



Sterically crowded triarylphosphines bearing cyano groups

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ABSTRACT

Sterically crowded triarylphosphines bearing one, two, and three cyano groups at 4-positions of aromatic substituents, namely, (4-cyano-2,6-diisopropylphenyl)_n(2,4,6-triisopropylphenyl)_{3-n}P (n = 1, 2, 3), were synthesized. Influence of the introduction of cyano groups is clearly reflected to the oxidation potentials and the fluorescence wavelengths. As the number of cyano groups increases, the oxidation potentials are raised and the fluorescence wavelengths are blue-shifted. Synthetic utility of the (cyanoaryl)phosphine is also demonstrated.

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A cyano group is a strong electron withdrawing substituent and is employed as a key substituent of typical electron acceptors such as DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), TCNQ (7,7,8,8-tetracyanoquinodimethane), and TCNE (tetracyanoethylene). In addition, a cyano group can coordinate to transition metals, and nitriles can serve as key synthetic intermediates to construct larger π -conjugated systems as shown in conversion to ketones,¹ cyclic π -conjugated systems,² and phthalocyanines.³ Aromatic amines bearing cyano groups have been reported to exhibit unique photophysical properties (Chart 1). 4-Dimethylaminobenzonitrile is a fluorescent molecule and has been studied as a typical TICT molecule,⁴ and can coordinate to transition metals.⁵ Tris(4-cyanophenyl)amine emits fluorescence in solution and solid with high quantum yield,^{6a} also works as a ligand for MOFs,^{6b} and has been studied as a candidate for SHG materials.^{6c,d} On the other hand, studies on 4-cyanophenylphosphines have been limited to the synthesis. Cyanophenylphosphines have been synthesized by Vilsmeier-Haack reaction of the corresponding amides,^{7a,7b} reaction of cyanophenylzinc reagents with chlorophosphines,^{7c,7f} nucleophilic substitution of phosphide anions with cyanophenyl fluorides,^{7d} palladium catalyzed phosphination of cyanophenyl bromides and triflates.^{7e} Sterically crowded triarylphosphines such as tris(2,4,6-triisopropylphenyl)phosphine (**1**)⁸ have planarized phosphorus atoms substituted by bulky substituents and can be reversibly oxidized to the corresponding radical cations at low potentials, because of the synergic effect of the high HOMO resulting from the phosphorus lone pair residing in the orbital of

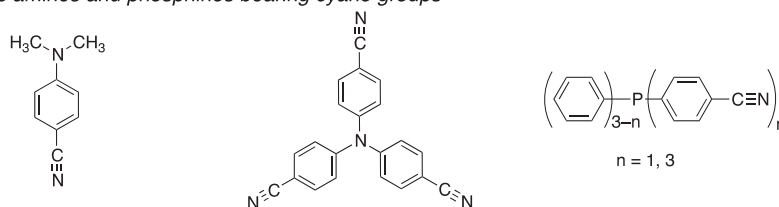
high p-character and the steric protection. Triarylphosphines similar to **1** have been employed as key functional sites in various π -electron systems and demonstrated to work as reversible redox sites.⁹ Among various π -electronic systems studied, sterically crowded triarylphosphines connected to acceptors such as carbonyl (**2**)^{9g} and quinone (**3**)^{9e,9h} moieties have been found to show typical donor-acceptor interaction such as intramolecular charge transfer. Therefore, the sterically crowded triarylphosphines bearing cyano groups are also expected to show unique properties taking characteristics of the triarylphosphines and the similarity to triaryl amines into consideration. In this letter, synthesis, structure, and properties of (cyanoaryl)phosphines **4a**, **4b**, and **4c** are described. Influence of the introduction of cyano groups was evaluated spectroscopically and electrochemically. Synthetic utility of the (cyanoaryl)phosphine is also presented.

We have synthesized various sterically crowded triarylphosphines bearing functional sites by using the (bromoaryl)phosphines as key intermediates.^{9c,9e,9g,9h} Triarylphosphines **4a**, **4b**, and **4c** bearing cyano groups were synthesized by the reaction of (bromoaryl)phosphines **5a**,^{9c} **5b**, and **5c**^{9e} with copper(I) cyanide in refluxing *N,N*-dimethylformamide, respectively (Scheme 1). Phosphines **4a**, **4b**, and **4c** were purified by column chromatography on aluminum and recrystallization, and obtained as yellow air-stable solids.

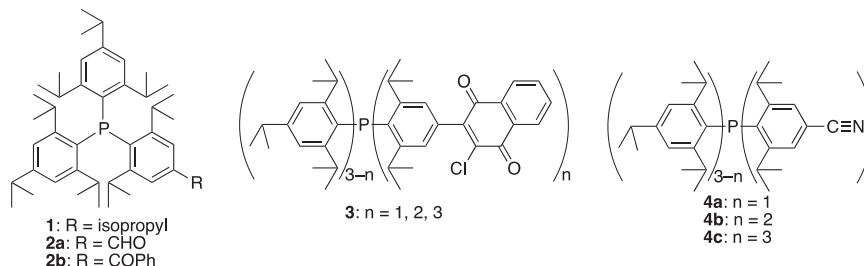
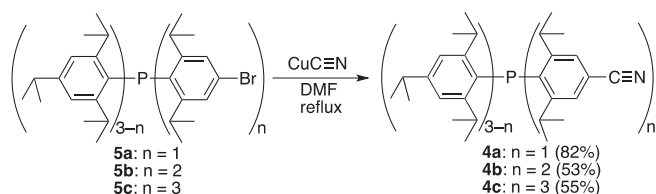
¹H (500 MHz, CDCl₃, 300 K) and ¹³C (126 MHz, CDCl₃, 300 K) NMR spectra of **4a**, **4b**, and **4c** exhibit inversion averaged signal patterns typical of the sterically crowded triarylphosphines such as **1**.^{8a,8c,8d} For example, symmetrical **4c** gives two methyl, one methyne, and one aromatic ¹H signals. The introduction of cyano groups leads to downfield shifts of ³¹P NMR resonances (δ_p -50.1 (**4a**), -47.7 (**4b**), -45.6 (**4c**), -51.9 (**1**)), upfield shifts of ipso-

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Aromatic amines and phosphines bearing cyano groups

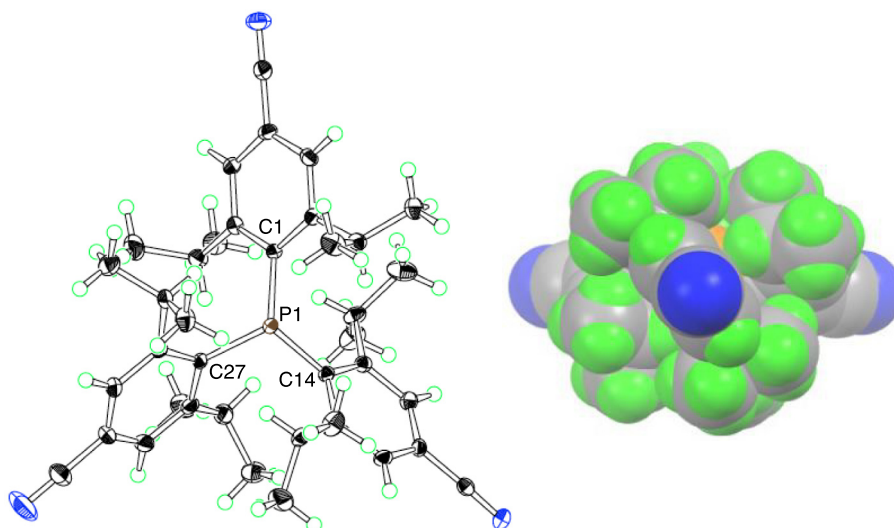


Sterically crowded triarylphosphines

**Chart 1.** Aromatic amines and phosphines bearing cyano groups and sterically crowded triarylphosphines.**Scheme 1.** Synthesis of (cyanoaryl)phosphines.

carbons of 4-cyanoaryl groups with smaller $^1J_{PC}$ (δ_c 143.5 (32.8 Hz) (**4a**), 141.2 (30.5 Hz) (**4b**), 139.1 (28.4 Hz) (**4c**)), and downfield shifts of *p*-carbons of cyanoaryl groups (δ_c 111.8 (**4a**), 113.0 (**4b**), 114.0 (**4c**), 112.41 (benzonitrile)¹⁰). Similar trend was observed in naphthoquinonyl substituted triarylphosphines **3**,^{9e} but the effect is larger for cyano groups. On the other hand, influences on the ^{13}C NMR chemical shifts and infrared absorptions ($\nu(CN)$) of the cyano groups are very limited (δ_c 119.8 (**4a**), 119.3 (**4b**),

118.8 (**4c**), 118.82 (benzonitrile);¹⁰ $\nu(CN)/cm^{-1}$ 2226 (**4a**), 2225 (**4b**), 2228 (**4c**), 2230 (benzonitrile)¹⁰). The structure of **4c** was investigated by X-ray crystallography (Fig. 1). The bond angles and lengths around the phosphorus atom (average 111.7°, 1.847 Å) are similar to those of **1** (111.5°, 1.845 Å).^{8a} The bond lengths around the cyano groups (CN 1.146(3), 1.144(3) 1.142(3); C–CN 1.442(3), 1.439(3), 1.449(3) Å) are within the typical values of aromatic nitriles (CN 1.138(1); C–CN 1.442(1))¹¹ such as benzonitrile (CN 1.137 (14); C–CN 1.401(14))¹² and tris(4-cyanophenyl) amine (CN 1.137(2), 1.137(2), 1.129(3); C–CN 1.429(2), 1.429(2), 1.434(3)).^{5c} The nitrogen atoms of **4c** in the crystal have contacts less than sum of the van der Waals radii with the aromatic (2.642, 2.658 Å) and methyl protons (2.679, 2.697 Å) to contribute tight packing (Fig. S27). Although the phosphorus atom still takes pyramidalized geometry, the whole shape of **4c** looks rather flat because the bent angles between the P–C bond and the aromatic ring calculated from the angle of the P–C bond and the C(*ipso*)–C(*para*) are deviated from 180° (P1–C1–C4 162.85°, P1–C14–C17 168.83°, P1–C27–C30 158.50°). Thus, **4c** is

**Figure 1.** An ORTEP drawing of **4c** (top view) obtained by X-ray crystallography with 50% thermal ellipsoids and a space filling model (side view). Selected bond angles (°) and lengths (Å): C1–P1–C14 114.57(9), C1–P1–C27 113.37(9), C14–P1–C27 107.03(9), P1–C1 1.846(2), P1–C14 1.844(2), P1–C27 1.851(2).

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