

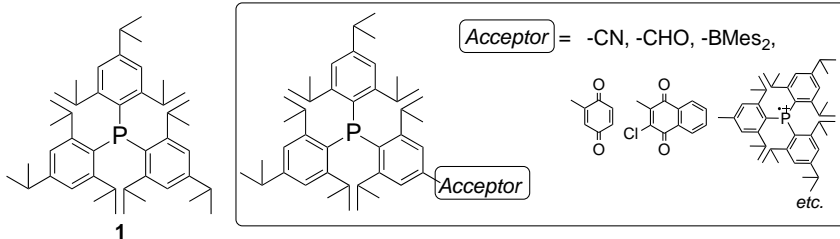
Sterically Crowded Triarylphosphines: Structure, Properties, Reactivities, and Construction of π -Electron Systems

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Sterically crowded triarylphosphines represented by tris(2,4,6-triisopropylphenyl)phosphine (**1**) are reversibly oxidized to the corresponding radical cation at low potential because of high HOMO, localized on the phosphorus lone pair, resulting from the planarized structure around the phosphorus atom and steric protection by three bulky aryl groups [1]. The sterically crowded triarylphosphines can be connected to functional sites such as donors including the triarylphosphine itself [2], acceptors [3], and radicals [4] to construct multistep redox systems. Triarylphosphines such as **1** have recently attracted attention as substrates for frustrated Lewis and radical pair [5].

We have continued synthetic studies toward triarylphosphines more crowded than **1**. Although widening of the bond angles around the phosphorus atom obtained by XRD seems to reach its maximum in **1**, triarylphosphines with further steric protection are still available. Structures, properties, reactivities of various sterically crowded triarylphosphines will be discussed with the aid of theoretical study. We have recently focused on the synthesis of sterically crowded triarylphosphines possessing acceptor moieties. Influence of the structures and properties of the acceptor moieties on the electronic structures of the phosphine moieties will be presented.



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