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Synthesis and characterization of stable tripodal silyl iron and nickel complexes

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ABSTRACT

The synthesis and reactivity of a series of iron and nickel complexes supported by tris(phosphino)silyl ligand (o-$(Ph_2P)C_6H_4)_3SiH$ (**1**) have been explored. Iron hydrido complex (o-$(Ph_2P)C_6H_4)_3SiFeH(PMe_3)$ (**2**) was generated by combination of **1** with $Fe(PMe_3)_4$. **1** reacted with $FeMe_2(PMe_3)_4$ delivered five-coordinate paramagnetic Fe(II) species (o-$(Ph_2P)C_6H_4)_3SiFeMe$ (**3**). **1** reacted with $Ni(PMe_3)_4$ in THF at room temperature afforded Ni(0) complex (o-$(Ph_2P)C_6H_4)(o$-$(Ph_2P)C_6H_4)_2(\eta^2$-(Si-H))$Ni(PMe_3)$ (**4**), whereas the oxidative addition product (o-$(Ph_2P)C_6H_4)_3SiNiH$ (**5**) was obtained by heating $Ni(PMe_3)_4$ and **1** in toluene at 80 °C for 20 h. The nickel halide complexes (o-$(Ph_2P)C_6H_4)_3SiNiX$ (X = Cl (**6**), Br (**7**), I (**8**)) were synthesized by combination of Cl_2MeSiH, EtBr, or CH_3I with **4**. Reaction of **1** with $NiMe_2(PMe_3)_3$ produced Ni(II) complex (o-$(Ph_2P)C_6H_4)_3SiNiMe$ (**9**). The molecular structures of complexes **2**, **5** and **6** were determined by X-ray single crystal diffraction.

1. Introduction

In past decades, chelate silyl ligands have emerged as a strategy for forming stable silyl metal complexes. These complexes might be the key intermediates in the catalytic processes [1–5]. Multidentate ligands, such as tridentate pincer ligand (o-$Ph_2PC_6H_4)_2SiMeH$, have been explored by several groups [6–12] and the tetradentate tripodal silyl ligands also attract much attention [13–15]. The tetradentate silyl ligand, $(Ph_2PCH_2CH_2)_3SiH$, designed by Stobart and co-workers has established a precursor "triPSiH" for forming cage-like Rh and Ir complexes [16,17]. Compared with this flexible ligand, the rigid tetradentate phosphorus silyl ligands, (o-$R_2PC_6H_4)_3SiH$ (R = Ph, *i*-Pr), pioneered by Peters exhibited an excellent effect for N_2 binding when installed with several late transition metals, such as Fe [18–20], Co [19], Ni [21], Ir [19] and Ru [22]. Furthermore, some weakly coordinated ligands, such as CH_2Cl_2, Et_2O, toluene and H_2, have been successfully installed to the Pt center [23]. The transition metals (Rh and Ir) carbonyl complexes supported by the rigid framework have been explored by Nakazawa group [24,25].

Recently, we reported the synthesis and characterization of a series of Ni, Co, and Fe complexes bearing a tridentate bis(phosphino)silyl ligand ((o-$Ph_2PC_6H_4)_2SiMeH$, [PSiP]-H). The hydrido iron(II) complex $[PSiP]Fe(H)(PMe_3)_2$ was found to be an excellent catalyst for hydrosilylation of aldehydes and ketones under mild condition [12]. In order to expand our exploration from tridentate to tetradentate ligands in this field, we present our recent research on installing several late transition metals on the tripodal ligand, ((o-$Ph_2P)C_6H_4)_3SiH$ (**1**), to afford a series of silyl metal complexes. The reactivity of these complexes has been explored. It is of interest to synthesize various Fe and Ni complexes with [Si–M–H] (M = Fe, Ni) moieties via Si–H bond activation. The resulting hydrido metal complexes might be employed in different catalytic processes, such as the reduction of unsaturated compounds.

2. Results and discussion

2.1. Preparation of complexes (o-$(Ph_2P)C_6H_4)_3SiFeH(PMe_3)$ (**2**) and (o-$(Ph_2P)C_6H_4)_3SiFeMe$ (**3**)

When **1** was treated with $Fe(PMe_3)_4$ in toluene, the color of the reaction mixture gradually changed from yellow-brown to orange and a great amount of yellow powder precipitated. After the volatiles were evaporated and the residue was washed with diethyl ether, the resulting hydrido iron(II) complex **2** was isolated in 77% yield (Scheme 1). In the IR spectrum of complex **2**, the stretching band of the Fe–H bond was found at 1967 cm^{-1}. In the ^1H NMR spectrum of complex **2**, the signal of the hydrido hydrogen was found at −15.00 ppm as a tdd (triplet of doublets of doublets) peak

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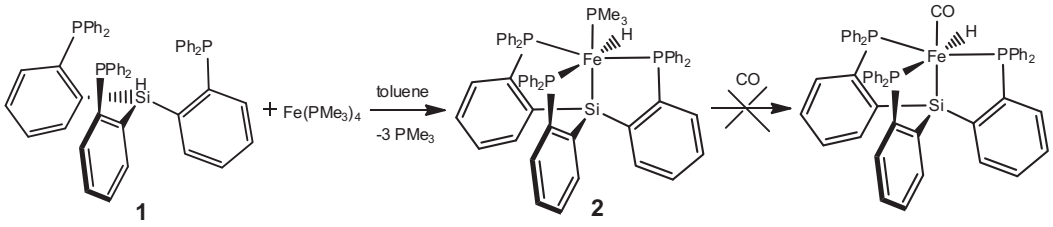


Scheme 1. Hydrido silyl iron(II) complex **2**.

with the coupling constants of $^{2}J_{PH}$ = 79.4, 78.8 and 10.8 Hz, respectively. In the ^{31}P NMR spectrum of complex **2**, three sets of signals (2:1:1) were observed at 82.0, 76.9, 5.3 ppm assigned to symmetric two –PPh_2, the third PPh_2 group opposite to the hydrido hydrogen, and the PMe_3 ligand.

X-ray crystallography has confirmed a hexa-coordinate distorted octahedral geometry of **2** with Fe atom in the center (Fig. 1). [P1P2P3H100] forms the equatorial plane and [Si1Fe1P4] is in the axial direction. The PMe_3 ligand is located in the opposite site of the silicon atom. The axial angle of Si1–Fe1–P4 is 176.59(2)° deviated from 180°. The bond lengths of Fe1–P1 (2.2388(5) Å) and Fe1–P4 (2.2514(5) Å) are a little bit longer than those of Fe1–P2 (2.1971(4) Å) and Fe1–P3 (2.2258(5) Å) due to the strong *trans*-influence of the coordinated silicon and hydrido hydrogen atom.

Recently, several hydrido iron pincer complexes have been explored as catalysts for the reduction of unsaturated compounds [26–29]. Our group has also reported iron hydride for the reduction of aldehydes and ketones [12,30–31]. These results inspired us to evaluate the catalytic activity of **2** for the related reactions. We chose several aldehydes, such as benzaldehyde, *o*-chlorobenzaldehyde, *p*-chlorobenzaldehyde, *o*-fluorobenzaldehyde, as substrates and $(EtO)_3SiH$ as hydrogen source with **2** as catalyst.

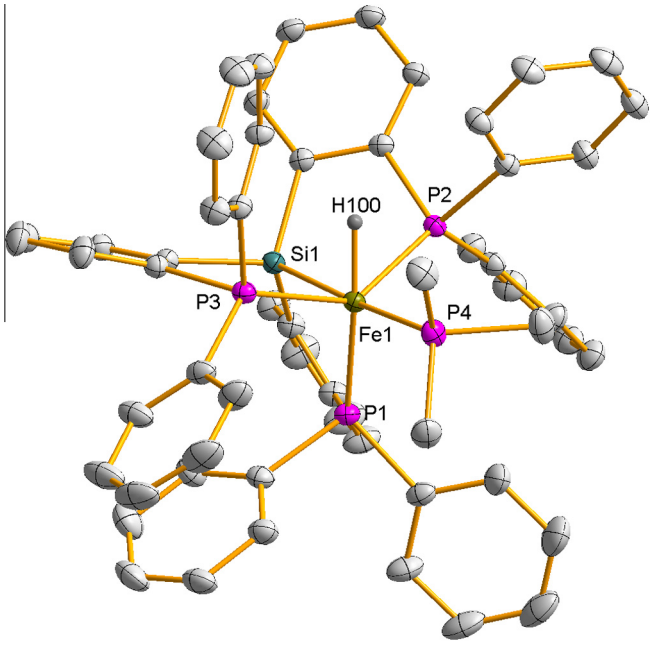
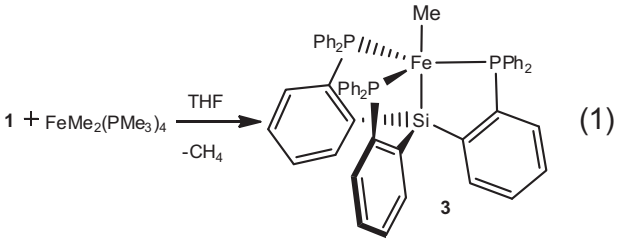


Fig. 1. ORTEP plot of complex **2** at the 50% probability level (hydrogen atoms except for Fe–H are omitted for clarity. Solvent attached has been squeezed). Selected bond lengths (Å) and angles (deg): Fe1–H100 1.42(3), Si1–Fe1 2.2718(5), Fe1–P2 2.1971(4), Fe1–P3 2.2258(5), Fe1–P1 2.2388(5), Fe1–P4 2.2514(5); P2–Fe–P3 139.43(2), P2–Fe1–P1 105.71(2), P3–Fe1–P1 106.71(2), P2–Fe1–P4 99.17(2), P3–Fe1–P4 96.78(2), P1–Fe1–P4 102.80(2), P2–Fe1–Si1 79.95(2), P3–Fe1–Si1 81.94(2), P1–Fe1–Si1 80.61(2), P4–Fe1–Si1 176.59(2).

Unfortunately, no conversion was found (determined by GC), even with 30 mol% loading or at the elevated temperature to 80 °C for a long time. The result might be explained by the steric effect of the chelating ligand. It can be seen from Fig. 2 that the iron atom is deeply buried in the nine benzene rings. This increases the stability of complex **2**. This stability was also reflected by the failed ligand replacement of PMe_3 by CO. Furthermore, the combination of **2** with excess MeI at 60 °C for 3 days did not afford any products. All of these results explain that complex **2** is very inert. It is worth mentioning that the crystals of **2** are stable in air for at least three months.



When **1** was combined with one equivalent of $FeMe_2(PMe_3)_4$ in THF at −78 °C, the solution color immediately changed from deep yellow to red-brown. Complex **3** was isolated as red powder in 79% yield (Eq. (1)). Originally, we thought the product would have a hexa-coordinate iron(II) structure, similar to that of **2**. However, the infrared spectrum data together with the paramagnetic NMR result indicate that **3** is a previously reported five-coordinate iron(II) complex, which could also be obtained from the reaction of a mixture of $FeCl_2$ and **1** with MeMgCl [20].

*2.2. Preparation of (o-(Ph_2P)C_6H_4)(o-(Ph_2P)C_6H_4)$_2$(η^2-(Si-H))Ni(PMe_3) (**4**) and (o-(Ph_2P)C_6H_4)$_3$SiNiH (**5**)*

Peters et al. previously reported the synthesis of a nickel hydride on $Si(PPh_2)_3$ by reaction of **1** with $Ni(COD)_2$ [21]. Here we report an alternative synthesis of such a complex using $Ni(PMe_3)_4$. When **1** was treated with one equivalent of $Ni(PMe_3)_4$ in THF, the color of the mixture changed from yellow to orange. After work-up, complex **4** as yellow cubic crystals was isolated in 74% yield from diethyl ether at 0 °C. Surprisingly, instead of a hydrido nickel(II)

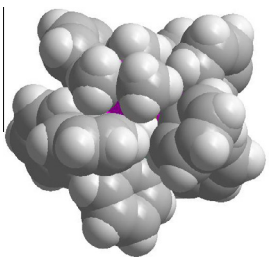


Fig. 2. Space-filling model of complex **2**.