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Synthesis, Structure, and Properties of Tris(2,6-diisopropyl-4-methoxyphenyl)phosphine

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Tris(2,6-diisopropyl-4-methoxyphenyl)phosphine (1) was synthesized to investigate substituent effect of methoxy groups on the properties of crowded triarylphosphines. Methoxy groups slightly lower the first oxidation potential of 1 and contribute blue-shift of UV-Vis absorption as compared with the corresponding 2,4,6-triisopropylphenyl derivative.

Keywords Oxidation potential; Triarylphosphine; UV-Vis spectrum

INTRODUCTION

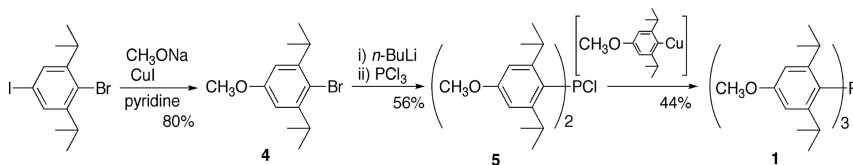
Unusual structure and physical properties of crowded triarylphosphines have attracted considerable attention for a long time.¹ Typical crowded triarylphosphines such as trimesitylphosphine (**2**)² and tris(2,4,6-triisopropylphenyl)phosphine (**3**)³ are reversibly oxidized to stable cation radicals, and they can be employed as redox centers of multistep redox systems.⁴ However, modification of properties of such redox systems by π -conjugated substituents, which are general in the second-row element systems such as triarylaminines, has been still limited and little is known for the effect of remote π -conjugated substituents on the properties of such compounds. Herein, we report synthesis and properties of tris(2,6-diisopropyl-4-methoxyphenyl)phosphine (**1**). Substituent effect of electron donating methoxy group on redox properties and electronic spectrum is discussed.

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RESULTS AND DISCUSSION

Triarylphosphine **1** was synthesized via **4** and **5** in a similar manner to related compounds (Scheme 1).^{3,4} X-ray crystallography of **1** revealed that average C–P–C bond angle (111.5°) and P–C bond length (1.850 \AA) are similar to those of **3** (111.5° , 1.845 \AA) (Figure 1).



SCHEME 1

Cyclic voltammogram of **1** exhibits reversible redox wave corresponding to oxidation to the cation radical and the oxidation potential ($E_{1/2} = 0.08 \text{ V}$ vs Ag/Ag^+) is lower than that of **3** (0.13 V) and tris(2,6-diisopropylphenyl)phosphine (**6**) (0.27 V),⁵ probably because of strong electron donating effect of methoxy group. UV-Vis spectrum of **1** in dichloromethane shows λ_{max} at $321 (16300) \text{ nm}$, which is blue-shifted as compared with **3** ($327 (13500) \text{ nm}$), and **6** ($328 (11000) \text{ nm}$) (Figure 2). Apparent blue shift of **1** seems to be attributed to higher LUMO of **1** considering the oxidation potentials.

Replacement of isopropyl group at 4 position of 2,4,6-triisopropylphenyl group with various substituents is expected to modulate electronic properties of crowded triarylphosphines without changing steric environment around the phosphorus. Because both isopropyl and methoxy groups are good electron donating substituents, effect of the replacement is limited for **1** and **3**. However, simple

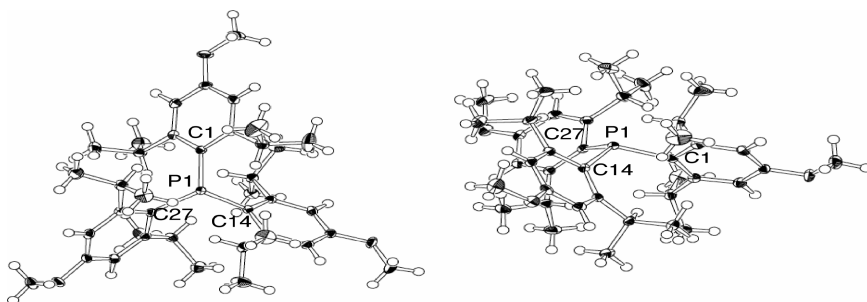


FIGURE 1 Molecular structure of **1**. Selected bond lengths (\AA) and angles ($^\circ$): P1–C1 $1.848(1)$, P1–C14 $1.850(1)$, P1–C27 $1.852(1)$, C1–P1–C14 $107.56(6)$, C1–P1–C27 $116.71(6)$, C14–P1–C27 $110.31(6)$.

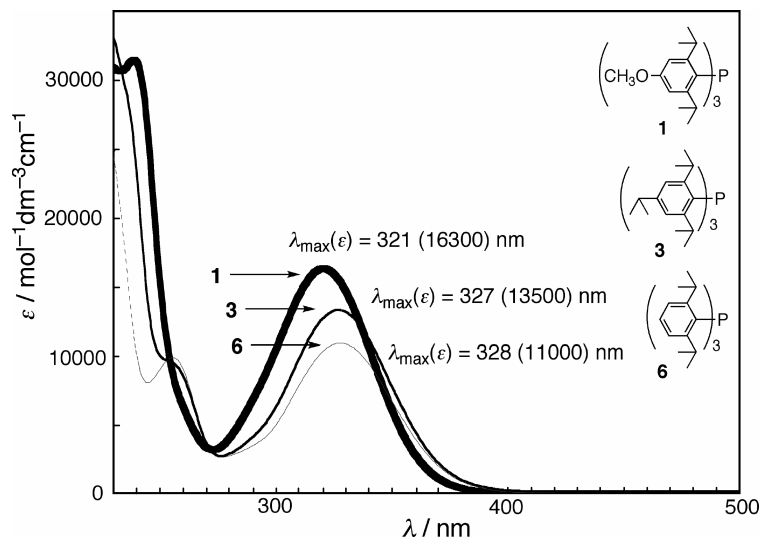


FIGURE 2 UV-Vis spectrum of **1** and related compounds in dichloromethane.

molecular design and synthetic strategy shown in this study is promising way to tune, even if limited, properties of crowded triarylphosphines and related compounds.

EXPERIMENTAL

Synthesis

2-Bromo-1,3-diisopropyl-methoxybromobenzene (4)

A mixture of 2-bromo-5-iodo-1,3-diisopropylbenzene (6.02 g, 16.4 mmol), CuI (3.05 g, 16.0 mmol), sodium methoxide (prepared from methanol (13.5 mL) and sodium (0.38 g, 16.4 mmol)) in pyridine (60 mL) was refluxed for 12 h. The resultant mixture was poured onto ice-water, extracted with ether, washed with 4 M HCl solution, saturated NaHCO₃ solution, and saturated NaCl solution, and dried over anhydrous MgSO₄. Drying agent was removed by filtration and the filtrate was concentrated under reduced pressure and purified by column chromatography (SiO₂, hexane) to give **4** (3.54 g, 13.1 mmol, 80%) as colorless oil. ¹H NMR (400 MHz, CDCl₃, 296 K) δ 6.68 (2H, s, arom.), 3.80 (3H, s, OCH₃), 3.47 (2H, sept, *J* = 6.66 Hz, CH), 1.20 (12H, d, *J* = 6.66 Hz, CH₃).

Chlorobis(2,6-diisopropyl-4-methoxyphenyl)phosphine (5)

Butyllithium (5.70 mmol, 1.58 mol L⁻¹ in hexane) was added to a solution of **4** (1.53 g, 5.65 mmol) in tetrahydrofuran (20 mL) at

–78°C, and the solution was stirred for 30 min. Phosphorus trichloride (0.23 mL, 2.64 mmol) was added and the mixture was allowed to warm to room temperature and stirred for 12 h. The mixture was concentrated under reduced pressure and purified by column chromatography (SiO₂, hexane) to give **5** (710 mg, 3.16 mmol, 56%) as colorless crystals.

M.p. 112.0–114.0°C. ¹H NMR (400 MHz, CDCl₃, 296 K) δ 6.65 (4H, d, *J* = 2.70 Hz, arom.), 3.79 (6H, s, OCH₃), 3.76 (4H, m, CH), 1.03 (12H, d, *J* = 6.68 Hz, CH₃), 1.02 (12H, d, *J* = 6.63 Hz, CH₃). ¹³C NMR (101 MHz, CDCl₃, 296 K) δ 160.86 (s, *p*-arom.), 153.87 (d, *J*_{PC} = 16.9 Hz, *o*-arom.), 128.06 (d, *J*_{PC} = 50.6 Hz, *ipso*-arom.), 110.06 (d, *J*_{PC} = 1.90 Hz, *m*-arom), 54.92 (s, OCH₃), 31.22 (d, *J*_{PC} = 18.9 Hz, CH), 24.28 (s, CH₃), 23.95 (s, CH₃). ³¹P NMR (162 MHz, CDCl₃, 296 K) δ 89.9 (s). IR (KBr) 3005, 2970, 2960, 2935, 2929, 2866, 2837, 1431, 1383, 1363, 1325, 1269, 1248, 1236, 1196, 1176, 1165, 1105, 1047, 1028, 937, 870, 849, 746, 625, 517, 484 and 463 cm^{–1}. Anal. calcd. for C₂₆H₃₈ClO₂P: C, 69.55; H, 8.53; Found: C, 69.84; H, 8.33.

Tris(2,6-diisopropyl-4-methoxyphenyl)phosphine (1)

Butyllithium (1.80 mmol, 1.58 molL^{–1} in hexane) was added to a solution of **4** (0.50 g, 1.84 mmol) in tetrahydrofuran (10 mL) at –78°C, and the solution was stirred for 30 min. CuCl (183 mg, 1.85 mmol) was added and the mixture was warmed to 20°C and stirred for 3.5 h. A solution of **5** (710 mg, 1.58 mmol) in tetrahydrofuran (3 mL) was added at –78 °C, and the mixture was warmed to room temperature and refluxed for 60 h. The mixture was concentrated under reduced pressure and purified by column chromatography (Al₂O₃, hexane, hexane:chloroform = 4:1) to give **1** (490 mg, 0.81 mmol, 44%) as colorless crystals.

M.p. 171.0–172.5°C. ¹H NMR (400 MHz, CDCl₃, 296 K) δ 6.61 (6H, d, *J* = 2.71 Hz, arom.), 3.79 (9H, s, OCH₃), 3.50 (6H, m, CH), 1.14 (18H, d, *J* = 6.68 Hz, CH₃), 0.70 (18H, d, *J* = 6.63 Hz, CH₃). ¹³C NMR (101 MHz, CDCl₃, 296 K) δ 160.18 (s, *p*-arom.), 155.07 (d, *J*_{PC} = 19.2 Hz, *o*-arom.), 126.56 (d, *J*_{PC} = 22.7 Hz, *ipso*-arom.), 109.61 (d, *J*_{PC} = 4.69 Hz, *m*-arom), 54.83 (s, OCH₃), 32.03 (d, *J*_{PC} = 18.0 Hz, CH), 24.41 (s, CH₃), 23.21 (s, CH₃). ³¹P NMR (162 MHz, CDCl₃, 296 K) δ –53.5 (s). UV-Vis (CH₂Cl₂, c = 3.29 × 10^{–5} molL^{–1}) λ_{max} (ε)/nm 321 (16300). IR (KBr) 2964, 2933, 2866, 2837, 1566, 1462, 1429, 1383, 1360, 1321, 1268, 1234, 1196, 1174, 1128, 1105, 1051, 1028, 937, 867, 849, 752, 652, 627, 580, 521, 492, 453 and 437 cm^{–1}. FT-ICR-MS (ESI) Calcd. for [C₃₉H₅₇O₃P+H]⁺: 605.4118, Found : 605.4118. Anal. calcd. for C₃₉H₅₇ClO₃P: C, 77.44; H, 9.50; Found: C, 77.04; H, 9.53.

Cyclic Voltammetry

Cyclic voltammetry was performed on a BAS CV-50W controller with a glassy carbon, Pt wire, and Ag/0.01 M AgNO₃/0.1 M *n*-Bu₄NClO₄/CH₃CN as a working, counter, and reference electrode, respectively (Ferrocene/Ferricinium = 0.18 V). A substrate *ca.* 10⁻⁴ M was dissolved in dichloromethane with 0.1 M *n*-Bu₄NClO₄ as a supporting electrolyte and the solution was degassed by bubbling with nitrogen gas.

Crystallographic Analysis of 1

Crystal data of **1**: C₃₉H₅₇O₃P, *M* = 604.85, colorless chunk grown from mixed solvent of hexane and ethanol (1:3), crystal dimensions 0.50 × 0.25 × 0.25 mm³, monoclinic, space group *P*2₁/n (no. 14), *a* = 11.9747(3), *b* = 22.2050(4), *c* = 13.6296(2) Å, β = 93.6097(6)°, *V* = 3616.9(1) Å³, *D*_c = 1.111 gcm⁻³, μ = 0.110 mm⁻¹, *T* = 140 K, *Z* = 4, *F*(000) = 1320.00. Of 28322 reflections measured (2θ_{max} = 51.0°), 6762 were observed [*I* > 0.0σ(*I*)] (*R*_{int} = 0.032). Variable parameters 389. Goodness of fit *S* = 1.23 for observed reflections, and *R*₁ = 0.040 for *I* > 2.0σ(*I*), *R* = 0.046, *R*_w = 0.067 for all reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.37 and -0.26 eÅ⁻³, respectively. CCDC 643412.

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