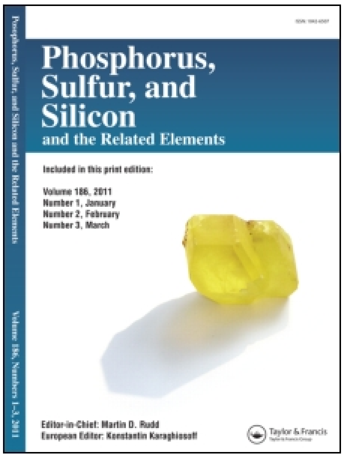

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Construction of Stable Redox Systems Composed of the Crowded Triarylphosphines

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CONSTRUCTION OF STABLE REDOX SYSTEMS COMPOSED OF THE CROWDED TRIARYLPHOSPHINES

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Extremely crowded triarylphosphines were synthesized by the reaction of arylcopper(I) reagents with chlorophosphines, and the relationship between molecular structure and redox properties was studied by X-ray crystallography and cyclic voltammetry. As the substituent on phosphorus became bulkier, bond lengths and angles around phosphorus atom became longer and larger, and oxidation potential was significantly lowered. Especially, tris(2,4,6-triisopropylphenyl)phosphine had an extremely crowded structure and was oxidized to a stable radical cation at an extraordinarily low oxidation potential. Novel redox systems possessing the crowded triarylphosphine structure as one of the redox sites were designed and synthesized.

Keywords: Bond angle; bond length; oxidation potential; redox systems; triarylphosphine

We have been interested in the construction of multistep redox systems possessing phosphorus functional group such as diphosphenes[1] and phosphaalkenes[2] as one of the redox sites. Crowded triarylphosphines such as trimesitylphosphine are known to have extremely large bond length and angles,[3] and some of them are reversibly oxidized to the

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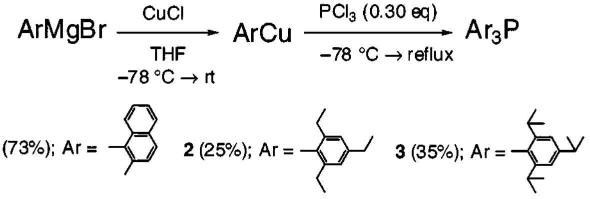

FIGURE 1

stable cation radicals.[4] In order to apply trimesitylphosphine structure as a redox site of multicentered redox systems, we optimized the method of preparation of trimesitylphosphine, which was originally prepared by the reaction of mesitylmagnesium bromide with phosphorus trichloride in 29% yield,[5] and obtained the quantitative yield by the addition of 3 equivalents of mesitylmagnesium bromide to a solution of phosphorus trichloride at −78°C in tetrahydrofuran.[6] The Grignard method was applied to the synthesis of aminophosphinobenzenes, which proved to be a quasireversible redox system,[6] but the method was not applicable to the introduction of an aryl group more sterically demanding than mesityl group. Therefore, arylcopper(I) reagents, which were reported for the synthesis of the crowded phosphine ligands,[7] were employed, and more crowded triarylphosphines such as **1**, **2**, and **3** were synthesized in moderate yields (Figure 1).

The structure of tris(2,4,6-triisopropylphenyl)phosphine **3**, the most crowded in this series, was investigated by X-ray crystallography as well as variable temperature NMR. Phosphine **3** has extremely large bond lengths and angles (average 1.845 Å and 111.5°, respectively) around the phosphorus atom, and temperature-dependent behavior was observed in ^{1}H-NMR most clearly for *o*-isopropyl groups. Due to the extremely crowded structure and sterically protecting effect of three 2,4,6-triisopropylphenyl groups, **3** was oxidized at significantly low potential (0.16 V vs. Ag/Ag^+) to the stable radical cation. Comparison of molecular structures and oxidation potentials of several triarylphosphines clearly revealed that oxidation potential drops as the bond length and angles around phosphorus become longer and larger. For example, bond angles and oxidation potentials of triphenylphosphine, trimesitylphosphine, and **3** are 103.0, 109.7,[8] and 111.5°, and 1.03, 0.41, and 0.16 V, respectively.

As model compounds of redox system possessing a phosphorus redox center, phenothiazinophosphinobenzene **4**, **5**, **6**, and **7** were synthesized (Figure 2). The trimesitylphosphine-type structures of **4** and **5** were constructed by the addition of aryl Grignard reagents to chlorophosphines. On the other hand, the more crowded structures of **6** and **7** were

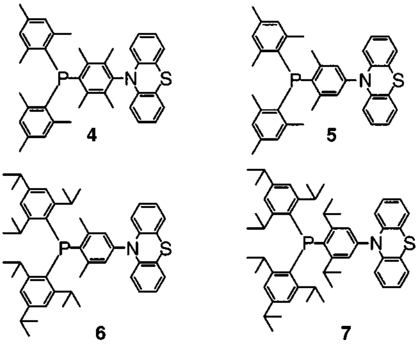

FIGURE 2

synthesized by using arylcopper(I) reagents. Cyclic voltammograms of **4** and **5** became two-step reversible only at low temperature. Removal of two methyl groups in the *o*-position to nitrogen did not improve stability of the redox system. However, structural change from the trimesitylphosphine- to the tris(2,4,6-triisopropylphenyl)phosphine-type structure greatly stabilized redox system. Two step reversible redox waves at $E_{1/2} = 0.21$ and 0.68 V were observed at room temperature for the most crowded **7**.

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