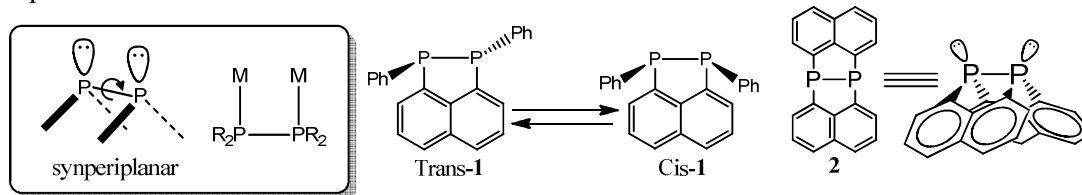


## 1G4b

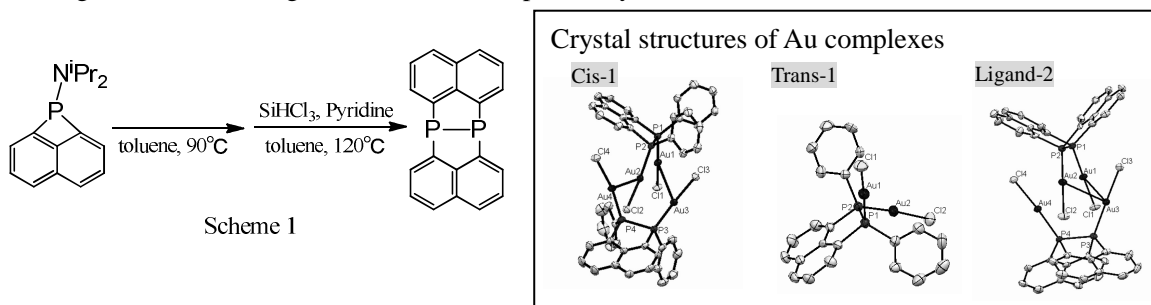
P—P Group Bound to 1,8-Positions of Naphthalene:  
Preparation of Cis Isomer and Synthesis of Binuclear Complex

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Diphosphine in a synperiplanar conformation is thought to be a useful ligand, because two metal centers can be coordinated to the respective phosphorus centers of the diphosphine moiety, and are linked in close proximity by a direct P—P bond. However, only a small number of reports have mentioned the ligands bearing such conformation. Here, we report the preparation of a thermodynamically less stable *cis* isomer of 1,2-diphosphacycle which has the synperiplanar conformation. We also synthesized a novel ligand **2**, a P-P bond of which is strongly fixed with two naphthalene units.



Diphosphine, in which a PhP—PPh bond bridges the 1,8-positions of naphthalene, 1,2-diphenyl-1,2-dihydronaphtho[1,8-cd][1,2]diphosphole (**1**), was prepared by the reaction of 1,8-dithionaphthalene with dichlorophenylphosphine [1]. The *trans* isomer of **1** was obtained as the major product. The *trans*-**1** was irradiated in tetrahydrofuran (THF) with UV-Vis light to reach equilibrium with *cis*-**1** in a *trans*:*cis* ratio of 1:2. When a similar photochemical conversion was carried out using a saturated hexane solution of *trans*-**1**, *cis*-**1** was precipitated in a good yield of 94% [2]. **2** was prepared by a ring-opening dimerization of 1-(diisopropylamino)-1H-naphtho[1,8-bc]phosphate, followed by reduction with SiHCl<sub>3</sub> (Scheme 1). *Cis*- and *trans*-**1** and **2** were used for the preparation of binuclear gold complexes. The crystal structures of (μ-*cis*-**1**)-[AuCl]<sub>2</sub> and (μ-**2**)-[AuCl]<sub>2</sub> demonstrated that the two lone pairs of *cis*-**1** and **2** are suitably directed for arrangement of the two gold centers in close proximity.



[1] T. Mizuta, S. Kunikata, K. Miyoshi, *J. Organomet. Chem.* 2004, 689, 2624.

[2] Y. Teramoto, K. Kubo, T. Mizuta, *J. Organomet. Chem.* 2011, 696, 3402.