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Synthesis, characterization, and catalytic behavior of a PSiP pincer-type ruthenium(II) complex

Yong-Hua Li^{a,c,*}, Xue-Hua Ding^a, Yuan Zhang^b, Wen-Rui He^a, Wei Huang^a

^a Jiangsu Key Laboratory of Organic Electronics & Information Displays, and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications, Nanjing, 210046, People's Republic of China

^b Department of Applied Chemistry, Nanjing College of Chemical Technology, Nanjing 211189, People's Republic of China

^c Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi,

Tsukuba, Ibaraki 305-8565, Japan

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ABSTRACT

The synthesis and characterization of a cyclometalated ruthenium(II) complex [RuCl(PSiP^{Cy})] containing monoanionic, tridentate coordinating PSiP-pincer ligand [κ^3 -(2-Cy₂PC₆H₄)₂SiMe]⁻ ([PSiP^{Cy}]) are reported. Complex **3** is one of the few examples of halogenated ruthenium(II) complexes supported by the pincer-like bis(phosphino)silyl ligand. The structure of complex **3** was unambiguously determined by multinuclear NMR and single crystal X-ray analysis. This compound has also been shown to catalyze the transfer hydrogenation of ketones to the corresponding secondary alcohols efficiently with 2-propanol as the hydrogen source instead of using molecular dihydrogen gas or hazardous reducing agents (e.g., NaBH₄ and LiAlH₄), and ^tBuOK as the base.

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Pincer ligands incorporating two phosphine arms and a central carbon atom have attracted a substantial amount of interest since the initial investigations of this type of ligands by Shaw et al. [1]. Such PCP ligands have been found to support a number of exciting catalytic and stoichiometric transformations [2,3]. Recently, several variations of the central donor atom Z(Z=N, S) have been explored [4]. However, the "PSiP" pincer-like transition metal complexes have rarely been reported [5]. Silvl ligands have strong σ -donating characters and show a stronger trans influence than do commonly used ligands in transition metal chemistry [6]. Silvl ligands would make an electron-rich metal center and coordinatively unsaturated species by its strong trans-labilizing effect. We have been working on the reaction of chelating disilyl compounds with group 10 transition metal complexes and reported a number of unusual complexes bearing chelating silyl ligands [7]. The above-mentioned unique character of the silyl ligands strongly affected the formation of such complexes. Therefore, "ancillary" silyl ligands would provide transition metal complexes having unique reactivities useful for catalysis. However, simple silyl ligands usually have high reactivity and can not stay on transition metals as "ancillary" ligands. Incorporation of silyl group in a multidentate ligand framework would be a useful strategy to make "ancillary" silyl ligands. There are two types of approaches for this kind of silyl ligands: 1) incorporation of one silyl group at the center of multidentate framework [8], and 2) attachment of two silyl groups in a rigid multidentate framework. The second approach is so far rather limited and the xanthsil ligand by Tobita and co-workers is a representative example [9]. Recently, transition metal complexes bearing other tridentate N₂Si, and S₂Si type ligands as well as tetradentate P₃Si and S₃Si type ligands have also been reported [10].

Hydrogen transfer catalysis is an attractive protocol for the reduction of ketones to alcohols in both academic and industrial research. The use of a hydrogen donor (e.g., 2-propanol) instead of using molecular dihydrogen gas or hazardous reducing agents (e.g., NaBH₄ and LiAlH₄) has a potential advantage in terms of mild reaction conditions and excellent regioselectivity [11].

Some pincer-like transition metal complexes of Ru, Ir, and Rh have been found to be active catalysts in (a)symmetric hydrogen transfer reactions of polar groups (e.g., ketones and imines) [11]. In recent years, a number of studies appeared on the successful use of cyclometalated ruthenium(II) complexes containing tridentate, cyclometalated PCP⁻, and NCN⁻ as catalyst precursors in hydrogen transfer reactions [12]. The great interest in the use of *E,C,E*-pincer ligands (*E*=N, P) arises from the remarkable stability of the corresponding metal complexes and the possibility to modulate the reactivity of the metal center by fine-tuning and control of the electronic and steric properties of the ligand framework [13].

We are interested in $[\{2-(R_2P)C_6H_4\}_2MeSi]^-$ ligands (=PSiP-R, R=Cy (cyclohexyl), ⁱPr, ^tBu), which would have high electron

^{*} Corresponding author at: Jiangsu Key Laboratory of Organic Electronics & Information Displays, and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications, Nanjing, 210046, People's Republic of China. Tel./fax: +86 25 85866396. *E-mail address:* liyhnju@hotmail.com (Y.-H. Li).

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donating property and higher rigidity than do $[(Ph_2P(CH_2)_n)_2MeSi]^$ ligands [14]. Herein we report the synthesis and structure of a rare cyclometalated ruthenium(II) complex $[RuCl(PSiP^{Cy})]$ **3** containing monoanionic, tridentate coordinating PSiP-pincer ligands $[\kappa^3-(2-Cy_2-PC_6H_4)_2SiMe]^-$ ($[PSiP^{Cy}]$), and its catalytic activity in the transfer hydrogenation of ketones with 2-propanol as the hydrogen source and ^tBuOK as the base. Dialkyl (aliphatic and cyclic), alkyl aryl, and diaryl ketones were all reduced in a good to high yield by this PSiP Ru(II) complex **3**.

Treatment of the parent tertiary silane, [PSiP]H (2) with an equimolar amount of [RuCl₂(COD)] in dry THF at ambient temperature in the presence of NEt₃ resulted in oxidative addition of the Si-H bond to the ruthenium(II) center, followed by reductive-elimination to give a Ru-(κ^3 -PSiP) complex in high yields (Scheme 1; isolated yield ca. 82%). Crystallization of compound 3 from benzene afforded X-ray quality single crystals, and its structure was unambiguously confirmed by single-crystal X-ray structure analysis (Fig. 1) [15,16]. To the best of our knowledge, complex **3** is one of the few examples of halogenated ruthenium(II) complexes supported by the pincerlike bis(phosphino)silyl ligand. Complex **3** crystallizes in the monoclinic group P-1 (Table 1). The pincer-like title compound contains two stable five-membered cyclometalated rings with the P-Ru-Si angles of 79.45(5) and 84.75(4)° (Table 2). The Ru atom is coordinated by two P atoms, one Si atom and two Cl atoms in a distorted squarepyramidal geometry, in which the silvl group occupies the apical coordination site, while the remaining phosphine arms of the [PSiP] ligand and the two bridging Cl atoms occupy basal sites. The bond distances of Ru1-Si1 and Ru1-Cl1 are 2.2729(11) and 2.4772(11) Å, respectively, which are similar to the other Ru analog with pincerlike tridentate PSiP ligand, Ru[SiMe(CH₂CH₂CH₂PPh₂)₂]Cl [14]. The two P donor atoms are almost in a cis arrangement with a P1-Ru1-P2 angle of $96.63(4)^\circ$, the methyl group on Si1 donor in **3** is positioned cis to Cl, and the P1 donor is trans to Cl1, with a P1-Ru1-Cl1 angle of 165.38(3)°. The four cyclohexane rings adopt the chair conformation and the two phenyl rings are, of course, planar, which are oriented at a dihedral angle of 79.89 (1)° (Table 2). The structure of complex 3 was also well identified by elemental analysis and multinuclear NMR.

Building on our synthetic investigations of [PSiP]-ligated metal complexes, we have begun to examine the utility of such species as catalysts in a range of substrate transformations. In particular, we are interested in exploring how the substitution of Si for C in a rigid tridentate ancillary ligand framework influences metal-mediated reactivity, given the strong electron donating and *trans*-labilizing abilities of Si. Reduction by means of hydrogen-transfer reactions has recently attracted much attention because of its practical simplicity and potential use at ambient pressure. Furthermore, the use of an alternative source of hydrogen may result in different reactivity patterns [11]. Recently, several Ru(II) PCP⁻, NCN⁻, CNC⁻, and CNN⁻ pincer complexes have been shown to catalyze the transfer hydrogenation of ketones [17], and it has been proposed that the Ru-C *o*-bond plays an important role in the formation of long-lived, catalytically active species [18]. In this context, we became interested in surveying the catalytic activity of ruthenium(II) complex





Scheme 1. Synthetic route of organosilicon complex Ru-(κ^3 -PSiP) (3).



Fig. 1. The structure of 3, showing the coordination environment of Ru atom. The hydrogen atoms and solvate molecules are omitted for clarity.

[RuCl(PSiP)] (3) containing monoanionic, tridentate coordinating PSiPpincer ligand in the transfer hydrogenation of ketones, employing basic ⁱPrOH as the hydrogen source. In contrast to the phosphinosilyl complexes previously reported by Stobart and co-workers that feature an aliphatic or benzylic ligand backbone, we anticipated that the reduced conformational flexibility associated with the rigid o-cyclohexyl backbone of [PSiP] could provide enhanced stability and selectivity in metal-mediated substrate transformations and the representative catalytic data obtained in our preliminary survey are summarized in Table 3. When employing 0.2 mol% of **3** with 5 mol% of KO^tBu at 80 °C, high conversion to the corresponding secondary alcohols was observed for several ketone substrates, including diaryl, dialkyl, and alkyl/aryl ketones (Scheme 2). The reactions are slow at room temperature but proceed at good rates at 80 °C and the catalyst system hydrogenates aliphatic ketones faster than aromatic ones. Although conditions have not yet been optimized, it is obvious that the activity of **3** as a catalyst in this reaction is comparable to that observed with phosphine and amine aryl pincer ruthenium complexes, but lower than the aminoalcohol based systems of Noyori [19]. As is the case for most metal-catalyzed transfer hydrogenation processes conducted in ⁱPrOH, lower conversion

Table 1

Crystal data and structure refinement parameters for 3.

Structure parameters	3
Empirical formula	C98H134Cl2P4Ru2Si2
fw	1765.15
Cryst syst	Triclinic
Space group	P − 1
a (Å)	14.607(3)
b (Å)	17.402(4)
c (Å)	20.728(4)
lpha (°)	109.35(3)
β (°)	97.94(3)
γ (°)	106.94(3)
<i>V</i> (Å ³)	4592.2(2)
Ζ	2
T (K)	293(2)
F (000)	1864
$ ho (\text{g cm}^{-3})$	1.277
Absorption coefficient (mm ⁻¹)	0.527
Goodness of fit on F ²	0.981
Total no. of data collected	14030
No. of unique data	11011
R indexes $[I > 2\sigma(I)]$	$R_1 = 0.0400$
	$wR_2 = 0.0976$
R (all data)	$R_1 = 0.0535$
	$wR_2 = 0.1040$
Largest diff map hole and peak (e $Å^{-3}$)	1.05 and -0.45

R1 = $\sum F_o |-|F_c|| / \sum -F_o |$; wR2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Selected	bond	lengths	and	angles	for	3
Selected	DOLLO	lenguis	dIIU	angles	101	э.

Ru(1) - P(1)	2.2373(11)	Ru(1) - Cl(1)	2.4772(11)
C(1) - Si(1)	1.869(4)	Ru(1) - P(2)	2.2367(12)
Si(1) - Ru(1)	2.2729(11)	P(1) - C(13)	1.853(3)
Si(1) - C(2)	1.900(4)	P(1) - Ru(1) - P(2)	96.63(4)
C(2) - Si(1) - C(8)	105.04(15)	P(1) - Ru(1) - Si(1)	84.75(4)
P(2) - Ru(1) - Si(1)	79.45(5)	Cl(1)-Ru(1)-Si(1)	90.94(4)
Cl(1) - Ru(1) - P(1)	165.38(3)	Cl(1) - Ru(1) - P(2)	96.30(4)
C(2) - Si(1) - Ru(1)	108.97(12)	C(1) - Si(1) - Ru(1)	118.93(13)
C(1) - Si(1) - C(2)	105.94(17)	C(3) - C(2) - C(7)	118.9(4)

Table 3

Transfer hydrogenation of ketones.

Entry	Catalyst	Substrate	Time (h)	Conversion (%)
1	3	Acetophenone	6	87
2	3	p-Methyl acetophenone	6.5	84
3	3	Benzophenone	8	85
4	3	2-Heptanone	5.5	90
5	3	Cyclohexanone	4	92
6	3	Cyclopentanone	3	94

was observed in the absence of KO^tBu as base. The preformed Ru complex **3** was similarly inactive for transfer hydrogenation of cyclohexanone in the absence of added KO^tBu, although 94% conversion was obtained when using 5 mol% KO^tBu along with 0.2 mol% **3** (entry 6, Table 3). Furthermore, these data show that the stability provided by the chelate ligand, and the potential for electronic/coordinative unsaturation are possible reasons for the activity observed. These preliminary results establish [PSiP]Ru complexes as a promising class of precatalysts for transfer hydrogenation. Further mechanistic studies of this reaction, as well as catalytic studies featuring these and other [PSiP] derivatives, are currently in progress.

In this contribution, convenient access to an Ru-(κ^3 -PSiP) complex with the bulky ligand $[\kappa^3 - (2 - Cy_2 PC_6 H_4)_2 SiMe]^-$ has been established from [RuCl₂(COD)]. We report the synthesis and preliminary coordination chemistry studies of the new coordinatively unsaturated group 8 pincer-like complex supported by the bis(phosphino)silyl ligand $[\kappa^3-(2-Cv_2PC_6H_4)_2SiMe]^-$ ([Cv-PSiP]⁻), as well as a preliminary investigation of the catalytic utility of [PSiP]Ru species in the transfer hydrogenation of ketones. The pincer-like ruthenium(II) complex 3 has been found to display high catalytic in the reduction of various ketones to the corresponding alcohols with ⁱPrOH as the hydrogen source and KOBu^t as the promoter. Under these conditions, the Ru-Si σ bond is stable and the [Ru(PSiP)Cl] fragment is preserved. The isolation of free 'pincer' type bis(phosphino)silyl ligands has opened new and easy synthetic routes to a variety of complexes with wide scope for functionalization and catalyst optimization and tuning. The synthesis of other 'pincer' complexes with catalytically important metals using this methodology is under way.

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 R^1 , $R^2 = alkyl$ or aryl

Scheme 2. Transfer hydrogenation of ketones.

Appendix A. Supplementary material

CCDC-819185 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.10.022.

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