

## A Chiral Diphosphine as *trans*-Chelate Ligand and its Relevance to Catalysis

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### Supplementary Information. Synthesis, Fluxionality, Structure

*R,R-trans*-1,2-C<sub>6</sub>H<sub>10</sub>(NHCOC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>, **1**, was a commercial sample.

#### [Au(**1**)]Cl, **2a**.

A solution of **1** (0.1686 g, 0.244 mmol) in dichloromethane (10 mL) was added to a solution of [AuCl(SMe<sub>2</sub>)] (0.0718 g, 0.244 mmol) in dichloromethane (10 mL). The mixture was stirred for 12 hours to give a white precipitate of the product which was collected, washed with n-pentane, and diethyl ether, and dried under vacuum. Yield 0.19 g, 85%. NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ(<sup>1</sup>H) = 1.21-1.92 [m, 8H, cyclohexyl]; 4.33 [m, 2H, CHN]; 6.93 – 8.19 [m, 28H, Ph and C<sub>6</sub>H<sub>4</sub>]; 9.19 [br, 2H, NH]; δ(<sup>31</sup>P) = 45.1 [s, AuP]. Anal. Calc. for C<sub>44</sub>H<sub>40</sub>AuClN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 57.25; H, 4.37; N, 3.03. Found: C, 57.09; H, 4.44; N, 2.94 %. Single crystals were grown by slow diffusion of n-pentane into a dichloromethane solution of **2a**. The complex [Au(**1**)]BF<sub>4</sub>, **2b**, was prepared by reaction of **2a** with Ag[BF<sub>4</sub>]. The NMR spectra were as for **2a**. Single crystals were grown by slow diffusion of n-pentane into a dichloromethane solution of **2b**.

#### [Ag(**1**)](CF<sub>3</sub>CO<sub>2</sub>), **2c**.

A mixture of ligand **1** (50 mg, 0.0723 mmol) and silver trifluoroacetate (0.0159 g, 0.0723 mmol) in THF (10 mL) was stirred for 12 hours to give a white precipitate which was collected, washed with n-pentane, and diethyl ether, and dried under vacuum. Yield 0.049 g, 74 %; NMR in CD<sub>2</sub>Cl<sub>2</sub>: δ(<sup>1</sup>H) = 1.29-1.95 [m, 8H, cyclohexyl]; 4.26 [m, 2H, CHN]; 6.69-7.7.63 [m, 28H, Ph and C<sub>6</sub>H<sub>4</sub>]; 8.06 [br, 2H, NH]; δ(<sup>31</sup>P) = 11.32 [m, AgP]. Anal. Calc. for C<sub>46</sub>H<sub>40</sub>AgF<sub>3</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>: C, 60.60; H, 4.42; N, 3.07. Found: C, 60.88; H, 4.46; N, 2.76 %. Single crystals were grown by slow diffusion on n-pentane into an acetone solution of **2c**.

**Activation energies for fluxionality.** The activation energies were calculated by use of the Eyring equation and the variable temperature NMR spectra, from coalescence of several different resonances in the <sup>1</sup>H NMR spectra and also from coalescence in the <sup>31</sup>P NMR spectra. The values given are averages.

#### Xray Structure Determinations

Unusual features are described below. Please note that the complexes are chiral so a centrosymmetric space group is not possible for any of these compounds. We have attempted refinements in the higher symmetry groups but they were not successful. Refinement in the final space groups reported was successful.

**Complex 2a.** The compound diffracted weakly and anisotropic refinement of light atoms was not justified. The water molecule was approximated as an oxygen atom without hydrogens, because the “riding atom” method used for other H-atoms does not apply.

**Complex 2b.** ADDSYM suggests added symmetry and the possible new space group P-1. However, the compound is chiral so the additional symmetry is impossible. Refinement was successful in P1 but not in P-1. The compound diffracted weakly and anisotropic refinement of light atoms was not justified.