Synthesis of a Sulfur-bridged Diphosphine Ligand and Its Unique Complexation Properties toward Palladium(II) Ion

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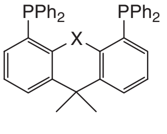
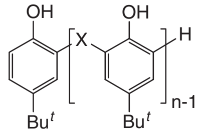
Sulfur-bridged phenol dimer $\mathbf{3_2}$ is converted into P–S–P ligand **5**, mono- and dinuclear palladium complexes of which are selectively synthesized and characterized by X-ray crystallography.

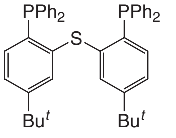
Diphosphines constitute a large ligand family useful for a variety of transition-metal-catalyzed transformations. Steric and electronic properties of a ligand often influence the rate and selectivity of catalysis, as well as the stability of its complexes. Recently, diphosphine ligands with a heteroatom linker between the two phosphino moieties have been developed and applied to catalysts. Of particular interest among such entities are Xantphos (**1**) and its derivatives, which were designed to enforce a large phosphorus–metal–phosphorus angle and have proven to be successful in tuning the activity and selectivity in various metal-catalyzed reactions.[1] A variety of coordination modes, i.e., bidentate cis and trans coordination and tridentate P–O–P coordination, have been achieved by tuning the substituents on the phosphine ligand and/or replacing the other ligands coordinating to the metal center.[1b,1c,1f] On the other hand, little attention has been paid to the corresponding P–S–P ligands.[1b,1f,2] Recently, Ohba et al. and we independently reported that sulfur-bridged phenol oligomers $\mathbf{3}_n$ exhibit high extractability toward soft metal ions in solvent extraction experiments, while their methylene-bridged counterparts $\mathbf{4}_n$ per se did not extract any metal ions, implying a vital role of the soft sulfur atoms in binding to metal ions.[3] We reasoned that all or a part of the hydroxy groups of $\mathbf{3}_n$ would be easily replaced with phosphino groups via a transition-metal-catalyzed Ar–O bond-cleavage reaction after conversion into triflate esters. This provides an easy access to a series of novel phosphine ligands with sulfur donors. As the first effort in this line, we report herein the preparation of P–S–P ligand **5** and its varied coordination modes, the latter being revealed by stepwise and quantitative introduction of $PdCl_2$ cores, taking advantage of good resistance of the Pd–Cl bonds toward substitution reactions.



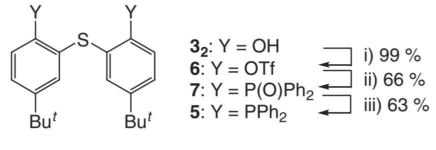
1: X = O
2: X = S



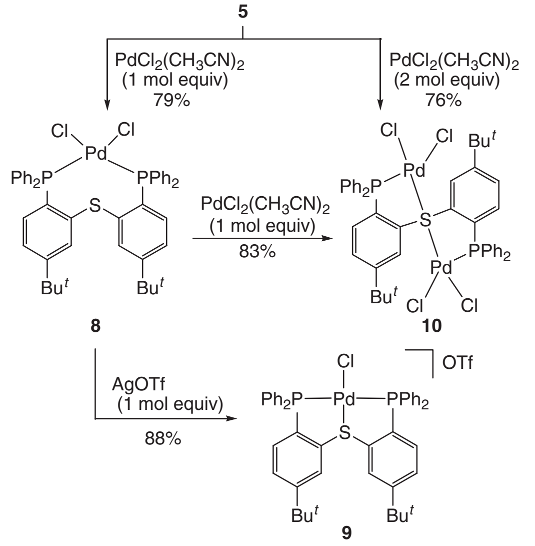
$\mathbf{3}_n$: X = S
$\mathbf{4}_n$: X = CH_2



5



Scheme 1. Reagents and conditions: i) Tf_2O, pyridine, rt, 2 h, ii) $Ph_2P(O)H$, $Pd(OAc)_2$, dppb, $^iPr_2EtN$, DMSO, 120 °C, 2.5 h, iii) $HSiCl_3$, Et_3N, toluene, reflux, 2 h.



Scheme 2.

Sulfur-bridged phenol dimer $\mathbf{3_2}$ was prepared by the reaction of *p-tert*-butylphenol with SCl_2 according to the literature procedure.[4] Esterification of $\mathbf{3_2}$ with triflic anhydride gave bistriflate **6**, which was submitted to palladium-catalyzed phosphorylation,[5,6] followed by reduction of the resulting phosphine oxide **7** with $HSiCl_3$ to afford diphosphine **5** in a good yield after purification by column chromatography (Scheme 1).

Treatment of diphosphine **5** with 1.0 mol equiv of $PdCl_2(CH_3CN)_2$ in refluxing benzene gave red complex **8**, the ^1H NMR spectrum of which showed one singlet for the Bu^t protons, indicating that this complex has a symmetric structure (Scheme 2).

The solid-state structure was determined by X-ray diffraction of a single crystal, which was obtained by slow diffusion of acetone into a dichloromethane solution of complex **8**. It was revealed that complex **8** has a mononuclear structure; the palladium(II) ion is centered on a distorted square plane defined by the two phosphorus atoms and two chloride ions (Figure 1). Ligand **5** coordinates to the metal center in a cis fashion with the two phosphorus atoms. The Pd–P (av 2.261 Å) and Pd–Cl (av 2.349 Å) bond lengths are within the range of normal values. The sulfur atom is forced into the apical position and a weak Pd–S bonding interaction seems to be present, judging from the interatomic distance between Pd–S (2.987 Å), as well as

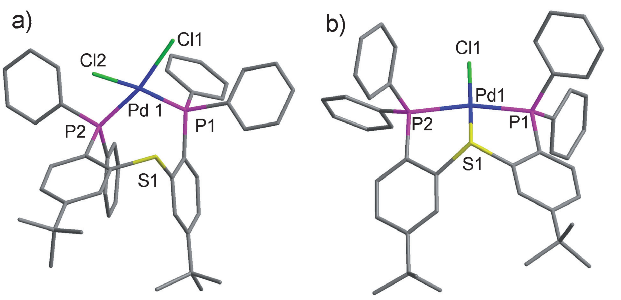


Figure 1. X-ray structures of a) complex **8** and b) complex **9**. Hydrogen atoms and triflate ion are omitted for clarity.

the geometry of the complex.[1b,8] It has been reported that bis[2-(diphenylphophino)ethyl]sulfide (PSP) coordinates to a platinum(II) ion in a tridentate fashion to form complexes formulated as [Pt(PSP)X]X ($X = Cl^-, Br^-$, and I^-).[2c] It has also been reported that Thioxantphos **2** forms [(Thioxantphos)-Pd(CH_3)]Cl and [(Thioxantphos)Pd(C_6H_4-*p*-CN)]Br, in which **2** serves as a tridentate ligand as evidenced by molar conductivity measurements.[1b] Therefore, it was a surprise to find that the soft sulfur atom did not expel one of the chloride ions to coordinate to the soft palladium center.

Interestingly, ionic complex **9** could be easily prepared by the treatment of **8** with 1.0 mol equiv of AgOTf under refluxing conditions in benzene (Scheme 2). Crystals suitable for X-ray structural analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **9**. In the crystal, the complex has a square-planar geometry, in which the two phosphorus atoms coordinate in a trans fashion with P1–Pd1–P2 angle of 167.52(10)° and the sulfur atom coordinates trans to the chloride ligand [Pd–S distance = 2.2685(30) Å].

On the other hand, the reaction of diphosphine **5** with $PdCl_2(CH_3CN)_2$ in the molar ratio of 1:2 afforded yellow complex **10**, the ^1H NMR spectrum of which was clearly different from that of complex **8** (Scheme 2). X-ray structural analysis of a single crystal, prepared by slow diffusion of diethyl ether into a dichloromethane solution of complex **10**, revealed that it is a dinuclear complex, in which the sulfur, one of the two phosphorus atoms, and two chloride ions coordinate to each palladium ion, forming a square-planar geometry (Figure 2). It is noteworthy that the sulfur atom takes part in the coordination to both the palladium ions by using the two lone pairs. The interatomic distance between Pd1–Pd2 (3.809 Å) indicates the absence of bonding interaction. To the best of our knowledge, such dinuclear metal complexes have not been reported for xanthene-type ligands **1** and **2**. Interestingly, complex **10** could also be prepared by the treatment of complex **8** with 1.0 mol equiv of $PdCl_2$-($CH_3CN)_2$. It seems that the conformational flexibility of ligand **5**, with the aid of the strong coordination ability of the epithio group to palladium(II) ion, enabled the transformation of mono- into dinuclear complexes, which may open an access to heterodinuclear complexes by a stepwise treatment of **5** with two different metal ions.

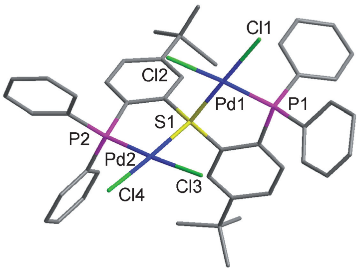


Figure 2. X-ray structure of compound **10**. Hydrogen atoms, solvents, and disordered carbon atoms are omitted for clarity.

In conclusion, we have shown here synthesis and unique complexation properties of ligand **5**. It serves as both bidentate P–P and tridentate P–S–P ligands, depending on the electron density of the palladium center, by changing the coordination mode of the two phosphino moieties between cis and trans fashions. The epithio linkage can coordinate to two palladium ions by using the two lone pairs to form a dinuclear complex, in which the two metal ions are placed close to each other. These properties are of special interest for the catalytic application of these palladium complexes.

References and Notes

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6 Detailed synthetic methods, spectral data, and crystallographic data of the compounds reported in this manuscript were deposited in Supporting Information.[7] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-670856–670858. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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