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Synthesis, structure, and catalytic behavior of a PSiP pincer-type iridium(III) complex

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ABSTRACT

The synthesis and characterization of a novel cyclometalated Iridium(III) complex [IrCl(H)(PSiP)] containing monoanionic, tridentate coordinating PSiP-pincer ligands $[\kappa^3\text{-}(2\text{-}^t\text{Bu}_2\text{PC}_6\text{H}_4)_2\text{SiMe}]^-$ ([PSiP]) is reported. Complex **(3)** is one of the few examples of bis(phosphino)silyl(hydrido)iridium(III) complexes structurally characterized by single crystal X-ray analysis. This compound has also been shown to catalyze the transfer hydrogenation of ketones to the corresponding secondary alcohols moderately with 2-propanol as the hydrogen source instead of using molecular dihydrogen gas or hazardous reducing agents (e.g., $NaBH_4$ and $LiAlH_4$), and ^{t}BuOK as the base.

Cyclometalated phosphine-based “PCP” pincer complexes of the transition-metals have been the subject of intense research since the initial investigations of this type of “PCP” ligands by Shaw et al. [1], owing to the remarkable stoichiometric and catalytic reactivity exhibited by such complexes [2,3]. Recently, significant effort has been devoted to the synthesis of structurally and/or electronically related systems where strategic alterations have been introduced to the pincer ligand architecture, including variation of the central and peripheral donor fragments, as well as the ancillary ligand backbone [4]. However, the “PSiP” pincer-like transition metal complexes have rarely been reported [5]. Although metal–silicon chemistry is well-precedented across the transition series, relatively little attention has been given to the incorporation of silyl donor fragments into the framework of a preformed tridentate and tetradentate ancillary ligand. Silyl ligands have strong σ-donating characters and show a stronger trans influence than do commonly used ligands in transition metal chemistry [6]. Silyl ligands would make an electron-rich metal center and coordinatively unsaturated species by its strong trans-labilizing effect. Therefore, “ancillary” silyl ligands would provide transition metal complexes having unique reactivities useful for catalysis. We have been working on the reaction of chelating disilyl compounds with group 10 transition metal complexes and obtained a number of unusual complexes bearing chelating silyl ligands [7]. Over the course of the research, we found simple silyl ligands usually have high reactivity and cannot 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 muntidentate 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 N_2Si, and S_2Si type ligands as well as tetradentate P_3Si and S_3Si 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., $NaBH_4$ and $LiAlH_4$) has a potential advantage in terms of mild reaction conditions and excellent regioselectivity.[11] Many 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

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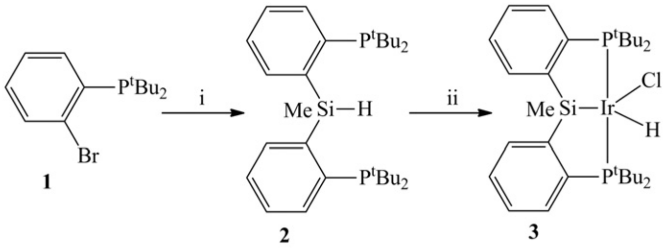
possibility to modulate the reactivity of the metal center by fine-tuning and control of the electronic and steric properties of the ligand framework [13].

We are interested in [{2-(R_2P)C_6H_4}$_2$MeSi]$^-$ ligands (=PSiP-R, R=Cy, ^{t}Bu, ^{i}Pr), which would have high electron donating property and higher rigidity than do [($Ph_2P(CH_2)_n$)$_2$MeSi]$^-$ ligands [14]. Herein we report the synthesis and structure of a novel cyclometalated iridium (III) complex [IrCl(H)(PSiP^{tBu})] **(3)** containing monoanionic, tridentate coordinating PSiP-pincer ligands [κ^3-(2-^{t}Bu$_2$PC_6H_4)$_2$SiMe]$^-$ ([PSiP^{tBu}]) (Fig. 1), and its catalytic activity in the transfer hydrogenation of ketones with 2-propanol as the hydrogen source and ^{t}BuOK as the base. Dialkyl (aliphatic and cyclic), alkyl aryl, and diaryl ketones were all reduced in a moderate yield by this PSiP Ir(III) complex **(3)**.

Treatment of the parent tertiary silane, [PSiP]H **(2)** with 0.5 equiv of [IrCl(COD)]$_2$ (cod = 1,4-cyclooctadiene) in dry toluene at 80 °C resulted in oxidative addition of the Si–H bond to the Iridium (I) center to give a 16-electron Ir(III)-(κ^3-PSiP) complex in high yields (Scheme 1; isolated yield ca. 90%) [15]. 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) [16,17]. To the best of our knowledge, there are only more than 10 examples of bis(phosphino)silyl(hydrido) iridium (III) complexes structurally characterized by single crystal X-ray analysis [14]. Complex **(3)** crystallizes in the monoclinic group P2$_1$/c (Table 1). The pincer-like title compound contains two stable five-membered cyclometalated rings with the P–Ir–Si angles of 85.92(3) and 85.70(4) °. The Ir atom is coordinated by two P atoms, one Si atom, one Cl atom and one H atom in a distorted square-pyramidal geometry, in which the silyl group occupies the apical coordination site, while the remaining phosphine arms of the [PSiP] ligand, the Cl and H atoms occupy basal sites. The bond distances of Ir1-Si1 and Ir1-Cl1 are 2.2668(9) and 2.3994(8) Å, respectively, which are similar to the other Ir analogue with pincer-like tridentate PSiP ligand, Ir(H)[SiMe($CH_2CH_2CH_2$ PPh_2)$_2$]Cl [14]. The two P donor atoms are almost in a *trans* arrangement with a P1-Ir1-P2 angle of 161.99(2) °, the methyl group on Si1 donor in compound **(3)** is positioned *trans* to hydrido group, and cis to Cl, with a Cl(1)–Ir(1)–H(52) angle of 163.0(13)°. The two phenyl rings are, of course, planar, which are oriented at a dihedral angle of 89.49 (2)° (Table 2). ^{1}H NMR spectroscopy of compound **(3)** showed the Ir-H signal as triplets with small ^{2}J(P,H) value of 14 Hz at around −23 ppm suggesting a *cis* relationship of the H and the two P atoms.



Reagents: (i) n-BuLi, CH_3SiHCl_2; (ii) [IrCl(COD)]$_2$.

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

Based 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 [18]. Recently, several Ru(II) PCP$^-$, NCN$^-$, CNC$^-$, and CNN$^-$ pincer complexes have been shown to catalyze the transfer hydrogenation of ketones [19], and it has been proposed that the metal-C σ-bond plays an important role in the formation of long-lived, catalytically active species [20]. In this context, we became interested in surveying the catalytic activity of iridium(III) complex [Ir(H)Cl (PSiP)] **(3)** containing monoanionic, tridentate coordinating PSiP-pincer ligand in the transfer hydrogenation of ketones, employing basic ^{i}PrOH as the hydrogen source. When employing 0.2 mol% of compound **(3)** with 5 mol% of KO^{t}Bu at 80 °C, moderate conversion to the corresponding secondary alcohols was observed for several ketone substrates, including diaryl, dialkyl, and alkyl/aryl ketones (Scheme 2). Although conditions have not yet been optimised, it is obvious that the activity of compound **(3)** as a catalyst in this reaction is comparable to that observed with phosphinosilyl complexes that feature an aliphatic or benzylic ligand backbone, and we found that reduced conformational rigidity associated with the flexible *o*-tertbutyl backbone of [PSiP] could provide moderate stability and selectivity in metal-mediated substrate transformations and the representative catalytic data obtained in our preliminary survey are summarized in Table 3. The reactions are slow at room

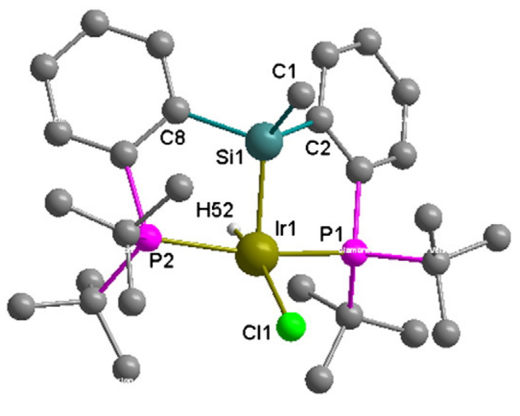


Fig. 1. The structure of **3**, showing the coordination environment of Ir atom. The hydrogen atoms are omitted for clarity.

Table 1
Crystal data and structure refinement parameters for **3**.

Structure parameters	3
Empirical formula	$C_{29}H_{48}ClIrP_2Si$
fw	714.35
cryst syst	monoclinic
space group	P 21/c
a (Å)	12.291(3)
b (Å)	15.050(2)
c (Å)	16.500(3)
α (°)	90.00
β (°)	98.57(3)
γ (°)	90.00
V (Å^3)	3017.8(11)
Z	4
T(K)	153(2)
F(000)	1440
ρ (g cm^{-3})	1.572
absorption coefficient (mm^{-1})	4.675
goodness of fit on F^2	0.941
total no. of data collected	21955
no. of unique data	6935
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0217$ $wR_2 = 0.0435$
R (all data)	$R_1 = 0.0263$ $wR_2 = 0.0441$
largest diff map hole and peak (e Å^{-3})	0.099 and −0.515

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