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Synthesis and Redox Properties of Sterically Hindered *meta*- and *para*-Aminophosphinobenzenes

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Abstract: *Meta*- and *para*- aminophosphinobenzenes composed of *para* substituted triarylamine and all *ortho* methylated triarylphosphine moieties were synthesized and their redox properties were investigated by cyclic voltammetry.
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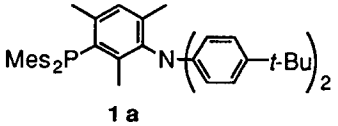
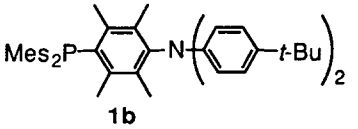
Para- and *meta*-phenylenediamines are one of the well-known skeletons for multi-step reversible redox systems and high-spin organic molecules, respectively, because charge delocalization stabilizes the radical cation and dication of *para*-phenylenediamine,[1] and topological symmetry and spin polarization of di(radical cation) of *meta*-phenylenediamine meet the prerequisite for intramolecular spin alignment.[2] Although *meta*- and *para*-phenylenediphosphines themselves have already been synthesized,[3] the phosphorus analogs of phenylenediamines have never been regarded as a redox system as above, because triarylphosphines are usually oxidized irreversibly. Trimesitylphosphine (**2**) is known as one of the most sterically hindered phosphines with unusual structure and properties. The phosphine **2** possesses very large C–P–C angles (average 109.7°)[4] as compared with those of triphenylphosphine (average 103.0°)[5] and gives a reversible redox system with a very low oxidation potential and a stable cation radical like *para* substituted triarylamines.[6] Thus, we considered that the trimesitylphosphine-type moiety was the most suitable and the only structure to evaluate to what degree extension of the well-known strategy of molecular design to heavier main-group elements is possible. In this communication, we would like to report on the synthesis and redox properties of *meta*- and *para*-aminophosphinobenzenes, **1a** and **1b**, which are composed of two expected reversible redox sites: all *ortho* methylated triarylphosphine and *para* substituted triarylamine moieties.



1a

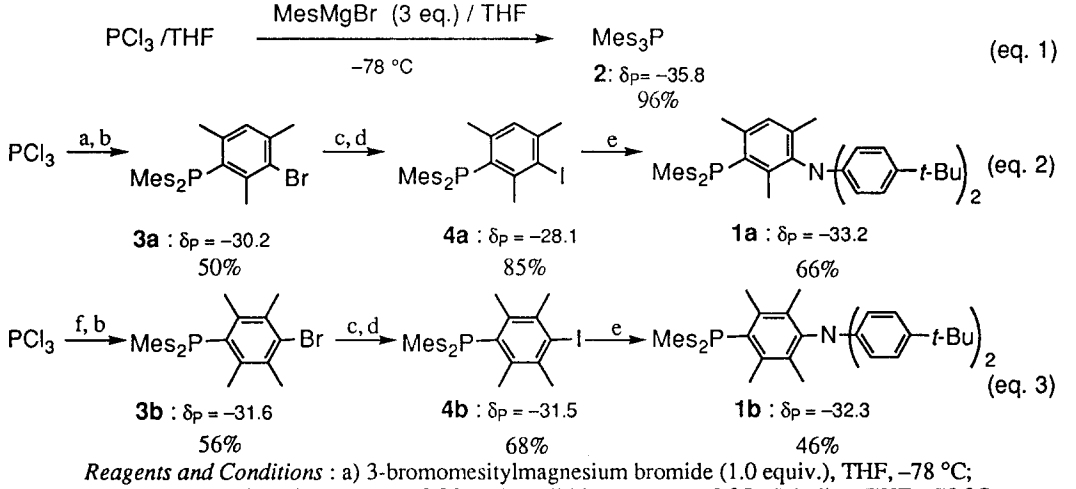


1b

2

Since introduction of the phosphorus atom might be a key step in the synthesis of the title compounds, synthesis of trimesitylphosphine (**2**) was optimized at first. Triarylphoshine is usually synthesized by the reaction of aryl Grignard reagents or aryl-lithium reagents with a phosphorus substrate such as phosphorus trichloride or trimethyl phosphite. The reported method,[7] the addition of phosphorus trichloride to a solution of the mesityl Grignard reagent at 0 °C, afforded trimesitylphosphine in 55% yield, if the Grignard reagent was

concentrated to a certain degree. However, the method was not applicable to further modification because the yield of **2** was strongly dependent on the reaction conditions such as concentration, and we could not suppress the formation of tetramesityldiphosphane (δ_P = –30.3). On the other hand, the addition of the mesityl Grignard reagent to a THF solution of phosphorus trichloride at –78 °C gave trimesitylphosphine in almost quantitative yield without any by-products (eq. 1). The more hindered 2,4,6-triethylphenyl Grignard reagent, however, gave tetrakis(2,4,6-triethylphenyl)diphosphane (δ_P = -32.4) almost quantitatively; therefore, trimesitylphosphine is considered to be one of the most hindered phosphines attainable by this method. Thus, (bromoaryl)dimesitylphosphines **3a** and **3b** were obtained in moderate yields by adding the third 2,6-dimethylaryl Grignard reagent to a solution of chlorodimesityl- or bromodimesitylphosphine at –78 °C. The bromides **3a** and **3b** were converted to the corresponding iodides **4a** and **4b** by lithiation followed by quenching with iodine. The Ullmann coupling[8] of the iodides **4a** and **4b** with bis(4-*t*-butylphenyl)amine afforded aminophosphinobenzenes **1a** and **1b**[9] as a stable solid in 66 and 46% yields, respectively, after chromatographic separation over silica gel using hexane-dichloromethane (7/1) with a small amount of triethylamine as eluent (eqs. 2, 3).[10]



Reagents and Conditions : a) 3-bromomesitylmagnesium bromide (1.0 equiv.), THF, –78 °C; b) MesMgBr (2.0 equiv.), THF, –78 °C; c) butyllithium, THF, –78 °C; d) iodine, THF, –78 °C; e) bis(4-*t*-butylphenyl)amine, Cu, K_2CO_3, 18-crown-6, *o*-dichlorobenzene, reflux (120 h); f) 4-bromodurylmagnesium bromide (1.0 equiv.), THF, –78 °C

The redox properties of **1a** and **1b** were investigated by cyclic voltammetry at 20 and –78 °C. The cyclic voltammograms of **1a** and **1b** at –78 °C along with trimesitylphosphine and bis(4-*t*-butylphenyl)mesitylamine are shown in Figure 1.[11] The cyclic voltammogram of **1a** at –78 °C was composed of the first and the second quasi-reversible waves (E_{ox} = 0.438 and 0.660 V, respectively), which became less reversible at 20 °C, followed by the third irreversible oxidation wave at 0.780 V. The first and the second redox waves could be attributed to the oxidation of the triarylphosphine and triarylamine moieties, respectively, by taking oxidation potentials of trimesitylphosphine and bis(4-*t*-butylphenyl)mesitylamine ($E_{1/2}$ = 0.379 and 0.548 V *vs.* Ag/Ag^+, respectively) into account. Probably, after the second oxidation, decomposition of the resultant di(radical cation) would cause generation of the re-oxidizable species. As a plausible explanation, we assume that the

coupling reaction at *ortho* positions of the nitrogen followed by deprotonation occurs to give a carbazole as reported in the electrochemical oxidation of triarylamines[12] and *m*-phenylenediamines,[2] although no decomposition products have been isolated. The redox behavior of **1a** is very similar and comparable to that of *m*-phenylenediamines which also give two-step reversible or quasi-reversible redox waves followed by the irreversible oxidation wave. The all *ortho* methylated triarylphosphine structure in **1a** could serve as a redox center comparable to *para* substituted triarylamine structures. On the other hand, **1b** did not afford two-step reversible redox waves, which are generally observed in *p*-phenylenediamines, even at –78 °C. *p*-Aminophosphinobenzene **1b** might be initially oxidized at 0.410 V to a cation radical which could be assigned as phosphorus-centered radical $\mathbf{1b}^{+\bullet}$. The second redox wave (0.162 V), which was not observed in the faster scanning (500 mV/sec), was ascribed to the oxidation of neutral amines generated by the decomposition of a phosphorus centered radical and the third oxidation wave (0.793 V) was assigned to the oxidation to the dication. The larger reduction current of the third wave than the first suggests that the decomposition mainly occurs at the phosphorus atom. Oxidation of **1b** afforded unstable radical cations in spite of *para* phenylene linkage between two reversible redox sites. A *para* amino substituent rather seemed to destabilize the phosphorus-centered radical cation. Less effective conjugation due to a long phosphorus-carbon bond, the more localized character of the phosphorus radical cation, and torsion between π-orbitals caused by *ortho* methyl substituents would be responsible for the redox behavior of **1b** thus observed.

Substitution of the bromine atom of the phosphines **3a** and **3b** with other redox active substituents to construct stable redox systems is in progress.

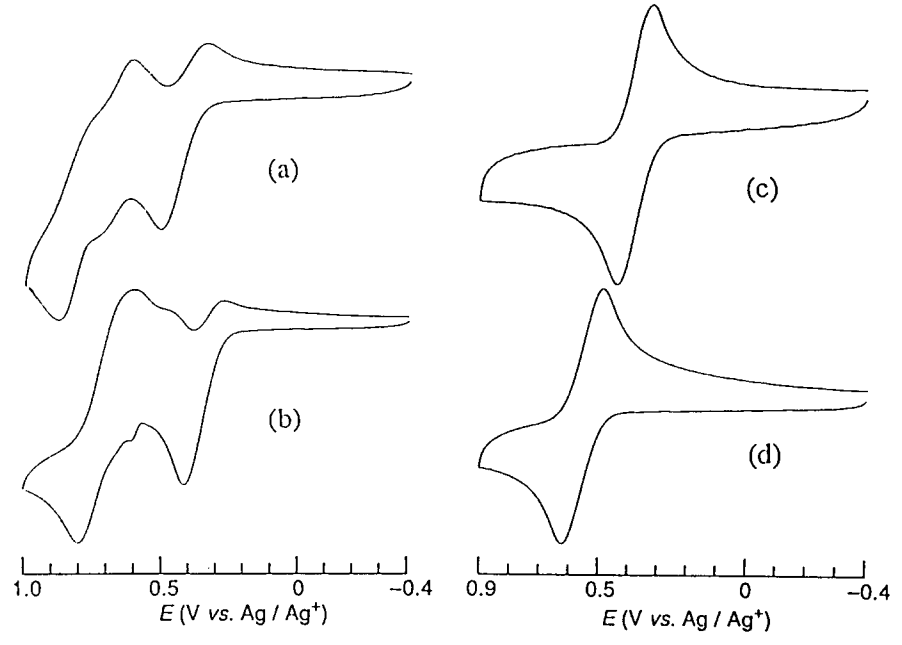


Figure 1. Cyclic voltammograms of (a) **1a** and (b) **1b** at –78 °C, and (c) trimesitylphosphine and (d) bis(4-*t*-butylphenyl)mesitylamine at r.t. Solvent: dichloromethane with 0.1 M *n*-Bu_4NClO_4 as a support electrolyte. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: Ag / 0.01 N $AgNO_3$ in acetonitlile with 0.1 M *n*-Bu_4NClO_4 ($E_{1/2}$(Ferrocene/Ferricinium) = 0.172 V). Scan rate: 50 mV/sec.

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9. **1a**: Colorless solid; mp 264.0–266.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.15 (4H, md, *J* = 8.8 Hz, arom.-3",5"), 6.90 (1H, d, *J* = 3.7 Hz, arom.-5), 6.83 (4H, md, *J* = 8.8 Hz, arom.-2",6"), 6.74 (4H, d, *J* = 3.1 Hz, arom.-3',5'), 2.22 (6H, s, Me-4'), 2.11 (3H, s, Me-4), 2.06 (12H, s, Me-2',6'), 1.97 (3H, s, Me-6), 1.79 (3H, s, Me-2), 1.28 (18H, s, *t*-Bu); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 143.36 (s, arom.-1"), 142.83 (s, arom.-4"), 142.60 (d, *J* = 14.1 Hz, arom.-2',6'), 142.39 (d, *J* = 17.7 Hz, arom.-2), 141.53 (d, *J* =6.1 Hz, arom.-1), 141.36 (d, *J* = 18.3 Hz, arom.-4), 137.91 (s, arom.-6), 137.43 (s, arom.-4'), 134.86 (d, *J* = 19.1 Hz, arom.-3), 131.64 (d, *J* = 5.1 Hz, arom.-5), 131.30 (d, *J* = 18.1 Hz, arom.-1'), 129.63 (d, *J* = 3.5 Hz, arom.-3',5'), 125.54 (s, arom.-3",5"), 118.62 (s, arom.-2",6"), 33.99 (s, $\underline{C}(CH_3)_3$), 31.40 (s, $C(\underline{C}H_3)_3$), 22.68 (d, *J* = 16.4 Hz, Me-2', 6'), 22.60 (d, *J* = 18.4 Hz, Me-4), 20.86 (s, Me-4'), 18.76 (s, Me-6), 18.08 (d, *J* = 16.0 Hz, Me-2); ^{31}P NMR (81 MHz, $CDCl_3$) δ = –33.2 (s); LRMS (70 eV, EI) *m/z* (rel. intensity) 667 (M^+; 100), 652 (M^+–CH_3; 50), 399 (M^+–Mes_2P+1; 6), 57 (*t*-Bu; 7). **1b**: Colorless solid; mp 111.0–113.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.18 (4H, d, *J* = 8.8 Hz, arom.-3",5"), 6.87 (4H, d, *J* = 8.8 Hz, arom.-2",6"), 6.81 (4H, d, *J* =2.6 Hz, arom.-3',5'), 2.27 (6H, s, Me-4'), 2.09 (18H, brs, Me-3, 5 and 2',6'), 1.93 (6H, s, Me-2,6), 1.29 (18H, s, *t*-Bu); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 143.59 (s, arom.-1"), 142.86 (s, arom.-1), 142.73 (s, arom.-4"), 142.34 (d, *J* =18.6 Hz, arom.-2',6'), 140.27 (d, *J* = 17.8 Hz, arom.-3,5), 137.37 (s, arom.-4'), 135.75 (d, *J* = 17.2 Hz, arom.-4), 134.26 (d, *J* = 4.1 Hz, arom.-2,6), 132.20 (d, *J* = 18.9 Hz, arom.-1'), 129.75 (s, arom.-3',5'), 125.65 (s, arom.-3",5"), 118.59 (s, arom. -2",6"), 34.05 (s, $\underline{C}(CH_3)_3$), 31.46 (s, $C(\underline{C}H_3)_3$), 22.79 (d, *J*= 16.1 Hz, Me-2',6'), 20.93 (s, Me-4'), 19.88 (d, *J* = 19.1 Hz, Me-3,5), 15.77 (s, Me-2,6); ^{31}P NMR (81 MHz, $CDCl_3$) δ = –32.3 (s); LRMS (70 eV, EI) *m/z* (rel. intensity) 681 (M^+; 100), 666 (M^+–CH_3; 51), 413 (M^+–Mes_2P+1; 10), 57 (*t*-Bu; 3).
10. The aminophosphinobenzenes **1a** and **1b** were oxidized to the corresponding phosphine oxides **5a** (δ_P = 27.7) and **5b** (δ_P = 28.9), respectively, during chromatographic purification without triethylamine.
11. The scannings upto 0.6 V for **1a** and **1b** gave almost reversible waves with $E_{1/2}$ = 0.397 and 0.350 V, respectively.
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