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Chiral memory effects in catalytic hydrogenations with dynamically chiral ligands

J.W. Faller *, Philip P. Fontaine

Yale University, P.O. Box 208107, New Haven, CT 06520-8107, United States

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Abstract

The low barrier for interconversion of chiral conformations of the dynamically chiral 2,2′-biphenyl ligand $NMe_2C_6H_4C_6H_4PCy_2$ is raised upon coordination. The individual enantiomers of the planar chiral arene-tethered complex $Ru(\eta^6{:}\eta^1\text{-}NMe_2C_6H_4C_6H_4PCy_2)Cl_2$ (**1**), however, do not undergo racemization readily. A second source of chirality, such as a chiral diamine, can be included by conversion of **1** into a dicationic analogue $[Ru(\eta^6{:}\eta^1\text{-}NMe_2C_6H_4C_6H_4PCy_2)((1S,2S)\text{-DPEN})](SbF_6)_2$ (**2**), which is a catalyst precursor for the hydrogenation of aryl ketones. Two epimers of **2**, R_{Ar},S,S and S_{Ar},S,S, are formed when starting from racemic **1**; this 1:1 mixture of diastereomers catalyzed the asymmetric hydrogenation of acetophenone. The enantiomerically pure diastereomers were obtained from resolved **1** and used separately to catalyze the reaction. Each diastereomer showed different selectivity, with S_{Ar},S,S-**2** being the more selective (61% ee for the hydrogenation of acetophenone). Our studies suggest that ruthenium hydride formation is accompanied by a decrease in hapticity of the η^6-arene and probable detachment of the ring from the metal. Nevertheless, the original conformational chirality of the biphenyl ligand appears to be at least partially retained during the catalysis.

Keywords: Catalysis; Memory effect; Fluxional; Ruthenium; Tether; Non-rigid

1. Introduction

The ruthenium catalyzed asymmetric hydrogenation of ketones developed by Noyori and coworkers [1–11] has emerged as a powerful method for the production of chiral non-racemic alcohols. These catalysts, which derive from complexes of the general form *trans*-$RuCl_2$(bisphosphine)(diamine) or *trans*-$RuCl_2$(phosphine)$_2$(diamine), are very active and selective for a variety of ketones [1–11]. The accepted mechanism involves a non-classical metal–ligand bifunctional catalysis, where the ancillary ligands play an active role in the reaction. Specifically, an *in situ* generated amido ligand is thought to aid in the activation of dihydrogen, and to then be involved in a proton transfer to the ketone [12–15]. There has been recent interest in systems in which the chirality of one ligand can be used to convey the chiral information to another conformationally flexible ligand [16–22]. A particularly effective case is that of $RuCl_2$(1*S*,2*S*-DPEN)(BIPHEP) where DPEN is configurationally stable diphenylethylenediamine and BIPHEP is dynamically chiral 2,2′-bis(diphenylphosphino)-1,1′-biphenyl [19].

During the course of our recent research with the planar chiral arene-tethered half-sandwich complex $Ru(\eta^6{:}\eta^1\text{-}NMe_2C_6H_4C_6H_4PCy_2)Cl_2$ (**1**) [23–25], we have found that a dicationic derivative, $[Ru(\eta^6{:}\eta^1\text{-}NMe_2C_6H_4C_6H_4PCy_2)((1S,2S)\text{-DPEN})](SbF_6)_2$ (**2**), is a catalyst precursor for the asymmetric hydrogenation of ketones under the conditions first reported by Noyori et al. [3], In **1** the configuration of the potentially dynamically chiral biphenyl ligand is locked in place by the coordination to the metal and the complex shows no propensity for racemization in solution. The dicationic complex, **2**, also retains its configuration in solution. As **2** is an 18-electron coordinately

* Corresponding author. Fax: +1 203 432 6144.
E-mail address: jack.faller@yale.edu (J.W. Faller).

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saturated species, its activation during its use in catalytic hydrogenation must involve the generation of open coordination sites to facilitate the binding of the substrate and/or the formation of one or more hydrides. Our initial investigations have suggested that the loss of the η^6-arene ligand during the catalysis furnishes the necessary binding sites, though this occurs with a high degree of retention of the ligand chirality. This report details the preliminary characterization and catalysis with **2**, with an emphasis on the analysis of the chiral elements of the complex and their respective effects on the catalytic selectivity.

2. Results and discussion

The dicationic complex **2** was prepared by the abstraction of the two chloride ligands of **1** with $AgSbF_6$ in the presence of the chiral diamine (1*S*,2*S*)-DPEN. The resulting dicationic complex is a robust air stable yellow solid that can be readily handled on the bench top. When starting from racemic **1**, two diastereomers in a 1:1 ratio are formed owing to the fixed chirality of the diamine ligand (Scheme 1). The ^{1}H NMR spectrum shows that, for both of the two isomers ($R_{Ar}S,S$-**2** and $S_{Ar}S,S$-**2**), each of the four amino protons are diastereotopic at room temperature. The protons attached to the chelate ring are readily identified by the larger coupling constants (~12 Hz) from geminal coupling on the NH_2 groups and *trans* couplings between the axial NH's and CH's, whereas the η^6-arene ring protons generally have couplings of up to ~7 Hz. The broadening from the quadrupolar ^{14}N provides identification of the protons attached to nitrogen. Cross peaks in a COSY experiment provided the connectivity, as is indicated for the R_{Ar},R,R diastereomer, which is shown in Fig. 1. Identification of which amino protons are *syn* or *anti* to the dimethylamino substituents was not straightforward, although one might speculate that an upfield shift would be expected for the axial NH proton (H_{1a}) owing to the ring current from the η^6 ring.That the four amino protons are diastereotopic is indicative fairly strong bonds between the diamine and the ruthenium center. A dynamic process involving hemilability of the diamine would eliminate the diastereotopic nature of the amino protons in the

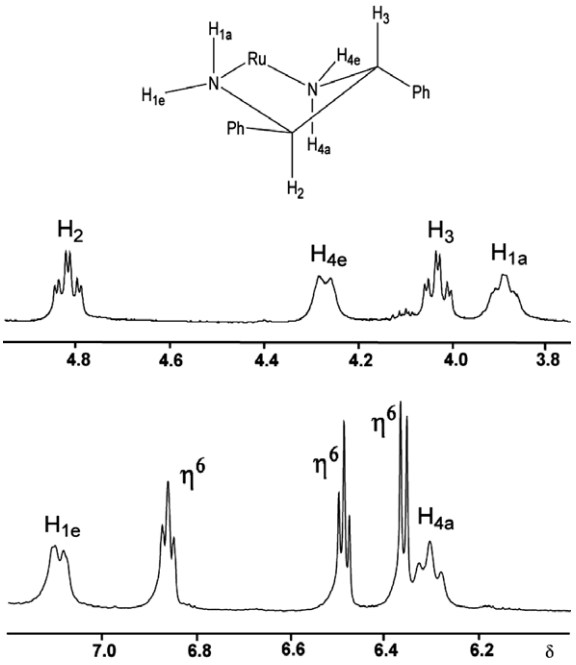
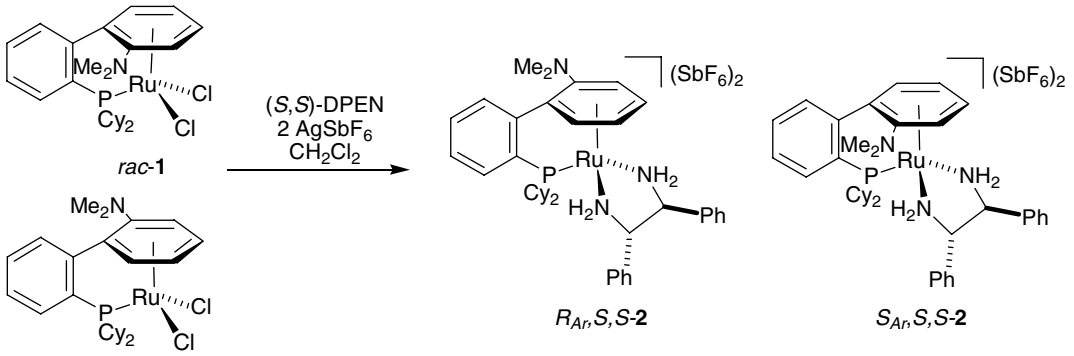


Fig. 1. Regions of the ^{1}H NMR Spectrum of R_{Ar},R,R-2.

NMR spectrum. Specifically, the dissociation of one of the amino ligands, which would result in a hemilabile 16-electron species, would at least make the two protons on the free amine equivalent owing to the fast N–C bond rotation and an umbrella-flip processes. That is, dissociation should allow for the facile interconversion of the two amino protons since the abovementioned dynamic processes would be expected to be fast relative to the NMR timescale upon the generation of a free amine and subsequent recoordination. The observance of four diastereotopic amino protons therefore precludes a hemilabile process that is fast on the NMR timescale.

Along these lines, the observance of the four diastereotopic amino protons reflects the differences in the two sides of the chelate. This is an effect of the planar chirality of the complex; more specifically, one of the amino groups is bound *syn* with respect to the NMe_2 moiety on the η^6-arene ring, while the other is *anti*. Here again, the rigidity of the complex is illustrated, as the aforementioned



Scheme 1. Synthesis of **2**.