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Synthesis, structure, and redox properties of crowded triarylphosphines carrying 2,6-diarylphenyl substituents

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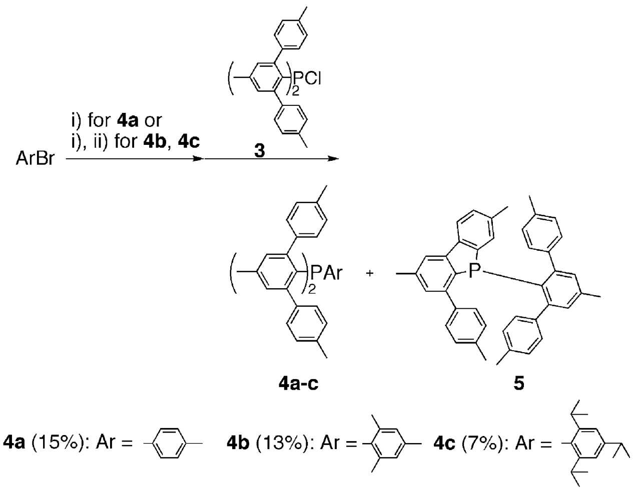
Abstract—Crowded triarylphosphines carrying 2,6-diarylphenyl and 2,4,6-trialkylphenyl groups were synthesized by the reaction of arylcopper(I) reagent with the chlorophosphines. The triarylphosphines had large bond angles and lengths around the phosphorus and were reversibly oxidized at significantly low potentials. X-ray crystallography of bis(2,4,6-triisopropylphenyl)[4-methyl-2,6-di(1-naphthyl)phenyl]phosphine revealed that two 1-naphthyl groups took *anti* conformation in the crystal.

Crowded triarylphosphines such as trimesitylphosphine (**1**) have been known to have unusual structure, large bond angles and length around phosphorus, and some of them are reversibly oxidized to the corresponding cation radicals at low potential.[1] Recently, we synthesized tris(2,4,6-triisopropylphenyl)phosphine (**2**) and clarified relation between molecular structure and redox properties.[2] 2,6-Diarylphenyl-type substituents, so called *m*-terphenyl ligands, are widely used as sterically protecting aryl groups[3] and the derivatives of various size and structure are available by the reaction of aryl Grignard reagents with polyhalobenzenes.[4] Herein, we report synthesis, structure, and redox properties of the crowded triarylphosphines carrying 2,6-diarylphenyl as well as 2,4,6-trialkylphenyl groups.

Chlorobis[4-methyl-2,6-bis(4-methylphenyl)phenyl]phosphine (**3**)[5] was synthesized by the reaction of the corresponding aryllithium with phosphorus trichloride. Since the reaction of phosphorus trichloride with 2 equiv of the arylcopper(I) reagent derived from the aryllithium did not give the corresponding triarylphosphine, whereas the reaction for 2,4,6-triisopropylphenyl group under similar conditions afforded **2**,[2] the less bulky aryl group should be employed as the third substituent. Chlorophosphine **3** was converted to triarylphosphine **4a** by the reaction with the corresponding aryl Grignard reagent. More crowded **4b** and **4c** were synthesized by the coupling of **3** with the corresponding arylcopper(I) reagent (Scheme 1). In addition to recovery of **3** (34–65%), yield of triarylphosphines suffered from formation of by-product, phosphole **5**,[5] which was regarded as a reduction product of **3**. Reaction of **3** with magnesium in THF also afforded phosphole **5** (24%) similarly to other bulky chlorophosphines[6] without formation of conventional product, tetraaryldiphosphane, and structure of **5** was confirmed by X-ray crystallography (Fig. 1).[7] On the other hand, reaction of the arylcopper(I) reagent carrying 2,6-diarylphenyl groups with



Scheme 1. Reagents and conditions: (i) Mg/THF, (ii) CuCl.

Keywords: Triarylphosphine; Arylcopper; Oxidation; Cation radical.

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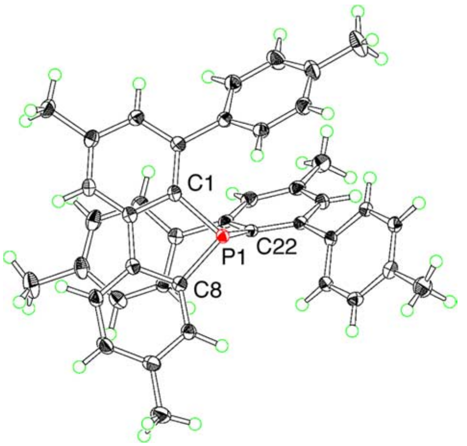
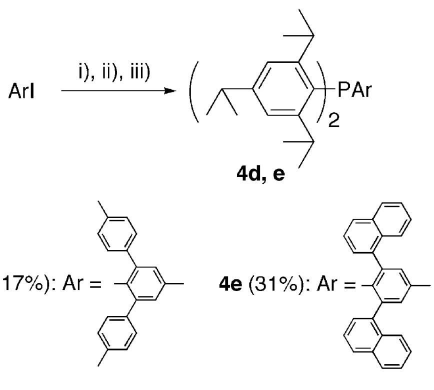


Figure 1. ORTEP drawing of **5** with 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): P1–C1 1.824(2), P1–C8 1.819(2), P1–C22 1.859(2), C1–P1–C8 89.88(7), C1–P1–C22 101.25(7), C8–P1–C22 112.94(7).

chlorobis(2,4,6-triisopropylphenyl)phosphine[8] afforded corresponding triarylphosphines **4d** and **4e**, and phosphine **4e** carrying 4-methyl-2,6-di(1-naphthyl)phenyl group, where *syn* and *anti* conformation of two 1-naphthyl groups were possible, was obtained as a single product (Scheme 2).

Triarylphosphines **4a**–**e** were characterized by conventional spectroscopy.[9] ^{31}P NMR signals of triarylphosphine **4b**–**e** appeared at high field typical of crowded triarylphosphines carrying 2,4,6-trialkylphenyl substituents, although introduction of 2,6-diarylphenyl-type substituents resulted in significant downfield shift (e.g., δ_P −32.5 (**4c**), −40.2 (**4e**), −52.4 (**2**)). ^{1}H and ^{13}C NMR spectra reflected crowded structure and severe broadening of aromatic protons of 4-methylphenyl groups was observed for **4b**–**d**. In spite of the introduction of three bulky aryl groups, **4e** was still observed as an averaged structure. The 4-methyl-2,6-di(1-naphthyl)phenyl group was observed as a C_2 symmetrical substituent, whereas the two 2,4,6-triisopropylphenyl groups gave signals for one completely unsymmetrical substituent. 2-Isopropyl groups (δ 2.421, 0.046, −0.299) and 3-aromatic protons (δ 6.371), which have spin-correlation with 5-aromatic protons (δ 6.880), displayed significant upfield shifts due to shielding by 1-naphthyl groups. These observation suggested slow enantiomerization of the propeller made of three aromatic rings bound to the phosphorus and rapid averaging between shielded sides (or deshielded sides) of the neighboring 2,4,6-triisopropylphenyl groups. Molecular structures of **4b** and **4e** were studied by X-ray crystallography (Figs. 2 and 3).[7] Phosphorus atom of **4b** was substituted by three bulky aryl groups that align propeller shape. Average C–P–C bond angle (109.2°) was close to that of trimesitylphosphine (**1**) (109.7°)[10] in spite of introduction of bulky 4-methyl-2,6-bis(4-methylphenyl)phenyl groups but average bond length (1.849 Å) was longer than **1** (1.837 Å). Two 1-naphthyl groups of phosphine **4e** took *anti* conformation to relieve steric



Scheme 2. Reagents and conditions: (i) *n*-BuLi/THF, (ii) CuCl, (iii) chlorobis(2,4,6-triisopropylphenyl)phosphine.

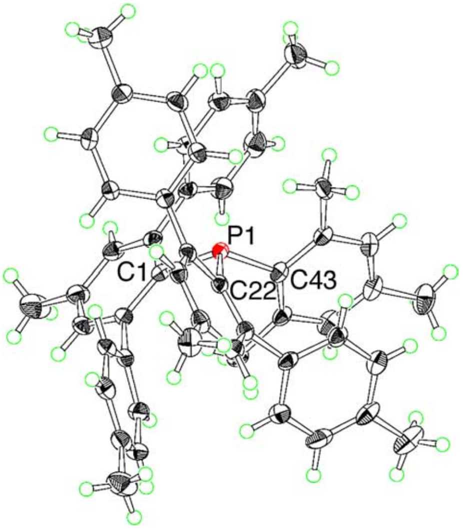


Figure 2. ORTEP drawing of **4b** with 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): P1–C1 1.853(2), P1-C-22 1.848(3), P1–C43 1.845(2), C1–P1–C22 110.0(1), C1–P1–C43 105.3(1), C22–P1–C43 112.3(1).

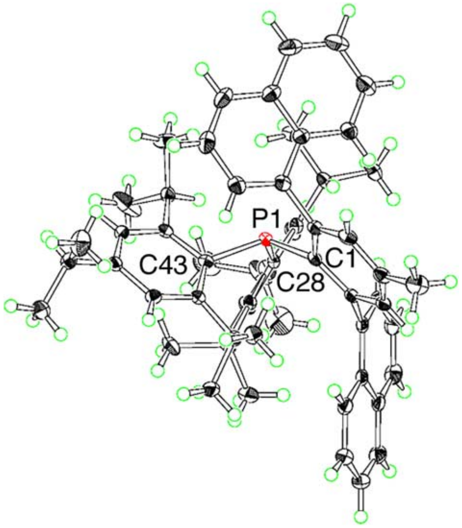


Figure 3. ORTEP drawing of **4e** with 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): P1–C1 1.850(2), P1–C28 1.855(2), P1–C43 1.859(2), C1–P1–C28 115.90(9), C1–P1–C43 107.08(9), C28–P1–C43 110.03(9).

Table 1. Average bond angles, lengths, oxidation potentials, and λ_{max} of triarylphosphines

Compound	C–P/Å	C–P–C/°	$E_{1/2}$/V[a]	λ_{max}(Log ε)/ nm[b]
Triphenylphosphine	1.828[c]	103.0[c]	1.03[d]	262 (4.06)
4a			0.32[d]	302 (3.97)
1	1.837[e]	109.7[e]	0.41	314 (4.19)
4b	1.849	109.2	0.17	346 (3.99)
2	1.845[f]	111.5[f]	0.16	327 (4.13)
4c			0.19	353 (3.94)
4d			0.18	336 (4.01)
4e	1.855	111.0	0.24	339 (4.02)
5	1.834	101.4	0.81[d]	297 (4.23)

[a] V versus Ag/Ag$^+$ in dichloromethane with 0.1 M n-Bu$_4$NClO$_4$ (Fc/Fc$^+$ = 0.20 V), scan rate 30 mV s^{-1}, reversible unless otherwise stated.
[b] Measured in dichloromethane.
[c] Ref. 11.
[d] Irreversible, peak potential.
[e] Ref. 10.
[f] Ref. 2.

repulsion and **4e** came to have two chiral centers originated from axial chirality of *anti*-4-methyl-2,6-di(1-naphthyl)phenyl group and helicity of the propeller composed of three aromatic rings substituted on the phosphorus. The three rings tilted in the direction of the minimum steric repulsion of the 1-naphthyl with 2,4,6-triisopropylphenyl groups and only one enantiomer of **4e** was observed in the chiral crystal. Average C–P–C bond angle (111.0°) was comparable to that of **2** (111.5°)[2] but average bond length (1.855 Å) was longer than that of **2** (1.845 Å) as a result of substitution of more bulky aryl groups than **2**.

Redox properties of triarylphosphines were studied by cyclic voltammetry. Oxidation potentials, average bond angles and lengths, and λ_{max} of UV–vis spectra of **4a–e**, **5** and related compounds were summarized in Table 1. Triarylphosphines **4b–e** showed reversible redox wave at considerably low potential corresponding to oxidation to cation radical although 4-methyl-2,6-di(1-naphthyl)phenyl group raised oxidation potential substantially. Chemical oxidation of **4c** in dichloromethane with tris(4-bromophenyl)aminium perchlorate afforded black solution and EPR spectra typical of cation radical of triarylphosphine ($g = 2.008$, $a(^{31}\mathrm{P}) = 27.8\,\mathrm{mT}$ in solution, $g_{\parallel} = 2.003$, $a_{\parallel}(^{31}\mathrm{P}) = 46.1\,\mathrm{mT}$, $g_{\perp} = 2.007$, $a_{\perp}(^{31}\mathrm{P}) = 19.8\,\mathrm{mT}$ in frozen solution) were observed (Fig. 4). Comparison of isotropic and anisotropic hyperfine coupling constants derived from $a_{\parallel}(^{31}\mathrm{P})$ and $a_{\perp}(^{31}\mathrm{P})$ ($a_{\mathrm{f}} = 28.6$, $a_{\mathrm{p}} = 8.8\,\mathrm{mT}$) with those of $\mathbf{2}^{+\bullet}$ ($a_{\mathrm{f}} = 22.6$, $a_{\mathrm{p}} = 8.2\,\mathrm{mT}$)[2] suggested that an unpaired electron of $\mathbf{4c}^{+\bullet}$ was more localized on 3s as well as 3p orbitals of the phosphorus atom than $\mathbf{2}^{+\bullet}$. On the other hand, phosphine **4a** and phosphole **5** showed irreversible oxidation peak. As can be seen from comparison of triphenylphosphine, **1**, with **2**, tris(2,4,6-trialkylphenyl)phosphines have larger bond angles and longer bond lengths, lower oxidation potentials, and longer λ_{max} as the molecules become more crowded. Similarly, as the substituent became more bulky from **4a**,**b** to **4c**, λ_{max} went longer wavelength, although clear relation was not observed for oxidation potentials.

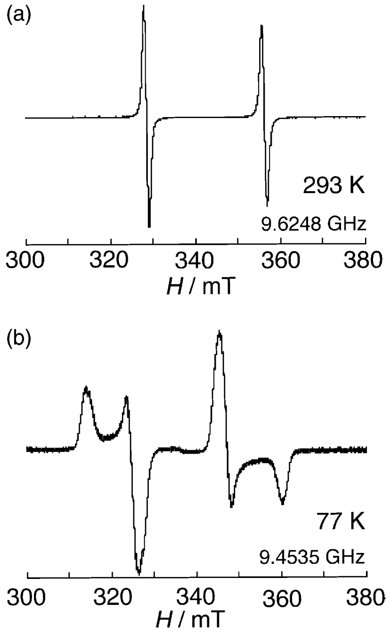


Figure 4. EPR spectra of $\mathbf{4c}^{+\bullet}$ in dichloromethane at (a) 293 K and (b) 77 K.

In conclusion, we synthesized crowded triarylphosphines carrying 2,6-diarylphenyl as well as 2,4,6-trialkylphenyl substituents and revealed structure and properties. Introduction of 2,6-diarylphenyl groups lead to diversity of structure as well as alternative choices of substituents for crowded triarylphosphines.

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Supplementary data

Experimental details and physical data for all compounds are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.10.084.

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7. Crystal data: **4b**: yellow block, $0.30 \times 0.30 \times 0.10\,\mathrm{mm}^3$, $C_{51}H_{49}P$, $M = 692.92$, monoclinic, $C2/c$ (#15), $a = 22.894(1)$, $b = 10.8719(3)$, $c = 34.217(1)$ Å, $\beta = 112.6261(8)°$, $V = 7861.3(5)$ Å^3, $Z = 8$, $Dc = 1.171\,\mathrm{g\,cm^{-1}}$, $F(000) = 2960.00$, $\mu(\mathrm{Mo\,K}_\alpha) = 0.104\,\mathrm{mm}^{-1}$, $T = 140\,\mathrm{K}$, reflection collected/unique = 22802/6002 ($2\theta_{\max} = 51.0°$, $R_{\mathrm{int}} = 0.043$), $R_1/R/R_{\mathrm{w}} = 0.059/0.069/0.102$, GOF = 1.39, max/min residual electron density 0.60/−0.59 eÅ^{-3}. Compound **4e**: yellow prism, $0.25 \times 0.25 \times 0.10\,\mathrm{mm}^3$, $C_{57}H_{65}P$, $M = 781.11$, orthorhombic, $P2_12_12_1$ (#19), $a = 16.7874(4)$, $b = 19.8546(4)$, $c = 14.2333(4)$ Å, $V = 4744.1(2)$ Å^3, $Z = 4$, $Dc = 1.094\,\mathrm{g\,cm^{-1}}$, $F(000) = 1688.00$, $\mu(\mathrm{Mo\,K}_\alpha) = 0.093\,\mathrm{mm}^{-1}$, $T = 130\,\mathrm{K}$, Reflection collected/unique = 35571/4891 ($2\theta_{\max} = 51.0°$, $R_{\mathrm{int}} = 0.046$), $R_1/R/R_{\mathrm{w}} = 0.036/0.040/0.045$, GOF = 1.13, max/min residual electron density 0.28/−0.33 eÅ^{-3}. Compound **5**: colorless block, $0.25 \times 0.15 \times 0.10\,\mathrm{mm}^3$, $C_{42}H_{37}P$, $M = 572.73$, triclinic, $P\bar{1}$ (#2), $a = 12.5906(4)$, $b = 13.6896(7)$, $c = 10.6150(4)$ Å, $\alpha = 105.331(2)$, $\beta = 99.871(2)$, $\gamma = 63.310(2)°$, $V = 1573.5(1)$ Å^3, $Z = 2$, $Dc = 1.209\,\mathrm{g\,cm^{-1}}$, $F(000) = 608.00$, $\mu(\mathrm{Mo\,K}_\alpha) = 0.116\,\mathrm{mm}^{-1}$, $T = 140\,\mathrm{K}$, Reflection collected/unique = 12313/5509($2\theta_{\max} = 51.0°$, $R_{\mathrm{int}} = 0.037$), $R_1/R/R_{\mathrm{w}} = 0.046/0.052/0.060$, GOF = 1.76, max/min residual electron density 0.52/−0.47 eÅ^{-3}. All data were collected on a Rigaku RAXIS-IV Imaging Plate. CCDC-240613 (**4b**), -240614 (**4e**), -240615 (**5**).
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9. Selected physical data: compound **3**: mp 244–246 °C; ^{1}H NMR (400 MHz, CDCl$_3$, 293 K): δ 6.982 (8H, d, $J = 8.02$ Hz), 6.888 (8H, br d, $J = 7.73$ Hz), 6.599 (4H, d, $J = 2.82$ Hz), 2.400 (12H, s), 2.236 (6H, s, Ar–CH$_3$); ^{31}P NMR (162 MHz, CDCl$_3$, 293 K): δ 94.8 (s). Compound **4a**: mp 193–195 °C; ^{1}H NMR δ 6.727 (10H, d, $J = 7.53$ Hz), 6.625 (4H, d, $J = 2.51$ Hz), 6.482 (10H, d, $J = 6.93$ Hz), 2.259 (12H, s), 2.247 (6H, s), 2.190 (3H, s); ^{31}P NMR δ −6.3 (s). Compound **4b**: mp 192–193 °C; ^{1}H NMR δ 7.115 (4H, br s), 7.016 (4H, br s), 6.9–6.3 (4H, br s), 6.796 (2H, br s), 6.518 (2H, br s), 6.167 (2H, d, $J = 2.40$ Hz), 6.025 (4H, br s), 2.373 (6H, br s), 2.248 (6H, s), 2.160 (6H, br s), 2.091 (3H, s), 1.501 (6H, br s); ^{31}P NMR δ −28.7 (s). Compound **4c**: mp 202–203 °C, ^{1}H NMR δ 6.970 (4H, br s), 6.871 (4H, br s), 6.712 (2H, br s), 6.517 (2H, d, $J = 3.09$ Hz), 6.385 (2H, br s), 5.986 (4H, br d, $J = 6.94$ Hz), 3.041 (2H, m, $J = 6.09$ Hz), 2.733 (1H, sept, $J = 6.86$ Hz), 2.433 (6H, s), 2.206 (6H, s), 2.085 (6H, s), 1.189 (3H, d, $J = 6.88$ Hz), 1.180 (3H, d, $J = 6.89$ Hz), 0.674 (6H, br s), 0.272 (6H, d, $J = 6.60$ Hz) (Four *m*-protons of Tol groups were not observed due to severe broadening); ^{31}P NMR δ −32.5 (s). Compound **4d**: mp 143–144 °C; ^{1}H NMR δ 7.093 (2H, br s), 7.060 (2H, br s), 6.873 (2H, dd, $J = 2.80$, 2.21 Hz), 6.774 (2H, d, $J = 2.87$ Hz), 6.525 (2H, dd, $J = 3.09$, 2.04 Hz), 6.331 (2H, br s), 6.202 (2H, br s), 3.722 (2H, m), 2.787 (2H, sept, $J = 6.86$ Hz), 2.761 (2H, m), 2.247 (3H, s), 2.180 (6H, s), 1.224 (6H, d, $J = 6.86$ Hz), 1.207 (6H, d, $J = 6.87$ Hz), 1.113 (6H, d, $J = 6.61$ Hz), 0.949 (6H, d, $J = 6.31$ Hz), 0.334 (6H, d, $J = 7.35$ Hz), 0.316 (6H, d, $J = 6.79$ Hz); ^{31}P NMR δ −42.3 (s). Compound **4e**: mp 107–108 °C; ^{1}H NMR δ 7.78–7.76 (2H, m), 7.49–7.41 (6H, m), 7.034 (2H, d, $J = 2.75$ Hz), 6.880 (2H, dd, $J = 3.04$, 2.02 Hz), 6.667 (2H, br d, $J = 6.64$ Hz), 6.623 (2H, t, $J = 7.49$ Hz), 6.371 (2H, br m), 3.777 (2H, m, $J = 6.86$ Hz), 2.741 (2H, sept, $J = 6.87$ Hz), 2.421 (2H, m, $J = 6.50$ Hz), 2.305 (3H, s), 1.194 (6H + 6H, d, $J = 6.82$ Hz), 1.180 (6H, d, $J = 6.88$ Hz), 0.647 (6H, d, $J = 6.45$ Hz), 0.046 (6H, d, $J = 6.48$ Hz), −0.299 (6H, d, $J = 5.74$ Hz); ^{31}P NMR δ −40.2 (s). Compound **5**: mp 263–264 °C; ^{1}H NMR δ 7.467 (1H, d, $J = 3.96$ Hz), 7.410 (1H, d, $J = 7.88$ Hz), 7.250 (2H, d, $J = 7.75$ Hz), 7.25–7.15 (2H, br s), 7.177 (2H, d, $J = 8.02$ Hz), 7.144 (1H, d, $J = 7.93$ Hz), 7.110 (1H, s), 7.071 (2H, d, $J = 7.83$ Hz), 7.052 (1H, d, $J = 1.94$ Hz), 6.872 (1H, dd, $J = 4.46$, 0.63 Hz), 6.666 (1H, d, $J = 1.34$ Hz), 6.5–5.5 (2H, br s), 6.308 (2H, br s), 2.432 (3H, s), 2.429 (3H, s), 2.413 (3H, s), 2.381 (3H, br s), 2.291 (3H, s), 2.157 (3H, s); ^{31}P NMR δ −20.3 (s).
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