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Synthesis and Redox Properties of Crowded Triarylphosphines Carrying a Nitroxide Radical and Related Compounds

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Crowded triarylphosphines carrying a nitroxide radical were synthesized to investigate intramolecular interaction between the crowded triarylphosphine redox centers and a neutral radical. A crowded triarylphosphine carrying a bromoaryl group was developed as a key synthetic intermediate. Lithiation of the (bromoaryl)phosphine, followed by reaction with 2-methyl-2-nitrosopropane, afforded a crowded triarylphosphine carrying a nitroxide after aerobic oxidation. Similar procedure using isoamyl nitrite (isoamyl = 3-methylbutyl) gave nitroxide and azobenzene derivatives with two crowded triarylphosphine moieties. The azobenzene derivative was alternatively prepared by photolysis of the corresponding (azidoaryl)phosphine. EPR spectra of the nitroxide radicals showed hyperfine couplings with ^{31}P nuclei, which were larger than previously reported phosphinoaryl nitroxide radicals. Cyclic voltammograms of the newly synthesized triarylphosphines showed reversible redox waves corresponding to the phosphorus redox centers. The two triarylphosphine moieties connected by a nitroxide linkage showed a reversible two-step oxidation reflecting considerable interaction between the phosphorus redox sites across the nitroxide linkage. Oxidation of the crowded triarylphosphines carrying a nitroxide and photolysis of the chemically oxidized (azidoaryl)phosphine was studied by EPR spectroscopy.

Crowded triarylphosphines have attracted broad interest due to their unique structure, properties, and reactivities. Introduction of bulky aryl groups leads to structural changes around the phosphorus represented by large C–P–C bond angles and unique dynamic process. Because structural changes raise the HOMO and the bulky aryl groups kinetically protect the phosphorus cation radical center, some crowded triarylphosphines can be reversibly oxidized at low potential to the stable cation radicals.[1] Trimesitylphosphine (**1**)[2] has long been known as a typical crowded triarylphosphine and its structure,[3] dynamic behavior,[4] and redox properties[1] have been studied multidimensionally. Recently, several triarylphosphines more crowded than **1** have been reported. Tri(9-anthryl)phosphine has a crowded structure[5] and unique photophysical properties,[6] arising from the anthryl groups. We have reported the synthesis and the redox properties of crowded triarylphosphines, such as tris(2,4,6-triisopropylphenyl)phosphine (**2**),[7] and have demonstrated the relation between structure and properties (Chart 1). Comparison of triphenylphosphine (average C–P–C bond angle: 103.0°,[8] $E_{\mathrm{ox}} = 1.01$ V vs. Ag/Ag$^+$), **1** (109.7°,[3] $E_{1/2} = 0.39$ V), and **2** (111.5°, 0.14 V)[7] clearly shows influence of the bulky aryl groups on the structure and properties. Steric effect of *ortho*-alkyl groups on the structure has been discussed for some crowded triarylphosphines.[9] In order to examine if the crowded triarylphosphines work as components of the functional molecules, we have synthesized crowded triarylphosphines carrying various functional sites. In addition to development of the practical materials, studies, such as how the newly developed redox sites behave in the model systems, are expected to clarify properties of the particular structure.

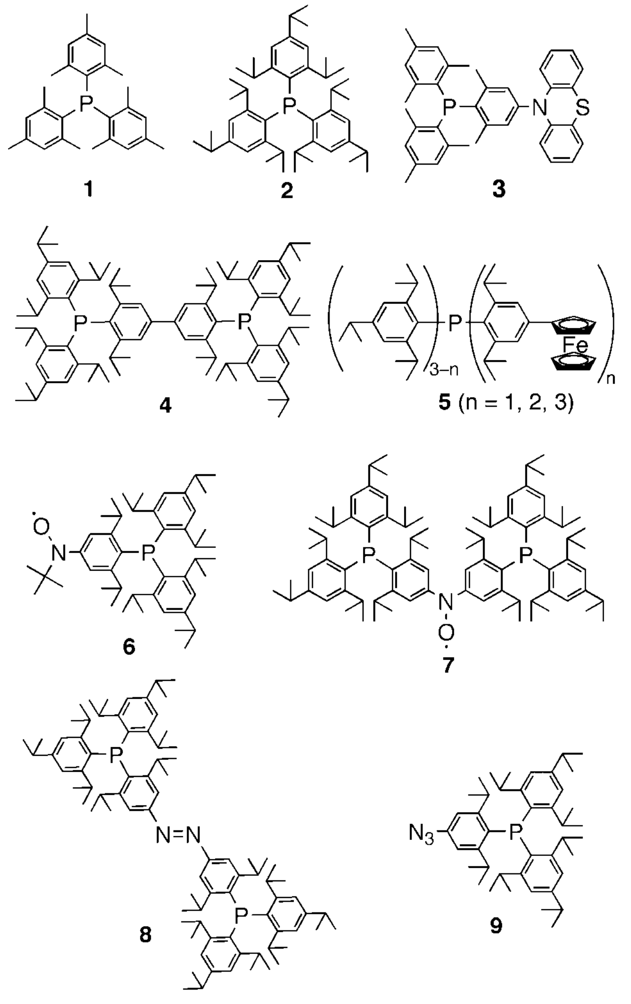

Chart 1. Crowded triarylphosphines.

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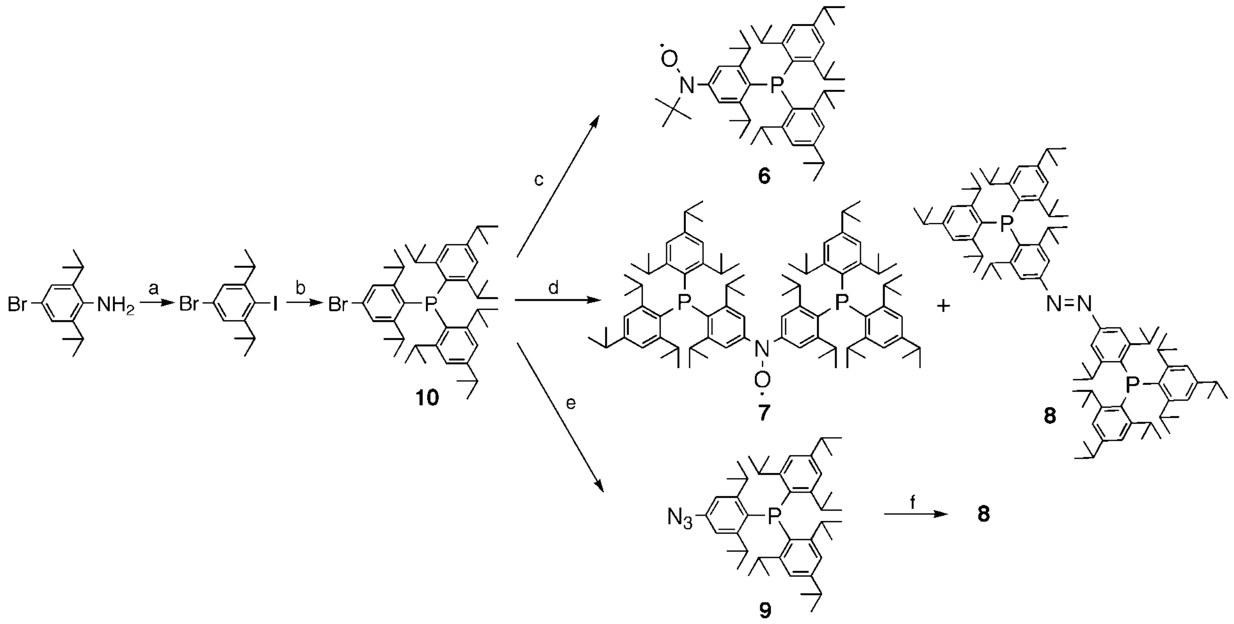


Scheme 1. Synthesis of triarylphosphines carrying a nitroxide and related compounds. Reagents and conditions: a, i) isoamyl nitrite/H_2SO_4/AcOH/0 °C, ii) KI/H_2O/0 to 20 °C (92%). b, i) *n*-BuLi/THF/−78 °C, ii) CuCl/−78 to 20 °C, iii) chlorobis(2,4,6-triisopropylphenyl)phosphine/−78 °C to reflux (50%). c, i) *t*-BuLi/THF/−78 °C, ii) 2-methyl-2-nitrosopropane/−78 to 20 °C, iii) air (9%). d, i) *t*-BuLi/THF/−78 °C, ii) isoamyl nitrite/−78 to 20 °C, iii) air (**7**: 33%, **8**: 41%). e, i) *n*-BuLi/THF/−78 °C, ii) TsN_3/−78 to 20 °C (49%). f $h\nu$/THF/0 °C (quant.).

Aminophosphinobenzene **3** shows a two-step nearly reversible redox waves only at low temperature.[10] On the other hand, introduction of the crowded triarylphosphine moieties similar to **2** improves stability of the phosphorus redox sites. Diphosphinobiphenyl **4**[11] and (ferrocenylaryl)phosphines **5**[12] work as multi-step redox systems at room temperature. In this article, we report synthesis and redox properties of the crowded triarylphosphines **6** and **7** carrying a nitroxide radical. There have been several research works on the triarylphosphines carrying nitroxide radicals. Spin delocalization on the phosphorus atoms[13] has been reported, and the phosphine moieties have been employed as coordination sites to transition metals to construct magnetic materials.[14] However, the phosphine moieties of **6** and **7** are severely shielded by six isopropyl groups and work as redox and/or radical sites rather than coordination sites. We discuss the delocalization of an unpaired electron on the phosphorus atoms and communication between the two phosphorus redox centers across the nitroxide linkage. Azobenzene **8** with the two triarylphosphine moieties was obtained in the course of the synthesis of **7**. Azide **9** was synthesized as a precursor to the triplet nitrene with a cation radical of the crowded triarylphosphine as well as an alternative synthetic intermediate for **8**. EPR studies on the generation of the triarylphosphine cation radicals with a nitroxide by oxidation of **6** and **7** and those with a triplet nitrene by oxidation of **9**, followed by photolysis, are also presented.

Results and Discussion

Synthesis and Structure. As it is unlikely that the nitroxide radicals survive under the reaction conditions for construction of the crowded triarylphosphines,[7] such as refluxing a mixture of the arylcopper(I) reagents and the phosphorus chlorides in tetrahydrofuran, (bromoaryl)phosphine **10** was employed as a key synthetic intermediate, and the nitroxide moiety was introduced in the final step (Scheme 1). The diazotization of 4-bromo-2,6-diisopropylaniline,[15] followed by reaction with potassium iodide, afforded 5-bromo-2-iodo-1,3-diisopropylbenzene. The reaction of an arylcopper(I) reagent, prepared from the bromoiodobenzene, with chlorobis(2,4,6-triisopropylphenyl)phosphine[16] gave **10**. (Bromoaryl)phosphine **10** was lithiated with *t*-butyllithium and allowed to react with 2-methyl-2-nitrosopropane, followed by aerobic oxidation during work-up, to afford nitroxide **6** as a purple solid. The lithiation of **10**, followed by reaction with isoamyl nitrite,[17] gave nitroxide **7** as a green solid after work-up, and azobenzene **8** was obtained as a by-product. Azobenzene **8** possibly forms by reduction of the initially produced nitrosobenzene derivative. Formation of azobenzenes by reduction of nitrosobenzenes has been reported.[18] Photolysis of azide **9**, prepared by the lithiation of **10**, followed by the reaction with *p*-toluenesulfonyl azide, also afforded **8** quantitatively. Azobenzene **8** was obtained as a single isomer (probably (*E*)) and no isomerization was detected by ^1H, ^{31}P NMR and UV–vis spectroscopy upon photolysis with Xe-lamp ($\lambda >$ 290 nm) in THF-d_8 at 0 °C. Azide **9** is less stable as compared with typical aryl azides, and a colorless solution of **9** became brown during evaporation. Nitroxides **6**, **7**, azobenzene **8**, and azide **9** were purified by column chromatography over Al_2O_3.

The UV–vis spectra of **6** and **7** reflect characteristics of the crowded triarylphosphine and nitroxide moieties (Fig. 1). Triarylphosphines **6** and **7** exhibit $\pi\pi^*$ absorption typical of such crowded triarylphosphines as **2** (λ_{max} (ε): **6**: 330 (17100); **7**: 338 (32200); **2**: 327 (13500) nm). *t*-Butyl aryl nitroxides generally exhibit strong absorption corresponding to $\pi\pi^*$ transition of the aromatic ring (ca. 290 nm) and weak nπ^* absorption at longer wavelength (ca. 500 nm).[19] Diaryl nitroxides

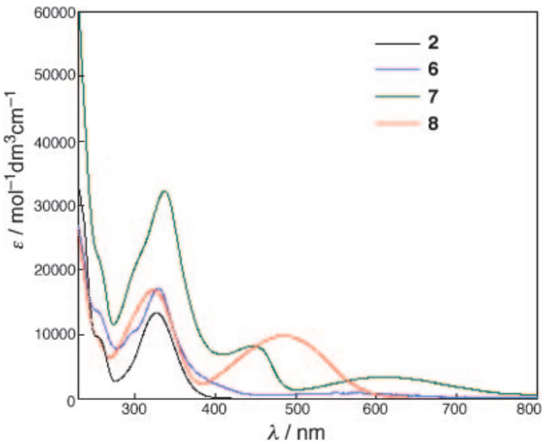


Fig. 1. UV–vis spectra of the crowded triarylphosphines in dichloromethane.

exhibit visible absorption at longer wavelength (ca. 520 nm).[20] 4-Aminophenyl nitroxides have been reported to exhibit broad band absorption up to 800 nm with λ_{max} at ca. 500 nm.[21] Both *t*-butyl derivative **6** and diaryl derivative **7** showed absorption in the longer wavelength region (λ_{max} (ε): **6**: 572 (932); **7**: 615 (3450); 446 (8150) nm) as compared to typical nitroxides, suggesting a significant interaction between the electron-donating crowded triarylphosphine and the electron-accepting nitroxide. On the other hand, azobenzene **8** showed red-shifted absorption corresponding to the azobenzene moiety (486 (9770) nm) as well as $\pi\pi^*$ transition similar to **2** (322 (16800) nm). The absorption of azobenzene moiety of **8** was similar to the corresponding absorption of analogous (*E*)-4,4′-bis(dimethylamino)-azobenzene (λ_{max} (ε, MeOH) 422 (19800), 457 (30600) nm)[22] rather than the parent (*E*)-azobenzene (λ_{max} (ε, CH_2Cl_2) 318 (21000), 443 (490) nm).[23]

The EPR spectra of nitroxides **6** and **7** were interpreted by assigning hyperfine couplings by ^{14}N, ^{31}P, and ^{1}H nuclei (**6**: $g = 2.0059$, $a(^{14}\text{N}) = 1.297$ (1N), $a(^{31}\text{P}) = 0.440$ (1P), $a(^{1}\text{H}) = 0.189$ mT (2H(*ortho*)); **7**: $g = 2.0056$, $a(^{14}\text{N}) = 0.990$ (1N), $a(^{31}\text{P}) = 0.600$ (2P), $a(^{1}\text{H}) = 0.188$ mT (4H(*ortho*))) (Fig. 2). Nitroxides **6** and **7** exhibited hyperfine couplings by ^{14}N and ^{1}H nuclei similar to the previously reported nitroxides carrying a phosphino group, *t*-butyl 4-diphenylphosphinophenyl nitroxide (**11**) ($a(^{14}\text{N}) = 1.160$ (1N), $a(^{31}\text{P}) = 0.226$ (1P), $a(^{1}\text{H}) = 0.222$ (2H(*ortho*)), 0.089 (2H(*meta*) mT)[13] and similar nitroxides as *t*-butyl phenyl nitroxide (**12**) ($a(^{14}\text{N}) = 1.195$ (1N), $a(^{1}\text{H}) = 0.213$ (3H(*ortho*, *para*)), 0.086 (2H(*meta*)) mT)[24] and diphenyl nitroxide (**13**) ($a(^{14}\text{N}) = 0.950$ (1N), $a(^{1}\text{H}) = 0.191$ (6H(*ortho*, *para*)), 0.082 (4H(*meta*)) mT)[25] (Chart 2). On the other hand, the hyperfine couplings with ^{31}P nuclei, which reflect unpaired electron density in the phosphorus 3s orbitals, were considerably larger than those of **11**. Taking higher p-character or higher hybridization ratio of the phosphorus lone pair of the crowded triarylphosphines into consideration, the phosphorus atoms of **6** and **7** were estimated to have a higher spin density than that of **11**. More effective π-conjugation arising form higher p-character of the phosphorus lone pair or intramolecular charge transfer due to low oxidation potential of the crowded triarylphosphines might be responsible for enhanced spin delocalization on the phosphorus.

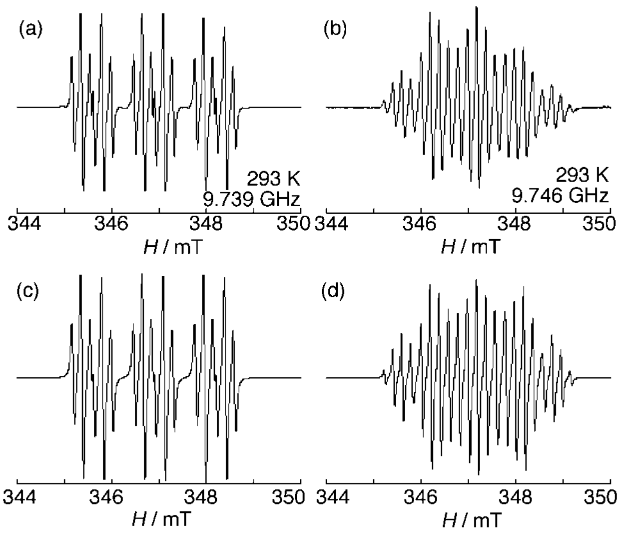


Fig. 2. EPR spectra of (a) **6** and (b) **7** in dichloromethane at 293 K, and simulated spectra of (c) **6** ($g = 2.0059$, $a(^{14}\text{N}) = 1.297$ (1N), $a(^{31}\text{P}) = 0.440$ (1P), $a(^{1}\text{H}) = 0.189$ mT (2H(*ortho*))) and (d) **7** ($g = 2.0056$, $a(^{14}\text{N}) = 0.990$ (1N), $a(^{31}\text{P}) = 0.600$ (2P), $a(^{1}\text{H}) = 0.188$ mT (4H-(*ortho*))).

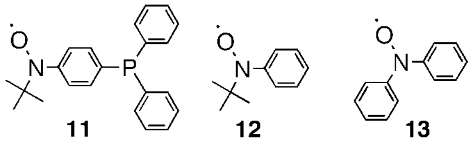


Chart 2. Nitroxide radicals.

Table 1. Redox Potentials of Crowded Triarylphosphines[a)]

Compound	$^{1}E_{1/2}$/V[b)]	$^{2}E_{1/2}$/V[b)]	$^{\text{red}}E_{1/2}$/V[b)]	ΔE/V[c)]
2	0.14			
4	0.19	0.35		0.16
6	0.09			
7	0.10	0.44	−1.11	0.34
8	0.23	0.35		0.12
9	0.22			
10	0.27			

a) Measured by cyclic voltammetry. Conditions: ca. 10^{-4} mol dm^{-3} in dichloromethane with 0.1 mol dm^{-3} *n*-Bu_4NClO_4 as a support electrolyte; working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/0.01 mol dm^{-3} $AgNO_3$ in acetonitrile with 0.1 mol dm^{-3} *n*-Bu_4NClO_4 ($E_{1/2}$(ferrocene/ferricinium) = 0.18 V); scan rate: 30 mV s^{-1}; temp.: 293 K. b) Reversible. c) $\Delta E = {}^{2}E_{1/2} - {}^{1}E_{1/2}$.

Redox Properties and Oxidation to Cation Radical. Cyclic voltammograms of **6**, **7**, **8**, **9**, and **10** showed that reversible oxidation of the crowded triarylphosphine moieties to the corresponding cation radicals occurred (Table 1). Phosphine **6** displayed one reversible oxidation at $E_{1/2} = 0.09$ V vs. Ag/Ag^{+}. On the other hand, **7** displayed two-step reversible oxidation ($E_{1/2} = 0.10$, 0.44 V) as well as reduction of the nitroxide moiety ($E_{1/2} = -1.11$ V) (Fig. 3, Scheme 2). The small difference between the oxidation and reduction potentials ($\Delta E = 1.21$ V) suggests that intramolecular charge

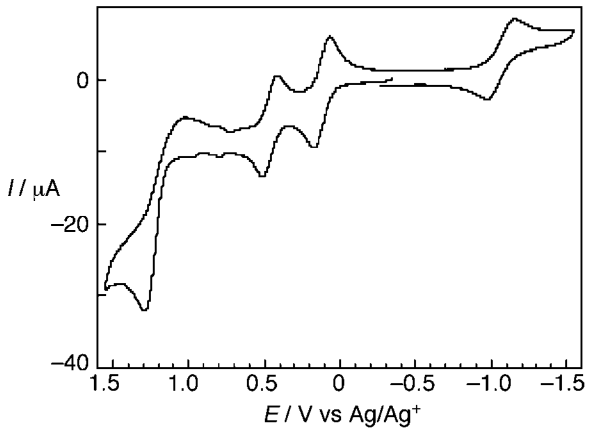


Fig. 3. Cyclic voltammograms of nitroxide **7** in dichloromethane with 0.1 mol dm^{-3} n-Bu$_4$NClO$_4$. Conditions: see Table 1.

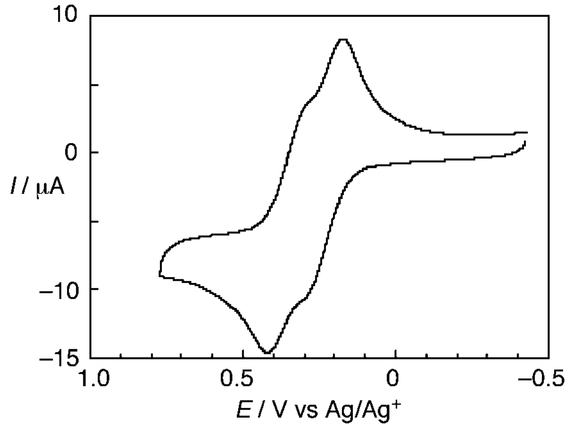
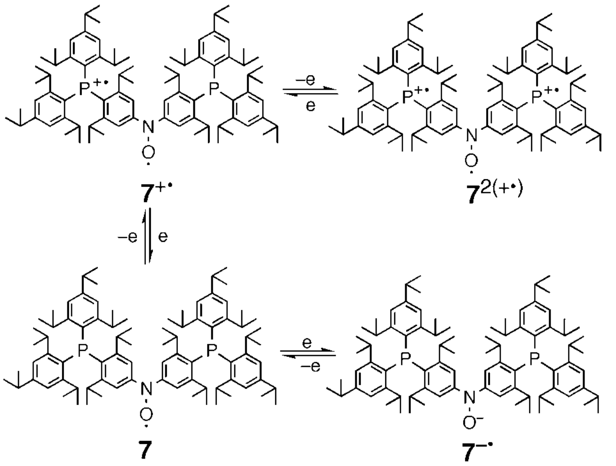


Fig. 4. Cyclic voltammograms of azobenzene **8** in dichloromethane with 0.1 mol dm^{-3} n-Bu$_4$NClO$_4$. Conditions: see Table 1.



Scheme 2. Oxidation and reduction of **7**.

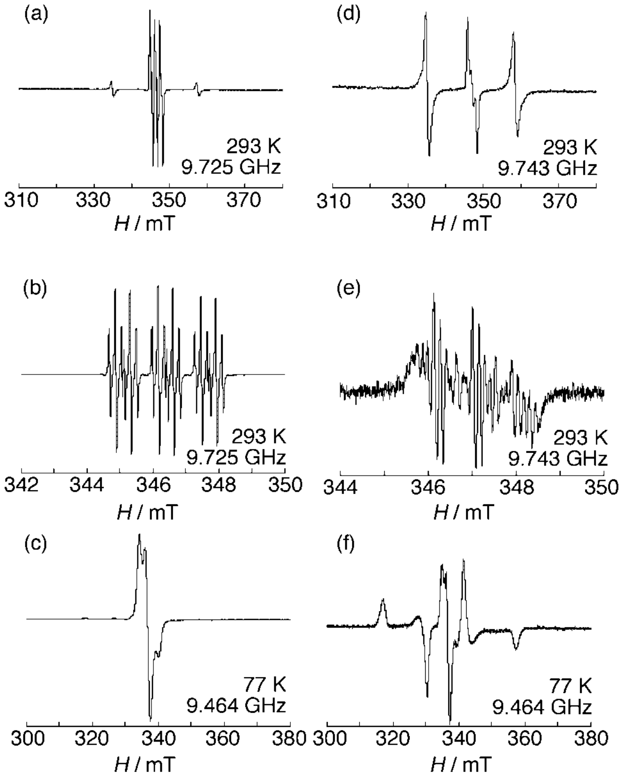
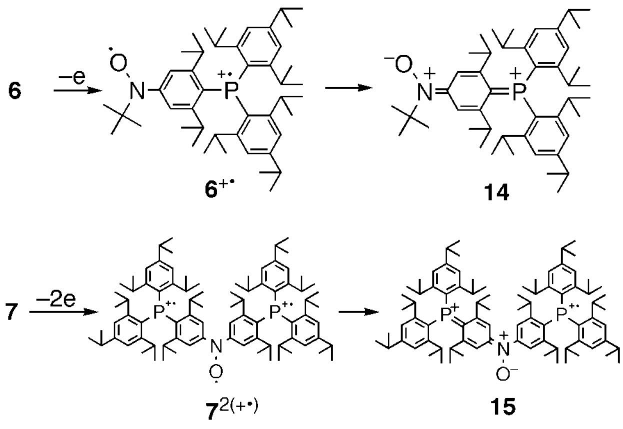


Fig. 5. EPR spectra of **6** and **7** obtained after oxidation with AgClO$_4$ in dichloromethane: **6** (a) at 293 K, (b) expansion around $g = 2$ at 293 K, (c) at 77 K. **7** (d) at 293 K, (e) expansion around $g = 2$, and (f) at 77 K.

transfer occurs between the phosphine and the nitroxide. Azobenzene **8** displayed two-step reversible oxidation with a slight difference of the potentials ($E_{1/2} = 0.23$, 0.35 V) (Fig. 4). The first oxidation potentials of the triarylphosphines are slightly affected by the substituents, and the substitution of the nitroxide at *para* to the phosphorus appears to lower the potential as compared with **2** ($E_{1/2} = 0.14$ V), which has an isopropyl group, whereas bromo, azido, and azo groups raise the potentials. Nitroxide **7** showed considerable difference between the first and the second oxidation potentials ($\Delta E = 0.34$ V). The difference was larger than those of **8** ($\Delta E = 0.12$ V) and **4**[6] ($\Delta E = 0.16$ V), suggesting significant electronic interaction between the two phosphorus atoms through the nitroxide linkage. The phosphorus cation radical center of $\mathbf{7}^{+•}$ induces the cationic character of the nitrogen atom through π-conjugation or intramolecular electron transfer, which mediates repulsion of the positive charges on the phosphorus atoms in the second oxidation. Irreversible oxidation peaks were observed for phosphines **6**, **7**, **9**, and **10** ($E_p = 1.09$ (**6**), 1.29 (**7**), 1.25 (**9**), 1.41 (**10**) V).

In order to generate cation radicals of the crowded triarylphosphines with a nitroxide radical, chemical oxidation of **6** and **7** was carried out and monitored by EPR spectroscopy (Fig. 5). Addition of AgClO$_4$ to a purple solution of **6** or a green solution of **7** in dichloromethane gave purple solutions. The EPR spectra of both solutions exhibited new doublet signals corresponding to the cation radical of the triarylphosphine (**6**: $g = 2.007$, $a(^{31}\mathrm{P}) = 22.6$ mT; **7**: $g = 2.007$, $a(^{31}\mathrm{P}) = 23.3$ mT) and reduced and less resolved signals corresponding to the nitroxide moieties. In the course of oxidation of **6**, the signals for nitroxides decreased and a weak doublet corresponding to the cation radicals of triarylphosphines was observed. On the other hand, the spectra of **7** were dominated by



Scheme 3. Oxidation of **6** and **7**.

the signals for the phosphorus cation radicals rather than nitroxides. Although the central signals displayed considerable change of subsidiary couplings, probably arising from decomposition on the phosphorus, unresolved signals did not allow detailed analysis, and there were no decisive signals indicative of the exchange interaction. The frozen solutions at 77 K exhibited superposition of the anisotropic EPR spectra of the cation radical of the triarylphosphine (**6**: $g_{//} = 2.005$, $a_{//}(^{31}\mathrm{P}) = 38.8\,\mathrm{mT}$, $g_{\perp} = 2.011$, $a_{\perp}(^{31}\mathrm{P}) = 17.0\,\mathrm{mT}$; **7**: $g_{//} = 2.006$, $a_{//}(^{31}\mathrm{P}) = 40.3\,\mathrm{mT}$, $g_{\perp} = 2.013$, $a_{\perp}(^{31}\mathrm{P}) = 11.1\,\mathrm{mT}$) on those of nitroxides (**6**: $g_x = 2.024$, $g_y = 2.008$, $g_z = 1.989$; **7**: $g_x = 2.019$, $g_y = 2.009$, $g_z = 1.993$), and did not show other meaningful signals, such as a $\Delta m_s = 2$ transition. Absence of new signals arising from dipole–dipole interaction as well as a $\Delta m_s = 2$ transition does not support formation of the triplet diradical or quartet triradical carrying the phosphorus cation radical and the nitroxide with detectable dipole–dipole interaction. Most probably, the cation radical of the triarylphosphine carrying nitroxides, such as $\mathbf{6}^{+\bullet}$ and $\mathbf{7}^{2(+\bullet)}$, is very reactive and decomposition of the nitroxide moiety does not allow direct observation in such conditions, although **6** and **7** exhibited reversible cyclic voltammograms and the cation radicals of the triarylphosphine are not so reactive to nitroxides at least intermolecularly. Even if the oxidation affords cationic species $\mathbf{6}^{+\bullet}$ and $\mathbf{7}^{2(+\bullet)}$ as expected, the phosphorus and the nitroxide radical centers could be independent or interact antiferromagnetically to give open-shell or closed-shell singlet moieties, such as quinoiminium *N*-oxides **14** and **15** (Scheme 3).

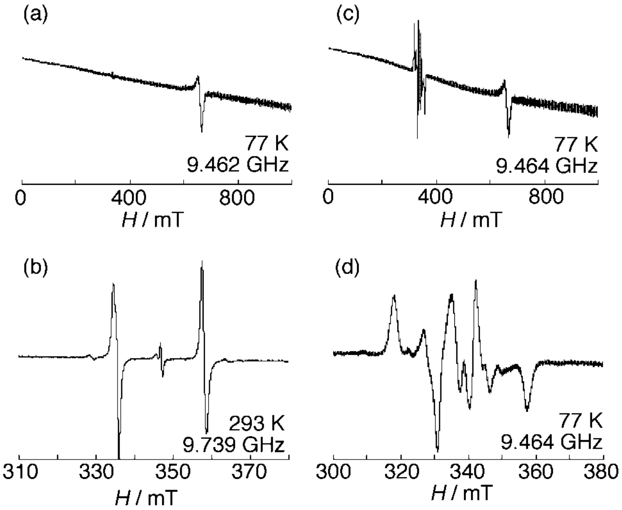
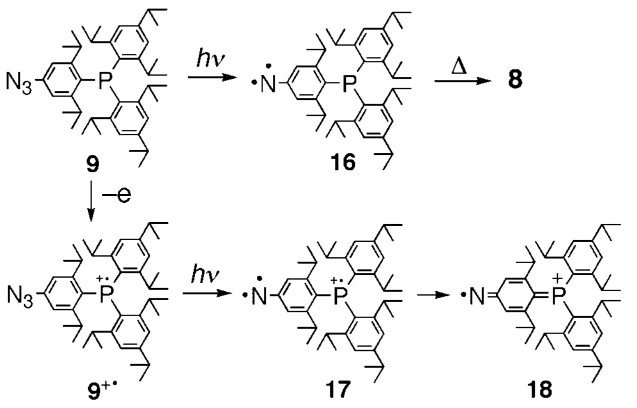


Fig. 6. EPR spectra of **9** in tetrahydrofuran obtained (a) after photolysis ($\lambda > 290\,\mathrm{nm}$) at 77 K, (b) after oxidation with tris(4-bromophenyl)aminium perchlorate at 293 K, (c) after oxidation with tris(4-bromophenyl)aminium perchlorate at 293 K and photolysis ($\lambda > 290\,\mathrm{nm}$) at 77 K, and (d) expansion around $g = 2$.



Scheme 4. Photolysis of **9**.

Photolysis of a cation radical of **9** is expected to give a triplet nitrene carrying a triarylphosphine cation radical moiety. In contrast to the cation radicals of **6** and **7**, which could lead to EPR silent singlet state, interaction of a triplet nitrene with the phosphorus cation radical is expected to give a quartet or doublet state. Photolysis of a frozen solution of **9** in THF with a Xe lamp ($\lambda > 290\,\mathrm{nm}$) at 77 K led to the formation of a green solid, and signals corresponding to a triplet nitrene[26] **16** ($D = 0.991$, $E = 0\,\mathrm{cm}^{-1}$) were observed (Fig. 6, Scheme 4). The green frozen solution became a red solution upon warming to 293 K, and azobenzene **8** was obtained. The oxidation of a solution of **9** with tris(4-bromophenyl)aminium perchlorate afforded a purple solution, and formation of the cation radical $\mathbf{9}^{+\bullet}$ was confirmed by EPR ($g = 2.007$, $a(^{31}\mathrm{P}) = 22.8\,\mathrm{mT}$). The sample was photolyzed with a Xe lamp ($\lambda > 290\,\mathrm{nm}$) at 77 K to give a green frozen solution. The EPR spectrum after the photolysis was the superposition of an axial symmetric powder pattern of the triarylphosphine cation radical ($g_{//} = 2.003$, $a_{//}(^{31}\mathrm{P}) = 39.2\,\mathrm{mT}$, $g_{\perp} = 2.010$, $a_{\perp}(^{31}\mathrm{P}) = 11.3\,\mathrm{mT}$) and a typical signal of the triplet nitrene ($D = 0.991$, $E = 0\,\mathrm{cm}^{-1}$). Additional signals around $g = 2$ were not decisive and neither a $\Delta m_s = 2$ transition nor a signal typical of a radical-substituted arylnitrene[27] was observed. The green frozen solution became a red solution upon warming to 293 K. Although **9** does not undergo a Staudinger reaction, the azide and the crowded triarylphosphine moieties are compatible with each other, and the azide group survived at least to some extent after the oxidation: The stability of the cation radical of the crowded triarylphosphines with an azido group $\mathbf{9}^{+\bullet}$ is suspect. Azide **9** itself is less stable as compared to typical aryl azides as mentioned above. Lack of the growing signals typical of a radical-substituted arylnitrene,[26] during the photolysis, excludes the formation of a triplet nitrene **17**, which is ferromagnetically coupled with the phosphorus cation radical center through the arylene linkage, although limited

π-conjugation as compared with the nitrogen radical systems and a large hyperfine coupling in the phosphorus system could lead to negligible dipole–dipole interaction or magnetically independent system. It is not so easy to pick up signals corresponding to a doublet molecule, such as **18**, resulting from antiferromagnetic interaction of the nitrene with the phosphorus cation radical center among other signals in the anisotropic spectra. However, lack of apparent growing and decreasing signals around $g = 2$ excludes the formation of such a doublet molecule.

Conclusion

We synthesized crowded triarylphosphines with a nitroxide radical, an azido group, or an azobenzene moiety from a common crowded (bromoaryl)phosphine. The (bromoaryl)phosphine is expected to be a useful intermediate for the synthesis of the crowded triarylphosphines carrying various functional sites. The crowded triarylphosphines with a nitroxide moiety, which have a phosphorus lone pair of enhanced p-character, exhibited considerable delocalization of an unpaired electron on the phosphorus atom as compared to the conventional triarylphosphines with a nitroxide. The nitroxide linkage significantly contributes to long-range communication between the two phosphorus redox centers and further extension of these units is expected to be unique electronic system. We could not fully clarify the intramolecular interaction between the cation radical of the triarylphosphine and a nitrogen radical center, probably due to instability of the phosphorus cation radical carrying a nitroxide as well as an azide. Synthetic studies towards further stabilization of the phosphorus radical centers is in progress to clarify interaction between the phosphorus and other radical centers.

Experimental

General. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a Bruker AV400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are expressed as δ downfield from external tetramethylsilane and calibrated to the residual proton of the deuterated solvents (δ 7.25 for chloroform-*d*, δ 7.20 for benzene-d_6, δ 5.32 for dichloromethane-d_2) or the carbon of the deuterated solvent (δ 77.0 for chloroform-*d*, δ 128.5 for benzene-d_6). ^{31}P NMR chemical shifts are expressed as δ downfield from external 85% H_3PO_4. Mass spectra were measured on a Hitachi M-2500S with electron impact (EI) ionization at 70 eV or a JEOL HX-110 with fast atom bombardment (FAB) ionization using the *m*-nitrobenzyl alcohol matrix. FT-ICR mass spectra were measured on a Bruker APEX III with electrospray ionization (ESI). Melting points were measured on a Yanagimoto MP-J3 apparatus without correction. Infrared and UV–vis spectra were measured on a Horiba FT-300 and a Hitachi U-3210 spectrometer, respectively. Microanalyses were performed at Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. Merck silica gel 60 and Sumitomo basic alumina (KCG-30) were used for the column chromatography. All reactions were carried out under argon unless otherwise specified. Tetrahydrofuran was distilled from sodium diphenylketyl under argon just prior to use. Cyclic voltammetry was performed on a BAS CV-50W controller with a glassy carbon, Pt wire, and Ag/0.01 mol dm^{-3} $AgNO_3$/0.1 mol dm^{-3} *n*-Bu_4NClO_4/CH_3CN as a working, counter, and reference electrode, respectively (ferrocene/ferricinium = 0.18 V). A substrate ca. 10^{-4} mol dm^{-3} was dissolved in dichloromethane with 0.1 M *n*-Bu_4NClO_4 as a supporting electrolyte and the solution was degassed by bubbling with nitrogen gas. X-band EPR spectra were measured on a Bruker ESP300E spectrometer equipped with a JEOL ES-UCD2X liquid nitrogen Dewar. Samples were dissolved in dichloromethane, which was distilled over calcium hydride, degassed by the freeze-and-thaw cycles, and transferred to a sample by bulb-to-bulb distillation. Oxidation was carried out in an H-shaped sealed tube. An Ushio UXL500D-O Xe lamp in a Model UI501C lamp house and a cut filter (UV-290) were used for the photolysis.

Synthesis. 5-Bromo-2-iodo-1,3-diisopropylbenzene: Acetic acid (75 mL) and sulfuric acid (25 mL) were added to 4-bromo-2,6-diisopropylaniline (7.26 g, 28.3 mmol), and the resultant hot mixture was stirred for 30 min. Isoamyl nitrite (6.8 mL, 56.4 mmol) was added at 0 °C, and the mixture was stirred for 20 min. A solution of potassium iodide (6.23 g, 37.5 mmol) in water (100 mL) was added at 0 °C, and the mixture was gradually warmed to 20 °C and stirred for 12 h. Aqueous solution of sodium hydrogensulfite was added to reduce iodine, and the mixture was extracted with hexane, washed with saturated sodium hydrogencarbonate solution and saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration, and the filtrate was concentrated under reduced pressure. The product was purified by column chromatography (SiO_2/hexane) to give 5-bromo-2-iodo-1,3-diisopropylbenzene (9.54 g, 26.0 mmol, 92%). **5-Bromo-2-iodo-1,3-diisopropylbenzene**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.18 (s, 2H, arom.), 3.37 (sept, $J_{HH} = 6.80$ Hz, 2H, C*H*), 1.21 (d, $J_{HH} = 6.80$ Hz, 12H, $CH(CH_3)_2$); ^{13}C NMR (101 MHz, $CDCl_3$, 296 K) δ 153.17 (s, 1,3-arom.), 126.86 (s, 4,6-arom.), 123.29 (s, 5-arom.), 106.99 (s, 2-arom.), 39.23 (s, *C*H), 23.16 (s, $CH(CH_3)_2$); IR (neat) 2964, 2927, 2885, 2870, 1558, 1462, 1423, 1404, 1387, 1363, 1340, 1317, 1298, 1238, 1169, 1153, 1130, 1107, 1068, 999, 933, 924, 887, 862, 800, 731, 701, and 665 cm^{-1}; LRMS (EI, 70 eV) *m*/*z* (rel intensity) 368 ($M^+ + 2$; 98), 366 (M^+; 100), 353 ($M^+ - CH_3 + 2$; 63), 351 ($M^+ - CH_3$; 65), 226 ($M^+ - CH_3 - I + 2$; 11), 224 ($M^+ - CH_3 - I$; 11), 211 ($M^+ - 2CH_3 - I + 2$; 7), 209 ($M^+ - 2CH_3 - I$; 4), 145 ($M^+ - CH_3 - BrI$; 14), 115 ($M^+ - 3CH_3 - IBr$; 13); HRMS (EI, 70 eV) Calcd for $C_{12}H_{16}{}^{79}BrI$: 365.9479. Found: 365.9471; Calcd for $C_{12}H_{16}{}^{81}BrI$: 367.9459. Found: 367.9462; Anal. Found: C, 39.85; H, 4.42%. Calcd for $C_{12}H_{16}BrI$: C, 39.27; H, 4.39%.

(4-Bromo-2,6-diisopropylphenyl)bis(2,4,6-triisopropylphenyl)phosphine (10). To a solution of 5-bromo-2-iodo-1,3-diisopropylbenzene (2.49 g, 6.78 mmol) in tetrahydrofuran (25 mL) was added butyllithium (1.56 mol L^{-1} in hexane, 4.4 mL, 6.86 mmol) at −78 °C, and the mixture was stirred for 30 min. Copper(I) chloride (716 mg, 7.23 mmol) was added at −78 °C, and the mixture was stirred at −78 °C for 30 min and at 20 °C for 2 h. A solution of chlorobis(2,4,6-triisopropylphenyl)phosphine (3.05 g, 6.45 mmol) in tetrahydrofuran (7 mL) was added to the mixture at −78 °C. The mixture was stirred for 20 min, gradually warmed, and refluxed for 10 h. The solvent was removed under reduced pressure, and hexane was added to the residue. Insoluble materials were removed by filtration, and the filtrate was concentrated under reduced pressure. The product was purified by column chromatography (Al_2O_3/hexane) followed by recrystallization (ethanol/hexane) to give **10** (2.30 g, 3.39 mmol, 50%). **10**: pale yellow prisms; mp 143.0–144.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 296 K) δ 7.15 (d, $J_{PH} = 2.82$ Hz, 2H, *m*-arom.(Ar)), 6.90 (d, $J_{PH} = 1.81$ Hz, 4H, *m*-arom.(Tip)), 3.46–3.36 (m, 6H, *o*-C*H*), 2.82 (sept, $J_{HH} =$

6.90 Hz, 2H, *p*-C*H*), 1.20 (d, $J_{\rm HH} = 6.90$ Hz, 12H, *p*-CH(C*H*$_3$)$_2$), 1.15 (d, $J_{\rm HH} = 6.59$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 1.14 (d, $J_{\rm HH} = 6.33$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 1.12 (d, $J_{\rm HH} = 6.59$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 0.73 (d, $J_{\rm HH} = 6.65$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 0.67 (d, $J_{\rm HH} = 7.31$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 0.65 (d, $J_{\rm HH} = 7.57$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, CDCl$_3$, 296 K) δ 155.43 (d, $J_{\rm PC} = 18.8$ Hz, *o*-arom.(Ar)), 153.05 (d, $J_{\rm PC} = 18.5$ Hz, *o*-arom.(Tip)), 152.94 (d, $J_{\rm PC} = 18.3$ Hz, *o*-arom.(Tip)), 149.58 (s, *p*-arom.(Tip)), 135.03 (d, $J_{\rm PC} = 28.8$ Hz, *ipso*-arom.(Ar)), 131.04 (d, $J_{\rm PC} = 22.7$ Hz, *ipso*-arom.(Tip)), 127.11 (d, $J_{\rm PC} = 4.0$ Hz, *m*-arom.(Ar)), 123.43 (s, *p*-arom.(Ar)), 122.12 (d, $J_{\rm PC} = 5.0$ Hz, *m*-arom.(Tip)), 122.06 (d, $J_{\rm PC} = 6.6$ Hz, *m*-arom.(Tip)), 34.07 (s, *p*-*C*H), 32.08 (d, $J_{\rm PC} = 17.8$ Hz, *o*-*C*H), 32.03 (d, $J_{\rm PC} = 18.0$ Hz, *o*-*C*H), 32.00 (d, $J_{\rm PC} = 17.1$ Hz, *o*-*C*H), 24.51 (s, *o*-CH(*C*H$_3$)$_2$(Tip)), 24.38 (s, *o*-CH(*C*H$_3$)$_2$(Ar)), 23.91 (s, *p*-CH(*C*H$_3$)$_2$), 23.24 (s, *o*-CH(*C*H$_3$)$_2$(Tip)), 22.98 (s, *o*-CH(*C*H$_3$)$_2$(Tip)), 22.67 (s, *o*-CH(*C*H$_3$)$_2$(Ar)); ^{31}P NMR (162 MHz, CDCl$_3$, 296 K) δ −50.9 (s); IR (KBr) 3045, 2966, 2933, 2904, 2868, 1601, 1560, 1462, 1419, 1383, 1362, 1308, 1236, 1155, 1103, 1057, 933, 879, 866, 802, 754, 650, 557, and 525 cm^{-1}; UV–vis (CH$_2$Cl$_2$, $c = 8.389 \times 10^{-6}$ mol L^{-1}) $\lambda_{\rm max}$ (ε)/nm 329 (13000); LRMS (EI, 70 eV) m/z (rel intensity) 678 ($M^+ + 2$; 100), 676 (M^+; 93), 635 ($M^+ - i$-Pr + 2; 8), 633 ($M^+ - i$-Pr; 7); FT-ICR-MS (ESI) Calcd for [C$_{42}$H$_{62}$PBr + H]$^+$: 677.3845. Found: 677.3850; Anal. Found: C, 74.23; H, 9.20; Br, 11.61%. Calcd for C$_{42}$H$_{62}$PBr: C, 74.42; H, 9.22; Br, 11.79%.

***t*-Butyl 3,5-Diisopropyl-4-bis(2,4,6-triisopropylphenyl)phosphinophenyl Nitroxide (6).** To a solution of (bromoaryl)phosphine **10** (200 mg, 0.296 mmol) in tetrahydrofuran (3 mL) was added *t*-butyllithium (1.40 mol L^{-1} in pentane, 0.42 mL, 0.588 mmol) at −78 °C, and the mixture was stirred for 30 min. A solution of 2-methyl-2-nitrosopropane dimer (28.1 mg, 0.162 mmol) in tetrahydrofuran (0.5 mL) was added at −78 °C, and the mixture was stirred at −78 °C for 5 min and at 20 °C for 12 h. The mixture was concentrated under reduced pressure and purified by column chromatography (Al$_2$O$_3$/hexane, hexane/ethyl acetate = 20/1) to afford **6** (18.5 mg, 0.027 mmol, 9%). **6**: purple solid; mp 49.5–52.0 °C; EPR (CH$_2$Cl$_2$) $g = 2.0059$, $a(^{14}{\rm N}) = 1.297$ (1N), $a(^{31}{\rm P}) = 0.440$ (1P), $a(^{1}{\rm H}) = 0.189$ (2H) mT; IR (KBr) 2960, 2931, 2908, 2868, 1701, 1599, 1552, 1462, 1417, 1383, 1362, 1311, 1192, 1165, 1103, 1068, 935, 879, 758, 650, and 525 cm^{-1}; UV–vis (CH$_2$Cl$_2$, $c = 8.473 \times 10^{-6}$ mol L^{-1}) $\lambda_{\rm max}$ (ε)/nm 572 (932), 330 (17100); FT-ICR-MS (ESI) Calcd for [C$_{46}$H$_{71}$NOP + H]$^+$: 685.5346. Found: 685.5341; Anal. Found: C, 79.19; H, 10.51; N, 1.90%. Calcd for C$_{46}$H$_{71}$NOP: C, 80.65; H, 10.45; N, 2.05%.

Bis[3,5-diisopropyl-4-bis(2,4,6-triisopropylphenyl)phosphinophenyl] Nitroxide (7). To a solution of (bromoaryl)phosphine **10** (200 mg, 0.296 mmol) in tetrahydrofuran (3 mL) was added *t*-butyllithium (1.40 mol L^{-1} in pentane, 0.42 mL, 0.588 mmol) at −78 °C, and the mixture was stirred for 30 min. To the resultant pale yellow solution was added isoamyl nitrite (0.02 mL, 0.149 mmol) at −78 °C, and the mixture was stirred at −78 °C for 5 min and at 20 °C for 12 h. The mixture was concentrated under reduced pressure and purified by column chromatography (Al$_2$O$_3$/hexane, hexane/ethyl acetate = 20/1) to afford **7** (60.0 mg, 0.0489 mmol, 33%). A fraction eluted with hexane was further purified by GPC (Jaigel 1H + 2H, chloroform) to give azobenzene **8** (74.0 mg, 0.0605 mmol, 41%). **7**: green solid; mp 131.5–134.0 °C; EPR (CH$_2$Cl$_2$) $g = 2.0056$, $a(^{14}{\rm N}) = 0.990$ (1N), $a(^{31}{\rm P}) = 0.600$ (2P), $a(^{1}{\rm H}) = 0.188$ (4H) mT; IR (KBr) 2958, 2927, 2906, 2868, 1601, 1552, 1462, 1419, 1383, 1362, 1309, 1101, 937, 879, 735, 650, and 523 cm^{-1}; UV–vis (CH$_2$Cl$_2$, $c = 1.120 \times 10^{-5}$ mol L^{-1}) $\lambda_{\rm max}$ (ε)/nm 615 (3450), 446 (8150), 338 (32200); FT-ICR-MS (ESI) Calcd for [C$_{84}$H$_{124}$NOP$_2$ + H]$^+$: 1225.9231. Found: 1225.9227; Anal. Found: C, 81.98; H, 10.40; N, 1.15%. Calcd for C$_{84}$H$_{124}$NOP$_2$: C, 82.30; H, 10.20; N, 1.14%.

(4-Azido-2,6-diisopropylphenyl)bis(2,4,6-triisopropylphenyl)phosphine (9). To a solution of (bromoaryl)phosphine **10** (197 mg, 0.291 mmol) in tetrahydrofuran (3 mL) was added butyllithium (1.58 mol L^{-1} in hexane, 0.3 mL, 0.474 mmol) at −78 °C, and the mixture was stirred for 30 min. A solution of *p*-toluenesulfonyl azide (116 mg, 0.544 mmol) in tetrahydrofuran (2 mL) was added, and the mixture was stirred at −78 °C for 5 min and at 20 °C for 12 h. The mixture was concentrated under reduced pressure and purified by column chromatography (Al$_2$O$_3$/hexane, hexane/ethyl acetate = 10/1) and GPC (Jaigel 1H + 2H, CHCl$_3$). A fraction containing **9**, which was obtained as a colorless solution, was concentrated under reduced pressure to afford **9** (92.0 mg, 0.143 mmol, 49%) as brown solid. **9**: brown solid; mp 108.5–110.0 °C (decomp.); ^{1}H NMR (400 MHz, CDCl$_3$, 296 K) δ 6.90 (d, $J_{\rm PH} = 3.12$ Hz, 4H, *m*-arom.(Tip)), 6.71 (d, $J_{\rm PH} = 2.74$ Hz, 2H, *m*-arom.(Ar)), 3.52–3.40 (m, 6H, *o*-C*H*), 2.82 (sept, $J_{\rm HH} = 6.82$ Hz, 2H, *p*-C*H*), 1.20 (d, $J_{\rm HH} = 6.82$ Hz, 12H, *p*-CH(C*H*$_3$)$_2$), 1.15 (d, $J_{\rm HH} = 7.04$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 1.14 (d, $J_{\rm HH} = 6.64$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 1.13 (d, $J_{\rm HH} = 7.04$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 0.72 (d, $J_{\rm HH} = 6.67$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 0.67 (d, $J_{\rm HH} = 6.69$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$), 0.65 (d, $J_{\rm HH} = 6.70$ Hz, 6H, *o*-CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, CDCl$_3$, 296 K) δ 155.32 (d, $J_{\rm PC} = 19.0$ Hz, *o*-arom.), 153.06 (d, $J_{\rm PC} = 18.4$ Hz, *o*-arom.), 152.88 (d, $J_{\rm PC} = 18.2$ Hz, *o*-arom.), 149.47 (s, *p*-arom.(Tip)), 139.88 (s, *p*-arom.(Ar)), 132.60 (d, $J_{\rm PC} = 26.7$ Hz, *ipso*-arom.(Ar)), 131.32 (d, $J_{\rm PC} = 23.1$ Hz, *ipso*-arom.(Tip)), 122.09 (d, $J_{\rm PC} = 4.6$ Hz, *m*-arom.(Tip)), 122.01 (d, $J_{\rm PC} = 4.6$ Hz, *m*-arom.(Tip)), 114.65 (d, $J_{\rm PC} = 4.4$ Hz, *m*-arom.(Ar)), 34.06 (s, *p*-*C*H), 32.08 (d, $J_{\rm PC} = 17.4$ Hz, *o*-*C*H), 32.03 (d, $J_{\rm PC} = 18.0$ Hz, *o*-*C*H), 32.01 (d, $J_{\rm PC} = 18.2$ Hz, *o*-*C*H), 24.51 (s, *o*-CH(*C*H$_3$)$_2$ × 2), 24.37 (s, *o*-CH(*C*H$_3$)$_2$), 23.90 (s, *p*-CH(*C*H$_3$)$_2$), 23.26 (s, *o*-CH(*C*H$_3$)$_2$), 22.98 (s, *o*-CH(*C*H$_3$)$_2$), 22.72 (s, *o*-CH(*C*H$_3$)$_2$); ^{31}P NMR (162 MHz, CDCl$_3$, 296 K) δ −51.1 (s); IR (KBr) 3045, 2960, 2933, 2904, 2866, 2104, 1601, 1589, 1554, 1462, 1427, 1419, 1383, 1362, 1325, 1281, 1163, 1101, 937, 877, 856, 723, and 650 cm^{-1}; UV–vis (CH$_2$Cl$_2$, $c = 1.433 \times 10^{-5}$ mol L^{-1}) $\lambda_{\rm max}$ (ε)/nm 334 (14500); FT-ICR-MS (ESI) Calcd for [C$_{42}$H$_{62}$N$_3$P + H]$^+$: 640.4754. Found: 640.4756; Anal. Found: C, 78.97; H, 9.83; N, 5.81%. Calcd for C$_{42}$H$_{62}$N$_3$P: C, 78.83; H, 9.77; N, 6.57%.

(*E*)-4,4′-Bis[bis(2,4,6-triisopropylphenyl)phosphino]-3,3′,5,5′-tetraisopropylazobenzene (8). A solution of azide **9** in tetrahydrofuran-d_8 (0.5 mL) was irradiated with Xe lamp ($\lambda > 290$ nm) at 0 °C. Quantitative conversion from **9** to **8** was confirmed by ^{31}P NMR after 5.5 h, and the solution was concentrated under reduced pressure and purified by column chromatography (Al$_2$O$_3$/hexane) to afford **8** quantitatively. **8**: red solid; mp 215.0–218.0 °C (decomp.); ^{1}H NMR (400 MHz, CDCl$_3$, 296 K) δ 7.68 (d, $J_{\rm PH} = 3.14$ Hz, 4H, *m*-arom.(Ar)), 6.92 (d, $J_{\rm PH} = 3.26$ Hz, 8H, *m*-arom.(Tip)), 3.53–3.45 (m, 12H, *o*-C*H*), 2.83 (sept, $J_{\rm HH} = 6.90$ Hz, 4H, *p*-C*H*), 1.24 (d, $J_{\rm HH} = 6.68$ Hz, 12H, *o*-CH(C*H*$_3$)$_2$), 1.21 (d, $J_{\rm HH} = 6.90$ Hz, 24H, *p*-CH(C*H*$_3$)$_2$), 1.16 (d, $J_{\rm HH} = 6.60$ Hz, 24H, *o*-CH(C*H*$_3$)$_2$), 0.79 (d, $J_{\rm HH} = 6.62$ Hz, 12H, *o*-CH(C*H*$_3$)$_2$), 0.73 (d, $J_{\rm HH} = 6.65$ Hz, 12H, *o*-CH(C*H*$_3$)$_2$), 0.66 (d, $J_{\rm HH} = 6.62$ Hz, 12H, *o*-CH(C*H*$_3$)$_2$); ^{13}C NMR (101 MHz, CDCl$_3$, 296 K) δ 154.15 (d, $J_{\rm PC} = 18.6$ Hz, *o*-arom.), 153.17 (d, $J_{\rm PC} = 17.9$ Hz, *o*-arom.), 153.10 (d, $J_{\rm PC} = 18.4$ Hz, *o*-arom.), 152.96 (s, *p*-arom.(Ar)), 149.61 (s, *p*-arom.(Tip)), 140.15 (d,

$J_{PC} = 29.2$ Hz, *ipso*-arom.(Ar)), 131.30 (d, $J_{PC} = 21.8$ Hz, *ipso*-arom.(Tip)), 122.14 (d, $J_{PC} = 4.2$ Hz, *m*-arom.), 122.10 (d, $J_{PC} = 4.3$ Hz, *m*-arom.), 118.59 (d, $J_{PC} = 3.8$ Hz, *m*-arom.), 34.09 (s, *p*-*C*H), 32.22 (d, $J_{PC} = 16.1$ Hz, *o*-*C*H), 32.17 (d, $J_{PC} = 18.0$ Hz, *o*-*C*H), 24.59 (s, *o*-CH(*C*H$_3$)$_2$), 24.56 (s, *o*-CH(*C*H$_3$)$_2$), 24.54 (s, *o*-CH(*C*H$_3$)$_2$), 23.91 (s, *p*-CH(*C*H$_3$)$_2$), 23.34 (s, *o*-CH(*C*H$_3$)$_2$), 23.01 (s, *o*-CH(*C*H$_3$)$_2$), 22.73 (s, *o*-CH(*C*H$_3$)$_2$); ^{31}P NMR (162 MHz, CDCl$_3$, 296 K) δ −49.5 (s); IR (KBr) 2960, 2931, 2906, 2868, 1601, 1552, 1462, 1419, 1383, 1362, 1311, 1234, 1165, 1120, 1101, 1066, 1057, 935, 901, 877, 756, 652, and 525 cm^{-1}; UV–vis (CH$_2$Cl$_2$, $c = 5.237 \times 10^{-6}$ mol L^{-1}) λ_{max} (ε)/nm 486 (9770), 322 (16800); FT-ICR-MS (ESI) calcd for $[C_{84}H_{124}N_2P_2 + H]^+$: 1223.9313. Found: 1223.9349; Anal. Found: C, 81.50; H, 10.17; N, 2.19%. Calcd for $C_{84}H_{124}N_2P_2$: C, 82.44; H, 10.21; N, 2.29%.

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Supporting Information

^{1}H, ^{13}C, and ^{31}P NMR spectra and cyclic voltammograms. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

References

1 a) M. Culcasi, Y. Berchadsky, G. Gronchi, P. Tordo, *J. Org. Chem.* **1991**, *56*, 3537. b) A. V. Il'yasov, Y. M. Kargin, A. A. Vafina, *Russ. J. Gen. Chem.* **1994**, *63*, 1833. c) C. Palau, Y. Berchadsky, F. Chalier, J.-P. Finet, G. Gronchi, P. Tordo, *J. Phys. Chem.* **1995**, *99*, 158. d) S. Sasaki, M. Yoshifuji, *Curr. Org. Chem.* **2007**, *11*, 17.

2 B. I. Stepanov, E. N. Karpova, A. I. Bokanov, *J. Gen. Chem. USSR* **1969**, *39*, 1544.

3 J. F. Blount, C. A. Maryanoff, K. Mislow, *Tetrahedron Lett.* **1975**, *16*, 913.

4 a) K. Mislow, *Acc. Chem. Res.* **1976**, *9*, 26. b) A. J. Bellamy, R. O. Gould, M. D. Walkinshaw, *J. Chem. Soc., Perkin Trans. 2* **1981**, 1099.

5 a) J. Wesemann, P. G. Jones, D. Schomburg, L. Heuer, R. Schmutzler, *Chem. Ber.* **1992**, *125*, 2187. b) D. M. P. Mingos, T. E. Müller, *J. Organomet. Chem.* **1995**, *500*, 251. c) T. E. Müller, J. C. Green, D. M. P. Mingos, C. M. McPartlin, C. Whittingham, D. J. Williams, T. M. Woodroffe, *J. Organomet. Chem.* **1998**, *551*, 313.

6 a) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Organomet. Chem.* **2002**, *646*, 277. b) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Organomet. Chem.* **2002**, *652*, 3.

7 S. Sasaki, K. Sutoh, F. Murakami, M. Yoshifuji, *J. Am. Chem. Soc.* **2002**, *124*, 14830.

8 a) J. J. Daly, *J. Chem. Soc.* **1964**, 3799. b) B. J. Dunne, A. G. Orpen, *Acta Crystallogr., Sect. C* **1991**, *47*, 345. c) J. Bruckmann, C. Krueger, F. Luts, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1995**, *50*, 351. d) A. N. Chekhlov, *Crystallogr. Rep.* **1993**, *38*, 467. e) H. Kooijman, A. L. Spek, K. J. C. van Bommel, W. Verboom, D. N. Reinhoudt, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, *54*, 1695.

9 R. T. Boeré, Y. Zhang, *J. Organomet. Chem.* **2005**, *690*, 2651.

10 a) S. Sasaki, F. Murakami, M. Yoshifuji, *Tetrahedron Lett.* **1997**, *38*, 7095. b) S. Sasaki, F. Murakami, M. Murakami, R. Chowdhury, K. Sutoh, M. Yoshifuji, *Phosphorus, Sulfur Silicon* **2002**, *177*, 1477. c) S. Sasaki, F. Murakami, M. Yoshifuji, *Organometallics* **2006**, *25*, 140.

11 S. Sasaki, F. Murakami, M. Murakami, M. Watanabe, K. Kato, K. Sutoh, M. Yoshifuji, *J. Organomet. Chem.* **2005**, *690*, 2664.

12 K. Sutoh, S. Sasaki, M. Yoshifuji, *Inorg. Chem.* **2006**, *45*, 992.

13 K. Torssel, *Tetrahedron* **1977**, *33*, 2287.

14 a) D. B. Leznoff, C. Rancurel, J.-P. Sutter, S. J. Rettig, M. Pink, O. Kahn, *Organometallics* **1999**, *18*, 5097. b) D. B. Leznoff, C. Rancurel, J.-P. Sutter, S. J. Rettig, M. Pink, C. Paulsen, O. Kahn, *J. Chem. Soc., Dalton Trans.* **1999**, 3593.

15 Z.-L. Lu, A. Mayr, K.-K. Cheung, *Inorg. Chim. Acta* **1999**, *284*, 205.

16 a) S. Freeman, M. J. P. Harger, *J. Chem. Soc., Parkin Trans. 1* **1987**, 1399. b) D. J. Brauer, F. Bitterer, F. Dörrenbach, G. Hessler, O. Stelzer, C. Krüger, F. Lutz, *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 1183.

17 C. Berti, *Synthesis* **1983**, 793.

18 R. Sanchez, G. Vest, W. Scott, P. S. Engel, *J. Org. Chem.* **1989**, *54*, 4026.

19 G. Chapelet-Letourneux, H. Lemaire, A. Rassat, *Bull. Soc. Chim. Fr.* **1965**, 444.

20 T. Ishida, H. Iwamura, *J. Am. Chem. Soc.* **1991**, *113*, 4238.

21 a) P. T. Frangopol, M. Frangopol, R. Baikan, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1975**, *24*, 2392. b) T. Itoh, K. Matsuda, H. Iwamura, *Angew. Chem., Int. Ed.* **1999**, *38*, 1791.

22 C. Haessner, H. Mustroph, *J. Prakt. Chem.* **1986**, *328*, 113.

23 A. Archut, F. Vögtle, L. De Cola, G. C. Azzellini, V. Balzani, P. S. Ramanujam, R. H. Berg, *Chem.—Eur. J.* **1988**, *4*, 699.

24 J. Yamauchi, Y. Deguchi, *Can. J. Chem.* **1988**, *66*, 1862.

25 J. Yamauchi, K. Okada, Y. Deguchi, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 483.

26 G. Smolinsky, E. Wasserman, W. A. Yager, *J. Am. Chem. Soc.* **1962**, *84*, 3220.

27 P. M. Lahti, B. Esat, Y. Liao, P. Serwinski, J. Lan, R. Walton, *Polyhedron* **2001**, *20*, 1647.