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Synthesis, Structure, and Hydrosilylation Catalysis of a Chiral A-Frame Rhodium(I) Dimer with Cis Diphosphite Ligands

Santiago Ini, Allen G. Oliver,[1] T. Don Tilley,* and Robert G. Bergman*

Department of Chemistry, University of California, and Division of Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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Summary: This paper reports the synthesis and structure of two new dinuclear chiral rhodium(I) complexes which feature a "cis-A-frame" geometry and their use as catalysts for the hydrosilylation of aromatic ketones.

Many dinuclear d^8 Rh^I, Ir^I, Pd^{II}, and Pt^{II} species exhibit "A-frame" type structures (Figure 1).[2] Complexes with two trans dppm ligands (dppm = bis(diphenylphosphino)methane), first reported by Eisenberg and co-workers,[3] are very common in rhodium(I) chemistry and have been carefully investigated.[4−6] In these complexes, the two metal centers are close to each other and each possesses a square-planar geometry. Surprisingly, analogous chiral complexes have received less attention, the first example being reported in 1995 by Ricard et al.[7] Due to the exceptional utility of rhodium(I) species in catalytic asymmetric synthesis,[8] and the unique properties of the dinuclear systems,[6,9,10] the preparation of new chiral, dinuclear rhodium complexes remains an important challenge.[11] Here we report the synthesis of a new chiral rhodium(I) dimer featuring a "cis-A-frame" geometry that is unique for this rhodium oxidation state (Figure 1) and its use as a catalyst for the hydrosilylation of ketones.

The ligands **1a** and **1b** were prepared by treating PCl_3 with (*S*)-(−)-1,1′-bi-2-naphthol followed by the appropriate resorcinol in the presence of Et_3N (Scheme 1).[12]

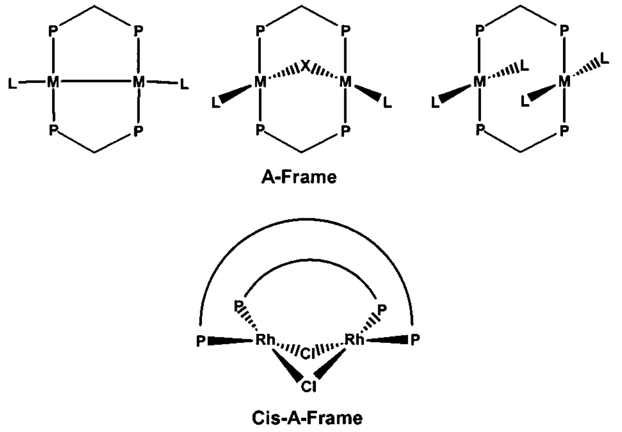

Figure 1. Schematic representations of the A-frame and cis-A-frame structures.

Reaction of **1a** and **1b** with $[Rh(COD)Cl]_2$ at room temperature results in the formation of a new complex in each case, as indicated by the appearance of a doublet of doublets in the ^{31}P NMR spectrum at δ 144.4 and 140.9 ppm ($J_{Rh-P} = 308$ Hz, $J_{P-P} = 65$ Hz) for **2a** and δ 143.8 and 140.9 ppm ($J_{Rh-P} = 308$ Hz, $J_{P-P} = 65$ Hz) for **2b**.[13] Both complexes are air-stable. The presence of two inequivalent phosphorus atoms together with the results of FAB-MS (*m*/*z* 1754 for **2a** and *m*/*z* 1814 for **2b**) suggested the presence of a dimer. The existence of the dimer in solution was confirmed by the Signer method for molecular weight determination,[14] which gave a molecular weight of 2140 for **2a**. The IR spectra of the complexes are not informative, since the low energy range characteristic of the phosphorus−oxygen bonds overlaps with other molecular frequencies.[15]

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[1] To whom questions concerning X-ray crystallography should be addressed.

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[11] Binuclear systems have become increasingly important in catalytic reactions. For example, Jacobsen and co-workers have demonstrated in the chromium-catalyzed asymmetric ring opening of epoxides that bimetallic systems can exhibit enhanced catalytic behavior relative to their monomeric analogues: Konsler, R. G.; Karl, J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 10780.

[12] These compounds were prepared by following a modified literature procedure.[25] Under a nitrogen atmosphere a solution of (*S*)-(−)-1,1′-bi-2-naphthol (2.00 g, 6.98 mmol) in 40 mL of THF at −40 °C was treated with PCl_3 (0.98 mL, 11.2 mmol) dissolved in 20 mL of THF followed by Et_3N (2.93 mL, 21.0 mmol). The white suspension was stirred at room temperature for 4 h. Filtration and evaporation of the solvent under reduced pressure left the crude naphtholatochlorophosphite as a white solid in 91% yield ($^{31}P\{^1H\}$ NMR (162 MHz): δ 179.0). The crude chlorophosphite was dissolved in 15 mL of THF and added dropwise to the appropriate resorcinol (1.71 mmol) dissolved in 15 mL of THF at −40 °C, and Et_3N (0.86 mL, 6.17 mmol) was subsequently added. The white suspension was stirred at room temperature for 12 h. The volatile materials were evaporated, and the resulting solid was dissolved in benzene and washed with 10% NaOH followed by brine and dried over Na_2SO_4. Evaporation of the solvent gave the analytically pure desired product.

[13] Complexes **2a** and **2b** were prepared by the addition of a solution of $[Rh(COD)Cl_2]_2$ (128 mg, 0.260 mmol) dissolved in 6 mL of CH_2Cl_2 to a solution of the respective ligand (0.52 mmol) dissolved in 6 mL of CH_2Cl_2. After the mixture was stirred for 1 h, the volatile materials were evaporated and the resulting solid was washed with ether followed by ethanol.

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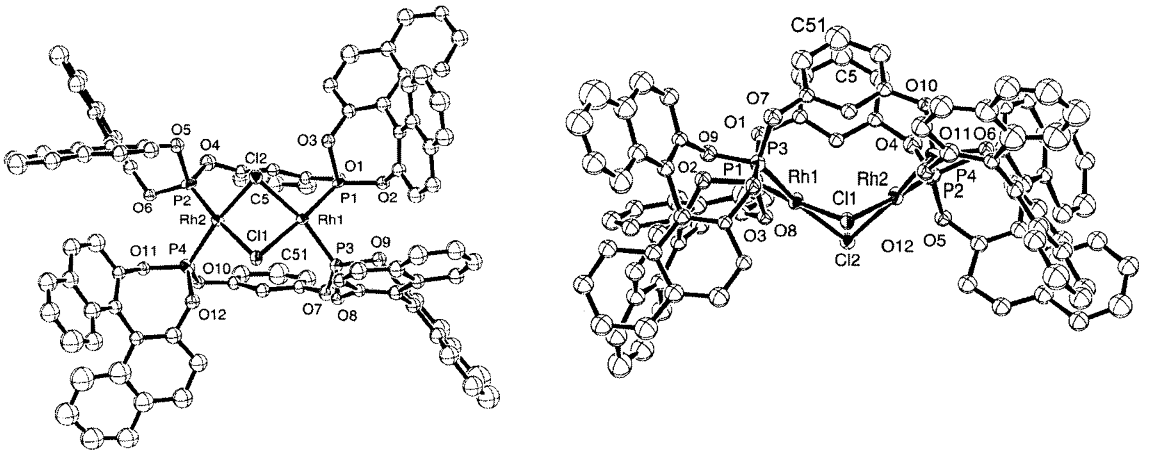
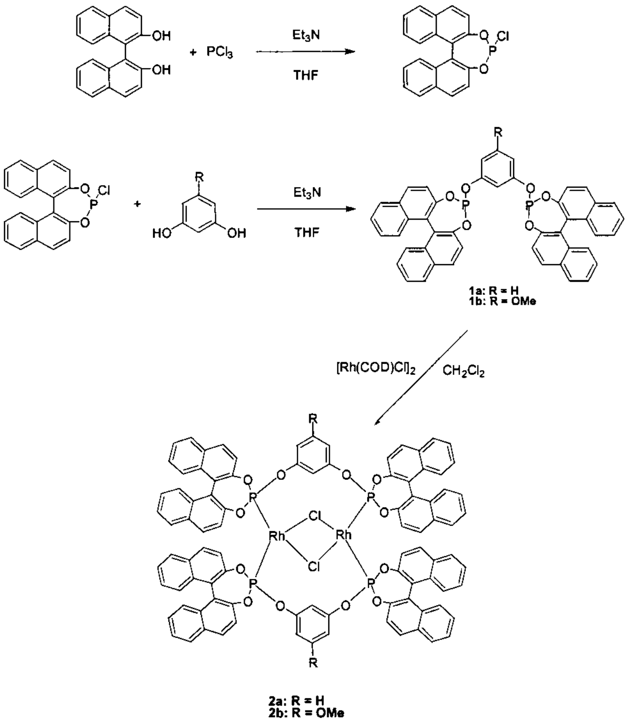


Figure 2. ORTEP view of **2a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Scheme 1. Synthesis



The structure of **2a** was established by X-ray diffraction.[16] The ORTEP view of complex **2a** is shown in Figure 2. In the crystal structure, each rhodium atom exhibits square-planar geometry (Table 1) and is bonded to two bridging chlorides and one phosphorus atom of each of the two bridging ligands. In contrast to the well-known A-frame structure, the phosphorus atoms are coordinated in a cis configuration. The complex has pseudo-2-fold rotation symmetry, with the axis centered between the chlorides (Figure 2). The distances between the phosphorus atoms of each ligand (P1−P2 = 5.480(6) Å and P3−P4 = 5.471(6) Å) are considerably larger than the distances between the phosphorus atoms bonding to a single rhodium (P1−P3 = 3.170(6) Å and P2−P4 = 3.159(6) Å). The long distance between the two phosphorus atoms in the ligand seemingly prohibits the formation of a monomeric chelating species. The Rh-(μ-Cl)$_2$Rh folding angle of 110.9° is more pronounced than those reported for analogous olefin and carbonyl complexes (116−124°).[17−22] The Rh−Rh distance of 3.103(2) Å is quite similar to those reported by Eisenberg and Kubiak for the A-frame systems[3] but shorter than that in the bimetallic rhodium complex ([Rh$_2$(nbd)$_2$(et,ph-P4)](BF$_4$)$_2$) reported by Stanley and co-workers (5.505 Å).[10] Although the ORTEP view hints at a possible interaction between the phenyl rings of the two bridging ligands, they are neither parallel to each other (24.6°)[15] nor exceptionally close, save for a contact

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2a

(a) Bond Lengths			
Rh(1)−P(1)	2.155(4)	Rh(2)−P(2)	2.148(4)
Rh(1)−P(3)	2.156(4)	Rh(2)−P(4)	2.157(4)
P(1)−P(2)	5.480(6)	P(2)−P(4)	3.159(6)
P(1)−P(3)	3.170(6)	P(3)−P(4)	5.471(6)
Rh(1)−Cl(1)	2.407(4)	Rh(2)−Cl(1)	2.418(4)
Rh(1)−Cl(2)	2.436(4)	Rh(2)−Cl(2)	2.421(4)
Rh(1)−Rh(2)	3.103(2)	C(5)−C(51)	3.423(2)
(b) Bond Angles			
Cl(1)−Rh(1)−Cl(2)	79.4(1)	Cl(1)−Rh(1)−P(1)	173.7(1)
Cl(1)−Rh(1)−P(3)	91.1(1)	Cl(2)−Rh(1)−P(1)	94.7(1)
Cl(2)−Rh(1)−P(3)	170.4(2)	P(1)−Rh(1)−P(3)	94.7(2)
Cl(1)−Rh(2)−Cl(2)	79.5(1)	Cl(2)−Rh(2)−P(2)	92.3(1)
Cl(1)−Rh(2)−P(4)	93.8(1)	P(2)−Rh(2)−P(4)	94.4(2)
Rh(1)−Cl(1)−Rh(2)	80.1(1)	Rh(1)−Cl(2)−Rh(2)	79.4(1)

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[16] Complex **2a** crystallizes as yellow columnar crystals from a CH$_2$Cl$_2$/hexane solution with a small amount of β-pinene. The crystals have the formula C$_{92}$H$_{56}$Cl$_2$O$_{12}$P$_4$Rh$_2$·3CH$_2$Cl$_2$ and a formula weight of 2008.86. They are orthorhombic, with a = 16.077(1) Å, b = 21.208(2) Å, c = 26.034(2) Å, and V = 8876(1) Å^3, space group $P2_12_12_1$ (No. 19), and Z = 4. X-ray diffraction measurements were made on a Bruker SMART diffractometer with a CCD area detector; Mo Kα radiation (λ = 0.710 69 Å), and a graphite monochromator. The data were collected at a temperature of −120 ± 1 °C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3°, counted for a total of 15.0 s per frame. Data were integrated to a maximum 2θ value of 46.5°. The data were corrected for Lorentz and polarization effects. An empirical absorption correction ($T_{\max}$ = 0.96, $T_{\min}$ = 0.59) based on a comparison of redundant and equivalent reflections was applied using SADABS (36 422 reflections measured). The final cycle of full-matrix least-squares refinement was based on 5851 observed reflections ($I > 3.00\sigma(I)$); R = 0.059.

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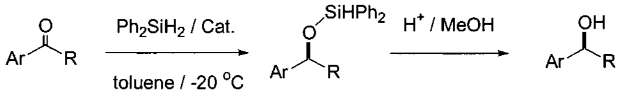
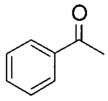
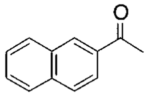
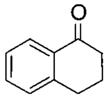
Table 2. Asymmetric Hydrosilylation of Ketones Catalyzed by 2a and 2b[b]



Cat.	ketone	yield (%)[a]	ee (%)[a]
2a		41	20
2b		60	6
2a		35	17
2a		58	4

[a] Determined by GC. [b] Conditions: ketone, 0.17 M; Ph_2SiH_2, 0.27 M; catalyst, 1.7 mM (1%); 1,3,5-trimethoxybenzene as internal standard in toluene at −20 °C, 5 days.

between C5 and C51 (3.42(2) Å) at the periphery of the molecule. In each ligand, the orientation of the planes of the binaphthol group lies approximately parallel to the C_2 axis and the other is nearly perpendicular to it, as seen in Figure 2. The molecular chirality of these complexes is created by the four binol-based phosphite moieties, which provide a unichiral[23] character to the complex.

To test the catalytic activity and the asymmetric induction of the catalyst, we investigated its reactivity in the hydrosilylation of aromatic ketones. We chose this reaction due to increasing utilization of rhodium and chiral phosphorus ligands in this process.[24] Complex **2a** displayed high catalytic activity in the hydrosilylation of acetophenone in toluene-d_8 at room temperature. Typically, 100% yield of the silyl ether was obtained after 2 h, as determined by NMR; a lower yield of alcohol was obtained after hydrolysis (52%). The catalyst remains unchanged after the reaction (on the basis of ^{31}P NMR spectroscopy). To determine whether the dimer dissociates into monomeric species under the catalytic conditions, a crossover experiment was carried out. A mixture of **2a** and **2b** was used in the hydrosilylation reaction. Analysis of the ^{31}P NMR spectrum of the mixture after the reaction showed no new resonances supplementing the two doublets of doublets corresponding to homodimers **2a** and **2b**; i.e., there was no evidence for the formation of a mixed dimer bearing one ligand with R = H and one with R = OMe. In the reaction carried out at low temperature, complexes **2a** and **2b** show catalytic activity in the hydrosilylation of acetophenone derivatives, although low enantiomeric excesses were obtained (Table 2). The poor enantioselectivity of catalyst **2b** could indicate that the methoxy substituents render the phenyl side of the complex inaccessible, forcing the reaction to occur on the opposite side, which is less crowded. We are currently examining the hydrosilylation mechanism in more detail.

In summary, we report here the synthesis and structure of the first rhodium(I) dimer having a "cis-A-frame" structure and its use as a catalyst for the reduction of ketones by hydrosilylation. Efforts to improve the enantioselectivity and to apply these catalysts to other processes are currently in progress.

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Supporting Information Available: Text giving details of the preparation and procedures and spectroscopic and analytical data for compounds **1** and **2** and ORTEP diagrams and tables giving crystallographic data for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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