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Synthesis and Redox Properties of a Diphosphene Carrying a Redox-Active Sterically Protecting Group

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Abstract

The 2,6-dimesityl-4-[bis(4-methoxyphenyl)amino]phenyl group was developed as a sterically protecting group carrying a reversible redox site at the 4-position and was applied to the construction of a novel redox system composed of the diphosphene and triarylamine units.

Keywords: amines; electrochemistry; phosphorus compounds; Ullmann reactions

Kinetically stabilized diphosphenes by sterically protecting groups, such as the 2,4,6-tri-*t*-butylphenyl [1] or tris(trimethylsilyl)methyl [2] group, are known to be reversibly reduced to give stable radical anions [3]. They are candidates for a component of functional molecules, such as redox sites of a multi-step redox system or spin centers of high-spin organic molecules. Recently, we [4] and others [5] have applied the 2,6-dimesitylaryl sterically protecting groups, which can be easily synthesized by the Hart reaction [6], to the stabilization of diphosphene and phosphaarsene. On the other hand, these compounds have already been used as protecting groups for low coordinated main-group elements as well as transition metal compounds as demonstrated by Power *et al.* [7]. As compared with the 2,4,6-tri-*t*-butylphenyl group, the 2,6-dimesitylaryl groups are assumed to have comparable bulkiness and less reactivity at the *ortho* substituent, judging from the reactivity of the corresponding phosphorus and arsenic compounds [4]. Furthermore, it should be mentioned that, from the synthetic viewpoint, the advantage of their employment would be the ease of introduction of functional groups at the 4-position of the aryl moieties. In this communication, we report the development of the 2,6-dimesityl-4-[bis(4-methoxyphenyl)amino]phenyl group, which is regarded to act not only as a sterically protecting group but also as a reversible redox site, and the application to the construction of a novel redox system composed of the diphosphene and triarylamine units.

Preparation of the 2,6-dimesityl-4-[bis(4-methoxyphenyl)amino]phenyl group is shown in Scheme 1. The Hart reaction [6] of 2,4,6-tribromoiodobenzene [8] with the mesityl Grignard

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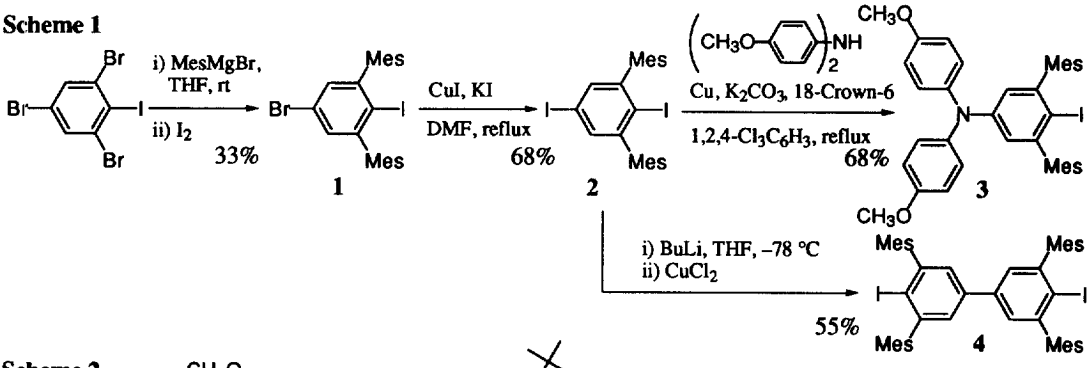
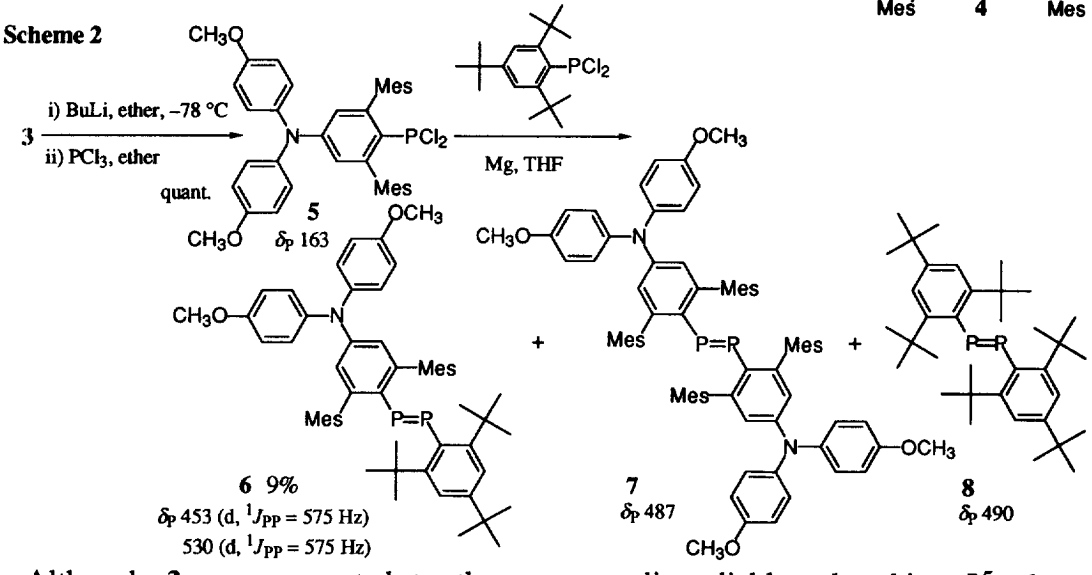
reagent, followed by the reaction with iodine, afforded bromoiodobenzene **1**[1], though the yield of **1** was suppressed by unknown side reactions. The bromine atom at the 4-position of **1** was then replaced with iodine by refluxing in dimethylformamide in the presence of large excess of both CuI and KI [9]. Diiodobenzene **2**[2] is a synthetic key intermediate for introducing a functional group at the 4-position of the sterically protected position, since iodine at the less hindered position can be selectively replaced with several functional groups by a variety of methods. For example, lithiation of **2** with butyllithium at –78 °C in THF, followed by quenching with water, afforded 2,6-dimesityliodobenzene [6] almost quantitatively and the lithiation of **2** followed by addition of $CuCl_2$ gave the novel sterically protecting group **4**[3] in 55%, where two hindered sites are linked by the 4,4'-biphenylene bridge. The Ullmann coupling also selectively proceeded at the less hindered position, and the copper-mediated coupling of **2** with bis(4-methoxyphenyl)amine in the presence of 18-crown-6 [10] afforded aminoiodobenzene **3**[4] as a stable colorless solid.

Scheme 1



Scheme 2



Although **3** was converted to the corresponding dichlorophosphine **5**[5] almost quantitatively by the conventional method [1], reductive coupling of **5** to diphosphene **7** was not successful in the presence of magnesium metal [1] probably due to the low reactivity of **5**. However, the reaction of a mixture of **5** and 0.7 molar amount of dichloro(2,4,6-tri-*t*-

butylphenyl)phosphine [1] with magnesium afforded a mixture of unsymmetrical diphosphene **6**,[6] symmetrical diphosphene **7**,[7] and **8** [1] in a ratio of 1:0.6:0.8 based on the ^{31}P NMR spectrum among other products (Scheme 2). Only **6** was isolated in the pure state from the mixture by repeated column chromatography on silica gel (hexane / benzene = 1 / 1 with a small amount of triethylamine) and GPC (Jaigel 1H + 2H / chloroform). Symmetrical diphosphene **7** could not completetly be separated from a by-product such as bis[2,6-dimesityl-4-{bis(4-methoxyphenyl)amino}phenyl]diphosphane.

Diphosphene **6** was characterized by a ^{31}P NMR signal at low field and a large coupling constant $^1J_{PP}$, typical values for unsymmetrical diphosphenes [11] [δ_P 453 (d, $^1J_{PP}$ = 575 Hz), 530 (d, $^1J_{PP}$ = 575 Hz)]. As expected, **6** gave a two-step reversible cyclic voltammogram at –78 °C (Figure 1), where the oxidation of the nitrogen and reduction of the phosphorus-phosphorus double bond appeared at $E_{1/2}$ = 0.49 and –2.19 V *vs.* Ag / Ag^+, respectively, although the redox wave at $E_{1/2}$ = 0.49 V became irreversible at 293 K. The redox potential of the phosphorus-phosphorus double bond ($E_{1/2}$ = –2.19 V) was nearly equal to those of **8** ($E_{1/2}$ = –2.16 V) [3] and bis(2,6-dimesityl-4-methylphenyl)diphosphene ($E_{1/2}$ = –2.16 V) [4, 5], measured under the identical conditions. The orthogonal alignment of the π-electron systems of the aromatic ring and the phosphorus–phosphorus double bond in diphosphenes carrying the aromatic bulky substituents [1] might cause the amino group at the 4-position to have only a slight effect on the redox properties of such diphosphenes. On the other hand, introduction of the phosphorus-phosphorus double bond at the 4-position of the amino group destabilized the corresponding radical cation. The effect of the amino group was most clearly demonstrated by the UV-Vis spectrum (Figure 2), where introduction of the amino group caused a red shift of the π-π* and n-π* transition [λ_{max} (logε) in hexane: **6**; 398 (3.70), 468 (3.45): **8** [1]; 343 (3.81), 463 (2.90)]. A hexane solution, mainly composed of **7**, clearly showed a red color with λ_{max} as 446 and 504sh, which suggested a further red-shift due to the second amino group. Thus, the color of the diphosphenes could be modified in a similar manner as azo dyes.

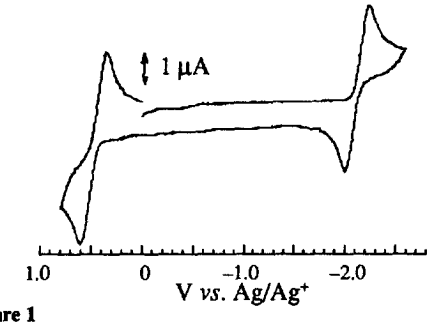


Figure 1
Cyclic voltammogram of **6** at –78 °C. 1 mmol L^{-1} in THF with 0.1 mol L^{-1} *n*-Bu_4NClO_4. Working electrode; grassy carbon, counter electrode; Pt, reference electrode; Ag / 0.01 mol L^{-1} $AgNO_3$ / 0.1 mol L^{-1} *n*-Bu_4NClO_4 / CH_3CN. Scan rate; 30 mV sec^{-1}.

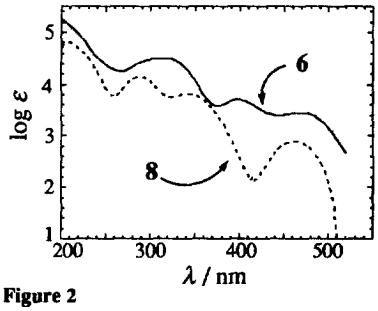


Figure 2
UV-Vis spectra of diphosphenes **6** and **8** in hexane.

In conclusion, we have developed a novel sterically protecting group possessing a reversible redox site at the 4-position of the protected functional group, and constructed the functional diphosphene possessing unique redox as well as optical properties. The

fundamental molecular design and synthetic strategy shown in this work can be applied to a variety of low-coordinated functional groups and pave the way to a new class of multifunctional molecules.

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[1] **1**: Colorless prisms (hexane), mp 107.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.00 (12H, s), 2.35 (6H, s), 6.96 (4H, br.s), and 7.26 (2H, s); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 20.2, 21.2, 106.3, 122.8, 128.1, 130.5, 135.1, 137.6, 140.7, and 149.0. Found: C, 55.43; H, 4.78; I, 24.58%. Calcd for $C_{24}H_{24}BrI$: C, 55.51; H, 4.66; I, 24.44%.

[2] **2**: Colorless needles (hexane-benzene), mp 250.0–251.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.99 (12H, s), 2.34 (6H, s), 6.95 (4H, br.s), and 7.43 (2H, s); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 20.3, 21.3, 94.5, 107.8, 128.2, 135.2, 136.4, 137.6, 140.6, and 149.2. Found: C, 50.89; H, 4.16; I, 44.84%. Calcd for $C_{24}H_{24}I_2$: C, 50.91; H, 4.27; I, 44.82%.

[3] **4**: Colorless needles (hexane-benzene), mp > 300.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.03 (24H, s), 2.35 (12H, s), 6.97 (8H, s), and 7.32 (4H, s); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 20.4, 21.2, 106.9, 125.9, 128.1, 135.3, 137.3, 140.2, 141.7, and 147.8; MS (FAB) *m/z* (rel intensity) 879 (M^++1; 56%), 878 (M^+; 48), 752 (M^+–126; 100), and 626 (M^+–252; 69).

[4] **3**: Pale yellow solid, mp 141.0–142.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.07 (12H, s), 2.34 (6H, s), 3.79 (6H, s), 6.74 (2H, s), 6.82 (4H, dm, J = 9.0 Hz), 6.95 (4H, br.s), and 7.10 (4H, dm, J = 9.0 Hz); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 20.2, 21.2, 55.4, 95.2, 114.8, 119.9, 126.5, 127.9, 135.3, 137.0, 140.5, 142.1, 147.1, 149.5, and 156.0; MS (EI, 70 eV) *m/z* (rel intensity) 667 (M^+; 100%), 652 (M^+–15; 8), and 540 (M^+–127; 6). Found: *m/z* 667.1948. Calcd for $C_{38}H_{38}INO_2$: M, 667.1948.

[5] **5**: Brownish yellow oil; ^{1}H NMR (200 MHz, C_6D_6) δ = 2.09 (6H, s), 2.27 (12H, s), 3.11 (6H, s), 6.56 (4H, d, J = 8.9 Hz), 6.74 (4H, s), 6.90 (2H, d, J = 2.9 Hz), and 7.02 (4H, d, J = 8.8 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ = 163 (s); MS (EI, 70 eV) *m/z* (rel intensity) 643 (M^++2; 16%), 642 (M^++1; 10), 641 (M^+; 22), 626 (M^+–15; 5), 571 (M^+–70; 4), 542 (M^+–99; 24), 541 (M^+–100; 48), and 526 (M^+–115; 8).

[6] **6**: Reddish-orange solid (hexane-benzene), mp 203.5–204.5 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.01 (18H, s), 1.27 (9H, s), 2.14 (12H, s), 2.26 (6H, s), 3.78 (6H, s), 6.67 (2H, s), 6.79 (4H, br.s), 6.80 (4H, dm, J = 8.9 Hz), 7.09 (4H, dm, J = 9.0 Hz), and 7.25 (2H, s); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 21.0, 21.3, 31.3, 33.8, 34.6, 38.1, 55.4, 114.7, 121.3, 122.0, 126.4, 128.4, 132.6 (d, J_{PC} = 45 Hz), 135.5, 136.5, 137.6 (d, J_{PC} = 64 Hz), 139.4, 140.7, 144.9, 148.9, 149.5, 153.3, and 155.8; ^{31}P NMR (81 MHz, $CDCl_3$) δ = 453 (d, J_{PP} = 575 Hz) and 530 (d, J_{PP} = 575 Hz); UV-Vis (hexane) λ (log ε) 315 (4.51), 398 (3.70), and 468 (3.45) nm; MS (EI, 70 eV) *m/z* (rel intensity) 848 (M^++1; 20%), 847 (M^+; 35), 791 (M^+–56; 10), 790 (M^+–57; 10), 602 (M^+–245; 8), 572 (M^+–275; 100), 556 (M^+–291; 29), 539 (M^+–308; 7), and 276 (7).

[7] **7**: Red solid; ^{1}H NMR (200 MHz, C_6D_6) δ = 2.00 (24H, s), 2.18 (12H, s), 3.15 (12H, s), 6.55 (8H, dm, J = 9.0 Hz), 6.70 (8H, s), 6.90 (4H, s), and 7.02 (8H, dm, J = 9.0 Hz); ^{31}P NMR (81 MHz, C_6D_6) δ = 487 (s); MS (FAB) *m/z* (rel intensity) 1143 (M^++1; 14%), 1142 (M^+; 15), 602 (M^+–540; 35), and 572 (M^+–570; 100).