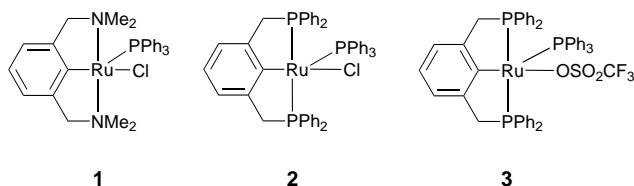


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## Hydrogen-Transfer Catalysis with Pincer-Aryl Ruthenium(II) Complexes\*\*

Paulo Dani, Thomas Karlen, Robert A. Gossage, Serafino Gladiali, and Gerard van Koten\*

Complexes of pincerlike aryl ligands such as **1–3** belong to a new class of homogeneous catalytic systems that contain a stable metal–carbon  $\sigma$  bond.<sup>[1, 2a]</sup> Such organometallic complexes have already been used in a number of metal-mediated organic transformations, for example, dehydrogenation,<sup>[2a]</sup> asymmetric allylic alkylation,<sup>[2b]</sup> asymmetric aldol condensation,<sup>[2c,d]</sup> Heck reactions,<sup>[1b]</sup> atom-transfer radical polymerization (ATRP), and Kharasch addition (ATRA).<sup>[2e,f]</sup> Additionally, the terdentate pincer ligand stabilizes complexes with unusual geometries or oxidation states.<sup>[2f–i]</sup>



Reduction by means of hydrogen-transfer reactions has recently attracted much attention because of its practical simplicity and potential use at ambient pressure.<sup>[3]</sup> Furthermore, the use of an alternative source of hydrogen may result in different reactivity patterns.<sup>[4]</sup> Coordination complexes containing bidentate ligands are normally used as catalysts in hydrogen-transfer reactions.<sup>[3]</sup> Herein we report that the pincer-type arylruthenium(II) complexes **1–3**,<sup>[5]</sup> containing the monoanionic, terdentate bis(amino)aryl  $[\text{C}_6\text{H}_3(\text{CH}_2\text{-NMe}_2)_2\text{-2,6}]^-$  (NCN) and bis(phosphanyl)aryl  $[\text{C}_6\text{H}_3(\text{CH}_2\text{-PPh}_2)_2\text{-2,6}]^-$  (PCP) ligands, are highly active catalysts for the reduction of various ketones to the corresponding alcohols with *i*PrOH as the hydrogen source and KOH as the promoter [Eq. (1)]. Representative types of ketones were chosen to evaluate the performance of **1–3** in such processes. Dialkyl (aliphatic and cyclic), alkyl aryl, and diaryl ketones were all

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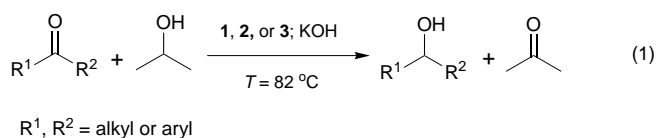










Table 1. Reduction of ketones by **1–3** with *i*PrOH/KOH as the reducing agent.<sup>[a]</sup>

Entry	Substrate	Product	Complex	Conversion [%] <sup>[b]</sup> ( <i>t</i> [h])	TOF [h <sup>−1</sup> ] <sup>[c]</sup>
1			<b>1</b>	> 98 (3.3)	1100
2			<b>2</b> <sup>[d]</sup>	> 98 (1.8)	10000
3			<b>2</b> <sup>[e]</sup>	> 98 (2.5)	900
4			<b>3</b> <sup>[d]</sup>	> 98 (1.3)	27000
5			<b>1</b> <sup>[f]</sup>	70 (44.0)	36
6			<b>3</b>	90 (0.5)	9000
7			<b>1</b>	90 (90.0)	83
8			<b>3</b>	> 98 (108.0)	100
9			<b>1</b>	90 (4.5)	1000
10			<b>3</b>	90 (1.5)	2000

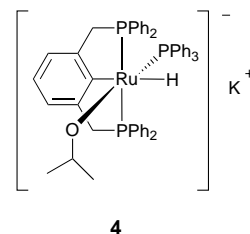
[a] The reactions were carried out on a 200-mmol scale in 200 mL of *i*PrOH under N<sub>2</sub> with [KOH]/[Ru] = 20. Unless otherwise noted, [Ru] = 0.1 mol % and *T* = 82 °C. [b] The conversion is equal to the yield of the product and was determined by gas chromatography. [c] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50 % conversion. [d] [Ru] = 0.01 mol %. [e] Reaction performed at 25 °C, [Ru] = 0.25 mol %. [f] Deactivation of the catalyst occurs.

reduced in a good to high yield by **1–3** (Table 1). The turnover frequencies (TOF) at 50 % conversion were higher with the [Ru(PCP)] complexes than with [Ru(NCN)].

In the case of cyclohexanone, more than 98 % conversion and a TOF of 1100 h<sup>−1</sup> were attained by using **1** (0.1 mol %) without removal of the acetone formed in the reaction (entry 1). The use of only 0.01 mol % of **2** or **3** under the same conditions resulted in higher TOFs of up to 10000 h<sup>−1</sup> and 27000 h<sup>−1</sup> (entries 2 and 4, respectively). These values are superior to those obtained with Ru<sup>II</sup> complexes that contain only monodentate phosphane ligands, such as [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>],<sup>[6]</sup> [RuCl(H)(PPh<sub>3</sub>)<sub>3</sub>], and [Ru(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>].<sup>[7, 8]</sup>

The experiments with **1–3** show a number of common features. Pretreatment of **1–3** with *i*PrOH containing KOH was essential for high catalytic activity. At a KOH/Ru molar ratio of 20/1, only traces of aldol products were formed.<sup>[9]</sup> Their formation increased at higher KOH concentration, as did the reaction rate. When a solution of the complexes in *i*PrOH/KOH was exposed to air before the addition of the ketone substrate, no reaction occurred, and paramagnetic Ru<sup>III</sup> complexes were formed. The rate of transfer-hydrogenation increased with increasing temperature, and the highest TOFs were obtained under reflux conditions (82 °C). However, **2** was able to reduce cyclohexanone at a reasonable rate even at room temperature (entry 3). In situ monitoring of **3** by <sup>31</sup>P NMR spectroscopy under catalytic conditions showed the absence of free PPh<sub>3</sub> or C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub> – **1,3**.

Neutral ruthenium(II) hydrido complexes have been claimed as the actual catalytic species in reductions mediated by low-valent Ru complexes.<sup>[10, 11]</sup> We have observed that when **3** is heated to reflux in *i*PrOH/KOH in the absence of a ketone substrate, a ruthenium hydrido species is formed in solution; it was assigned the ionic structure **4** on the basis of NMR spectroscopic data. Anionic ruthenium hydrido complexes have been used as catalyst precursors in the reduction of ketones by H<sub>2</sub>,<sup>[12]</sup> and their participation in hydrogen abstraction from alcohols has been proposed.<sup>[13]</sup> However, to the best of our knowledge, this is the first time that such a species was detected in the course of a hydrogen-transfer process in *i*PrOH.<sup>[14]</sup>



These observations indicate that: 1) the structural unit [Ru(PCP)PPh<sub>3</sub>] is retained in the course of the catalytic cycle, 2) a ruthenium hydride is most probably the true catalyst in this process, and 3) the ruthenium hydrido complex **4** represents a resting state of the catalyst before the addition of the substrate. We regard this species as the reservoir that delivers the actual catalyst once the substrate is added. Although this ruthenium hydrido complex does not correspond to the known [Ru(H)(PCP)PPh<sub>3</sub>],<sup>[5c]</sup> the latter may play some role in the catalysis.

In conclusion, the pincer-aryl ruthenium(II) complexes **1–3** form active catalysts in the reduction of ketones by hydrogen transfer in *i*PrOH. Under these conditions, the σ Ru–C bond is stable and the [Ru(PCP)PPh<sub>3</sub>] fragment is preserved. We are currently testing the performance of chiral Ru<sup>II</sup> complexes of pincer-aryl ligands in this reaction.

### Experimental Section

Typical procedure for the catalytic hydrogen-transfer reaction: A suspension of **3** (0.0197 g, 0.02 mmol) and KOH (10 mL, 0.2 M in *i*PrOH) in *i*PrOH (30 mL) was heated to reflux under nitrogen for 1 h. The resulting brown solution was quickly transferred to a solution of the ketone (200 mmol) in *i*PrOH (170 mL), and the mixture was subsequently heated to 82 °C. The acetone formed was not distilled off. Yields were determined by GC analysis with *n*-undecane as internal standard.

**4**: <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS): δ = −8.50 (br dt, <sup>2</sup>J(H,P) = 18, 20 Hz, 1 H, RuH), 1.20 (brs, 6 H, CH<sub>3</sub>), 3.68 (brd, <sup>2</sup>J(H,H) = 14 Hz, 2 H, PCH), 4.00 (brs, 1 H, CH–O), 4.30 (doublet of virtual triplets (dvt), <sup>2</sup>J(H,H) = 14 Hz, <sup>3</sup>J(H,P) not resolved, 2 H, CH–P), 6.50–7.60 (m, 34 H, ArH) 7.70–7.80 (m, 4 H, *o*-H of PCP); <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, 85 % H<sub>3</sub>PO<sub>4</sub>): δ = 47.31 (t, 1 P, PPh<sub>3</sub>), 71.80 (d, <sup>2</sup>J(P,P) = 19 Hz, 2 P, PCP).

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## Synthesis and Characterization of an Open-Framework Antimony(III) Phosphate: [H<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>1.5</sub>[(SbO)<sub>2</sub>(SbF)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>]\*\*

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Nanoporous aluminosilicate zeolites find technological applications in areas such as catalysis, separations, and ion exchange.<sup>[1]</sup> After Flanigen et al. reported a series of open-framework aluminophosphates (AlPO<sub>4</sub>s),<sup>[2]</sup> others successfully incorporated transition and other main group metals into open frameworks.<sup>[3]</sup> Unlike the zeolites and many AlPO<sub>4</sub>s, which are based upon corner-sharing [XO<sub>4</sub>] tetrahedra, many of the newer materials are based on other polyhedra that give rise to new topologies. For example, several open-framework tin(II) phosphates<sup>[4]</sup> were prepared in which the stereochemically active electron lone pair associated with each Sn<sup>II</sup> center leads to trigonal [SnO<sub>3</sub>] and square pyramidal [SnO<sub>4</sub>] units. One of these materials<sup>[4f]</sup> is truly nanoporous and exhibits reversible dehydration and ion-exchange properties. We therefore extended the search for open frameworks into the Sb<sub>2</sub>O<sub>3</sub>/P<sub>2</sub>O<sub>5</sub> system.

Open frameworks containing Sb<sup>III</sup> include the antimony(III) sulfides<sup>[5]</sup> and the mineral cetineite and related synthetic phases.<sup>[6]</sup> While a number of Sb<sup>V</sup> [7] and mixed-valent Sb<sup>III</sup>/Sb<sup>V</sup> [8] phosphates have been made, until recently the only known materials based solely on [Sb<sup>III</sup>O<sub>x</sub>] and [P<sup>V</sup>O<sub>4</sub>] polyhedra were condensed SbPO<sub>4</sub><sup>[9]</sup> and layered SbO(H<sub>2</sub>PO<sub>4</sub>)·H<sub>2</sub>O.<sup>[10]</sup> Layered antimony(III)fluoride phosphates have also been synthesized: KSbF<sub>2</sub>(HPO<sub>4</sub>)<sup>[11]</sup> and MSbFPO<sub>4</sub>·nH<sub>2</sub>O (M = NH<sub>4</sub>, Na, K, Rb, Cs, CN<sub>3</sub>H<sub>6</sub>, n = 0–1.5)<sup>[12, 13]</sup>, as well as a chain-type structure: CsSbF<sub>3</sub>(H<sub>2</sub>PO<sub>4</sub>).<sup>[13]</sup> The three-dimensional structure of a new Sb<sup>III</sup>-based material, NaSb<sub>3</sub>O<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>,<sup>[14]</sup> although not microporous, suggested that Sb<sup>III</sup> could be incorporated into an open framework phosphate. By using a structure-directing agent (SDA) under hydrothermal synthesis conditions<sup>[15]</sup> we synthesized the material described below.

The asymmetric unit of [H<sub>3</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>]<sub>1.5</sub>[(SbO)<sub>2</sub>(SbF)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] contains 29 crystallographically independent non-hydrogen atoms (Figure 1). As in many other open frameworks for which fluorine is used as a mineralizer,<sup>[16–19]</sup> fluorine is incorporated into the structure. This framework is based upon a network containing: 1) pseudo-octahedral [SbO<sub>5</sub>E] and [SbO<sub>4</sub>FE] units (E = lone pair), 2) pseudo-trigonal-bipyramidal [SbO<sub>4</sub>E] and [SbO<sub>3</sub>FE] units (the lone pairs of electrons occupy axial and equatorial positions in the

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