricenium = 0.18 V); scan rate, 50 mV s^{-1}.

was observed as a two-step oxidation with a difference in oxidation potential of 0.16 V. The two amino groups weakly interact with each other through space or through the P=P bond. However, replacement of *o*-mesityl groups with the 2,4,6-triisopropylphenyl groups did not improve the stability of the oxidation of the triarylamine moieties and the oxidation of the amino group became irreversible at room temperature. The reduction potential of **1** was similar to those typical of diphosphenes, and the amino groups seem to have little effect on the reduction potential of the diphosphene moiety.

Scheme 2. *Redox Cycle of Diphosphene* **1**



Conclusions. – Diphosphene **1** was synthesized and revealed to be a three-step reversible redox system with intense red color. The cyclic voltammogram and the electronic spectrum demonstrated that the triarylamine structures played key roles as redox sites as well as as auxochromes. These findings not only deepen our understanding of the fundamental properties of the P=P bond, but also pave the way for novel functional molecules that carry the heavier main-group elements in the low-coordination states.

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Experimental Part

General. THF was distilled from sodium benzophenone ketyl (=sodium oxidodiphenylmethyl) under Ar just prior to use. All reactions were carried out under Ar. Column chromatography: *Merck* silica gel *60*. Gel-permeation chromatography: *Japan-Analytical-Industry LC-908* device, *JAIGEL-1 H* and *JAIGEL-2 H* columns, $CHCl_3$ as eluent. M.p.: *Yanagimoto MP-J3* apparatus; not corrected. Cyclic voltammetry: under N_2; *BAS-CV-50W* voltammetric analyzer. UV/VIS Spectra: *Hitachi U-3210* spectrophotometer; $\lambda_{max}(\log \varepsilon)$ in nm. ^{1}H-, ^{13}C-, and ^{31}P-NMR Spectra: *Bruker AC-200P* or *AV-400* spectrometer; δ(H) and δ(C) in ppm downfield from external $SiMe_4$, δ(P) in ppm downfield from external 85% H_3PO_4 soln.; *J* in Hz. MS: *Hitachi M-2500S* with electron impact (EI) ionization at 70 eV or *Jeol HX-110* with fast-atom-bombardment (FAB) ionization and the 3-nitrobenzyl alcohol matrix; in *m/z* (rel. %).

2,6-Bis(2,4,6-triisopropylphenyl)-4-bromoiodobenzene (**3**). To a THF soln. of 2,4,6-triisopropylphenylmagnesium bromide, prepared from 2,4,6-triisopropylbromobenzene (25.7 g, 90.8 mmol) and Mg (2.20 g, 90.8 mmol) in THF (50 ml), was added a soln. of 2,4,6-tribromoiodobenzene (10.0 g, 22.7 mmol) in THF (50 ml) within 60 min, and the mixture was stirred for 12 h. The mixture was cooled to 0° and a THF (50 ml) soln. of I_2 (17.3 g, 68.1 mmol) was added. The resultant dark brown mixture was stirred for 12 h, and excess I_2 was quenched with $NaHSO_3$ soln. The org. layer was extracted with Et_2O, the extract washed with brine, dried ($MgSO_4$), and evaporated, and the residue recrystallized from $CHCl_3$: **3** (7.97 g, 50%). Colorless powder. M.p. 236–238°. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.32 (*s*, 2 arom. H); 7.05 (*s*, 4 H, *m*-Tip); 2.95 (*sept.*, *J* = 6.86, 2 H, *p*-C*H*Me$_2$); 2.47 (*sept.*, *J* = 6.81, 4 H, *o*-C*H*Me$_2$); 1.30 (*d*, *J* = 6.91, 12 H, *p*-CH*Me*$_2$); 1.21 (*d*, *J* = 6.86, 12 H, *o*-CH*Me*$_2$); 1.12 (*d*, *J* = 6.81, 12 H, *o*-CH*Me*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): 148.88; 148.59; 145.40; 138.96; 130.70; 121.67; 120.83; 109.59; 34.16; 30.88; 24.83; 24.00; 23.32. EI-MS: 688 (100, $[M+2]^+$), 686 (94, M^+), 673 (6, $[M+2-Me]^+$), 671 (5, $[M-Me]^+$), 645 (5, $[M-CHMe_2]^+$), 643 (5, $[M+2-CHMe_2]^+$), 546 (3, $[M+2-Me-I]^+$), 544 (3, $[M-Me-I]^+$). HR-EI-MS: 686.1987 ($C_{36}H_{48}BrI^+$, M^+ calc.; 686.1984).

2,6-Bis(2,4,6-triisopropylphenyl)-1,4-diiodobenzene (**4**). A mixture of **3** (2.00 g, 2.90 mmol), CuI (8.51 g, 43.6 mmol), and KI (14.5 g, 87.3 mmol) in *N,N*-dimethylformamide (80 ml) was refluxed for 22 h and cooled to r.t. Ice-water as well as aq. ammonia was added to dissolve insoluble copper salts, and the mixture was extracted with Et_2O. The extract was dried ($MgSO_4$) and evaporated: anal. pure **4** (2.13 g, 99%): Colorless powder. M.p. 266–269°. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.52 (*s*, 2 arom. H); 7.05 (*s*, 4 H, *m*-Tip); 2.95 (*sept.*, *J* = 6.91, 2 H, *p*-C*H*Me$_2$); 2.49 (*sept.*, *J* = 6.83, 4 H, *o*-C*H*Me$_2$); 1.31 (*d*, *J* = 6.91, 12 H, *p*-CH*Me*$_2$); 1.22 (*d*, *J* = 6.87, 12 H, *o*-CH*Me*$_2$); 1.12 (*d*, *J* = 6.81, 12 H, *o*-CH*Me*$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$): 148.85; 148.71; 145.39; 138.84; 136.55; 120.82; 110.94; 93.09; 34.17; 30.89; 24.80; 24.02; 23.34. EI-MS: 734 (100, M^+), 719 (5, $[M-Me]^+$), 691 (4, $[M-CHMe_2]^+$, 480 (16, $[M-2I]^+$. HR-EI-MS: 734.1839 ($C_{36}H_{48}I_2^+$, M^+, calc. 734.1846). Anal. calc. for $C_{36}H_{48}I_2$: C 58.86, H 6.59, I 34.55; found: C 58.83, H 6.78, I 34.95.

4-[Bis(4-methoxyphenyl)amino]-2,6-bis(2,4,6-triisopropylphenyl)iodobenzene (**5**). A mixture of **4** (4.95 g, 6.73 mmol), bis(4-methoxyphenyl)amine (2.00 g, 0.97 mmol), copper powder (876 mg, 13.8 mmol), potassium carbonate (3.75 g, 27.1 mmol), and [18]crown-6 (380 mg, 1.40 mmol) in 1,2,4-trichlorobenzene (53 ml) was refluxed for 46 h. The mixture was chromatographed (SiO_2, hexane, benzene) and recrystallized from benzene: **5** (3.50 g, 61%). Colorless prisms. M.p. 267–269°. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.03 (*d*, *J* = 8.92, 4 arom. H); 6.99 (*s*, 4 H, *m*-Tip); 6.78 (*s*, 2 arom. H); 6.74 (*d*, *J* = 8.94, 4 arom. H); 3.74 (*s*, 2 MeO); 2.90 (*sept.*, *J* = 6.90, 2 H, *p*-C*H*Me$_2$); 2.63 (*sept*, *J* = 6.84, 4 H, *o*-C*H*Me$_2$); 1.26 (*d*, *J* = 6.92, 12 H, *p*-CH*Me*$_2$); 1.23 (*d*, *J* = 6.88, 12 H, *o*-CH*Me*$_2$); 1.07 (*d*, *J* = 6.85, 12 H, *o*-CH*Me*$_2$). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 155.78; 148.16; 148.10; 146.68; 145.41; 140.68; 140.23; 126.22; 120.99; 120.62; 114.70; 99.15; 55.47; 34.09; 30.87; 24.86; 24.02; 23.30. FAB-MS: 835 (100, M^+) 707 (28, $[M-I-2]^+$).

Bis{4-[bis(4-methoxyphenyl)amino]-2,6-bis(2,4,6-triisopropylphenyl)phenyl}diphosphene (**1**). To a soln. of **5** (180 mg, 0.22 mmol) in THF (6 ml), 1.54M *t*BuLi in pentane (0.34 ml, 0.52 mmol) was added at −78° and stirred for 20 min. PCl_3 (0.0564 ml, 0.65 mmol) was added, and the mixture was warmed to r.t. The mixture was evaporated and extracted with Et_2O. The extract was washed with ice-water, dried ($MgSO_4$), and evaporated: **6** as a yellow oil, which was used in the next step without further purification. ^{31}P-NMR (81 MHz, C_6D_6): 160.2.

To a soln. of crude **6** in THF (5 ml), 1.54M *t*BuLi in pentane (0.21 ml, 0.32 mmol) was added at −78°. The resulting red soln. was warmed up to r.t., diluted with hexane, and evaporated. The residue was purified by repeated column chromatography (SiO_2, hexane, benzene) and gel-permeation chromatography: **1** (17.2 mg, 11%). Red solid. M.p. 198–206° (dec.); UV/VIS (CH_2Cl_2): 306 (4.53), 460 (4.12), 530 (3.83). ^{1}H-NMR (200 MHz, C_6D_6): 7.02 (*s*, 8 H, *m*-Tip); 6.96 (*d*, *J* = 8.55, 8 arom. H); 6.85 (*s*, 4 arom. H); 6.49 (*d*, *J* = 8.55, 8 arom. H); 3.08 (*s*, 12 H, MeO); 3.00 (*sept.*, *J* = 6.70, 4 H, *p*-C*H*Me$_2$); 2.79 (*sept.*, *J* = 7.00, 8 H, *o*-C*H*Me$_2$); 1.24 (*d*, *J* =

6.90, 24 H, *p*-CH*Me*$_2$); 1.16 (*d*, *J* = 6.80, 24 H, *o*-CH*Me*$_2$); 1.05 (*d*, *J* = 6.80, 24 H, *o*-CH*Me*$_2$). ^{31}P-NMR (81 MHz, C_6D_6): 506.5. FAB-MS: 1480 (5, M^+), 696 (100, $[M/2 - C_3H_7 - 1]^+$).

REFERENCES

[1] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.* **1981**, *103*, 4587; **1982**, *104*, 6167; M. Yoshifuji, in 'Multiple Bonds and Low Coordination in Phosphorus Chemistry', Eds. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, 1990, p. 321.

[2] M. Culcasi, G. Gronchi, J. Escudie, C. Couret, L. Pujol, P. Tordo, *J. Am. Chem. Soc.* **1986**, *108*, 3130; A. J. Bard, A. H. Cowley, J. E. Kilduff, J. K. Leland, N. C. Norman, M. Pakulski, G. A. Heath, *J. Chem. Soc., Dalton Trans.* **1987**, 249.

[3] K. Tsuji, S. Sasaki, M. Yoshifuji, *Tetrahedron Lett.* **1999**, *40*, 3203.

[4] E. Urnezius, J. D. Protasiewicz, *Main Group Chemistry* **1996**, *1*, 369; S. Shah, S. C. Burdette, S. Swavey, F. L. Urbach, J. D. Protasiewicz, *Organometallics* **1997**, *16*, 3395; B. Twamley, C. D. Sofield, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1999**, *121*, 3357.

[5] C.-J. F. Du, H. Hart, K.-K. D. Ng, *J. Org. Chem.* **1986**, *51*, 3162.

[6] M. B. Goldfinger, K. B. Crawford, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 4578.

[7] S. Gauthier, J. M. J. Fréchet, *Synthesis* **1987**, 383.

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