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Communication

Iron(II) hydrides bearing a tetradentate PSNP ligand

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ABSTRACT

A new class of iron(II) hydrides based on a tetradentate PSNP ligand were synthesized and fully characterized. All the iron(II) complexes feature a folded PSNP ligand with *cis* reactive sites. The hydrido iron complex $[2\text{H}(\text{NCMe})](\text{BF}_4)_2$ is capable of catalyzing aldehyde hydroboration by pinacolborane (HBpin) and with extremely high efficiency at room temperature. Aldehydes with various functional groups are compatible.

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Iron-based catalysts have drawn much attention because they are earth abundant, cheap, and environment benign [1]. In recent years, iron-based complexes have been explored for a variety of transformations, such as hydrogenation [1,2], hydrosilylation [3–5], hydroboration [6–8], proton reduction [9], H₂ splitting [10–12], and CO₂ reduction [13]. Significantly, iron hydride species was thought to be the key intermediate in those transformations [14].

Iron complexes with tetradentate ligand have exhibited high reactivity for both stoichiometric and catalytic reactions [15–22]. For example, iron-based complexes with different types of diimino diphosphine ligands, as known as P₂N₂, have shown high reactivity in asymmetric hydrogenation and asymmetric transfer hydrogenation of ketones and imines [15,16]. The P₂N₂ type ligand is usually coordinated to the Fe center in a planar arrangement which results in two active sites *trans* to one another in an octahedral geometry (Fig. 1). Unlike P₂N₂, diphosphinodithio ligand (P₂S₂) was found to coordinate to iron center in a folded way that the two active sites are in a *cis-α* disposition. Although the reactivity of iron(II) hydrides in $[(\text{P}_2\text{S}_2)\text{Fe}(\text{H})\text{X}]^{n+}$ series (X = CO, MeCN or H[−]) has been investigated [23], they are inactive in catalytic hydroboration or hydrosilylation of organic carbonyl substrates.

By switching one of S atoms in P₂S₂ to N, we describe here a series of well-characterized iron(II) hydride complexes supported by PSNP tetradentate ligands. The combination of soft-hard donating atoms stabilizes such iron(II) hydrides for investigations

and increases their reactivity for catalysis, *i.e.*, catalytic hydroboration of aldehydes at mild conditions.

The tetradentate ligands **2** and **3** were synthesized from the same precursor, compound **1** (Scheme 1). In the presence of NaH, the reaction of 1,2-NH₂C₆H₄SH with 2-(diphenylphosphino)benzyl chloride [24,25] afforded **1** in 95% yield. Treatment of **1** with 1.1 equiv. of *n*-butyllithium and further reaction with 2-(diphenylphosphino)benzyl chloride produced **2** (yield: 70%). Condensation of **1** and 2-(diphenylphosphino)benzaldehyde in the presence of 10% *p*-toluenesulfonic acid gave ligand **3**. The ³¹P NMR spectrum of **1** exhibits a single peak at δ −17.0 (Fig. S2 in Supporting information), while NH₂ protons are shown as a broad peak at δ 4.08 in ¹H NMR spectrum (Fig. S1 in Supporting information). The ³¹P NMR spectrum of **2** displayed two phosphorus resonances at δ −15.9 and −17.2 (Fig. S4 in Supporting information). By contrast, the ³¹P signals of **3** were observed at δ −14.4 and −16.7 (Fig. S6 in Supporting information).

Treatment of the CH₂Cl₂/MeCN (1:1, v/v) solution of **2** with 1 equiv. of $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ provided bis(acetonitrile) iron complex $[\text{2}(\text{NCMe})_2](\text{BF}_4)_2$, which was isolated as pink solids in 86% yield (Scheme 2). The ³¹P NMR spectrum shows two doublets peak at δ 37.4 and 29.6 (*J*_{P-P} = 121.3 Hz) (Fig. S8 in Supporting information). Such a large ³¹P–³¹P coupling constant suggests the two P atoms are *trans* to each other.

By diffusion of diethyl ether into a MeCN solution of $[\text{2}(\text{NCMe})_2](\text{BF}_4)_2$, single crystals suitable for X-ray diffraction were obtained (Fig. 2). Crystallographic analysis $[\text{2}(\text{NCMe})_2](\text{BF}_4)_2$ reveals that the iron center is coordinated to the folded PSNP ligand and two MeCN molecules, which are in *cis* position. In the *pseudo*-octahedral

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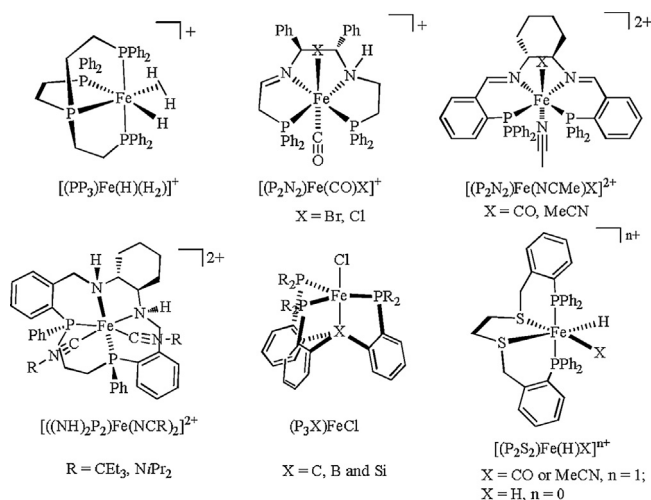
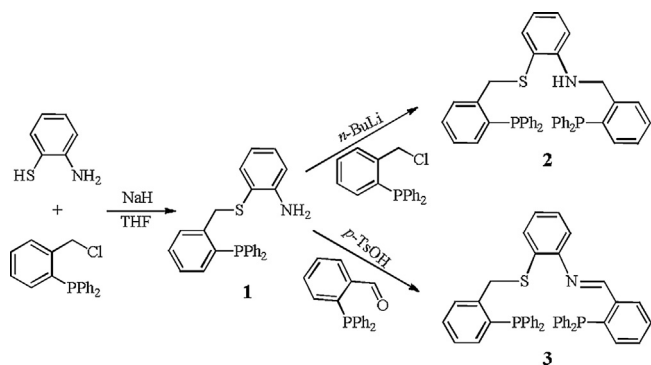
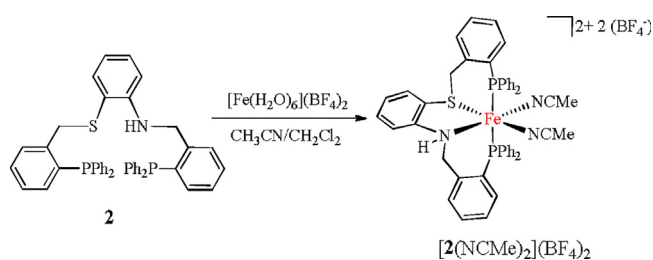


Fig. 1. Structures of iron(II) complexes with tetradentate ligands.



Scheme 1. Synthetic route of the ligands **2** and **3**.



Scheme 2. Synthesis of bis(acetonitrile) iron complex $[2(\text{NCMe})_2](\text{BF}_4)_2$.

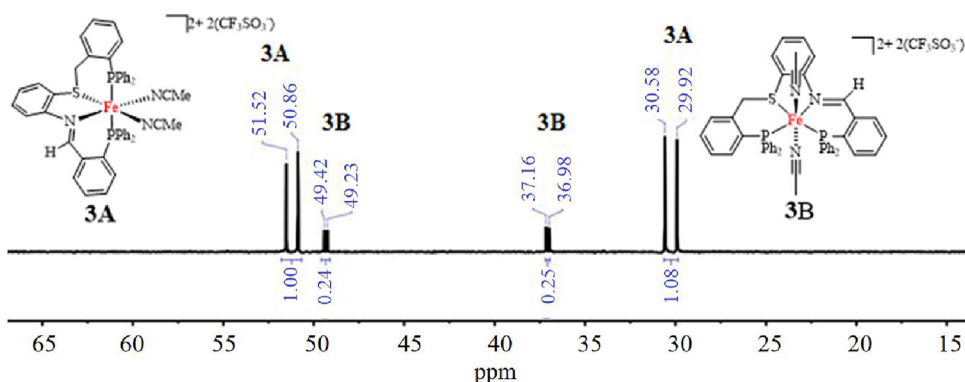


Fig. 3. ^{31}P NMR spectrum of $[3(\text{NCMe})_2](\text{CF}_3\text{SO}_3)_2$ exhibiting two isomers **3A** and **3B**.

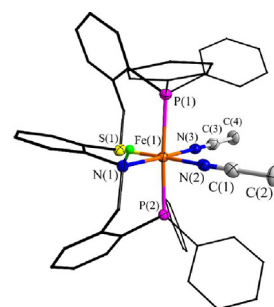


Fig. 2. Structure (50% thermal ellipsoids) of $[2(\text{NCMe})_2](\text{BF}_4)_2$. For clarity, the anion and hydrogen atoms bonded to carbon atoms are omitted. Selected distances (Å) and angles (deg.): Fe(1)–P(1) 2.3398(1), Fe(1)–P(2) 2.3062(1), Fe(1)–S(1) 2.2276(1), Fe(1)–N(1) 2.059(3), Fe(1)–N(2) 1.930(4), Fe(1)–N(3) 1.915(3), N(2)–C(1) 1.135(5), N(3)–C(3) 1.136(5), P(1)–Fe(1)–P(2) 176.42(5), N(1)–Fe(1)–S(1) 86.69(1), N(2)–Fe(1)–N(3) 91.05(1).

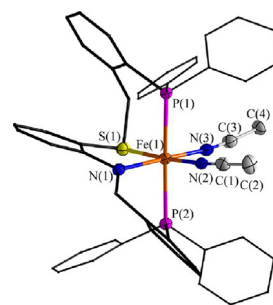


Fig. 4. Structure (50% thermal ellipsoids) of **3A**. For clarity, the anion and hydrogen atoms are omitted. Selected distances (Å) and angles (deg.): Fe(1)–P(1) 2.3448(9), Fe(1)–P(2) 2.2803(9), Fe(1)–S(1) 2.2332(9), Fe(1)–N(1) 1.986(3), Fe(1)–N(2) 1.934(3), Fe(1)–N(3) 1.915(3), N(2)–C(1) 1.132(4), N(3)–C(3) 1.135(4), P(1)–Fe(1)–P(2) 171.90(4), N(1)–Fe(1)–S(1) 85.43(8), N(2)–Fe(1)–N(3) 91.05(1).

geometry, the S and N atoms in PSNP and another two N atoms in MeCN groups are essentially coplanar. Two P atoms are *trans* to the plane with a P–Fe–P angle of $176.42(5)^\circ$, which is in agreement with the observations in the ^{31}P NMR spectrum. The structure of $[2(\text{NCMe})_2](\text{BF}_4)_2$ is very similar to $[\text{Fe}(\text{P}_2\text{S}_2)(\text{NCMe})_2](\text{CF}_3\text{SO}_3)_2$ and $\text{Fe}(\text{P}_2\text{O}_2)(\text{CO})_2$ complexes described previously [3,23,26].

Complex $[3(\text{NCMe})_2](\text{CF}_3\text{SO}_3)_2$ was prepared by the reaction of **3** with $\text{Fe}(\text{CF}_3\text{SO}_3)_2$ in $\text{MeCN}/\text{CH}_2\text{Cl}_2$ (1:1, v/v) at room temperature. The ^{31}P NMR spectrum of $[3(\text{NCMe})_2](\text{CF}_3\text{SO}_3)_2$ exhibits four sets of doublets, which are assigned as two isomers **3A** and **3B** (Fig. 3). The ratio of **3A**/**3B** is approximately 4:1. The two doublets at δ 51.2 and 30.3 with $J_{\text{P-P}} = 132.7$ Hz is indicative of two unique *trans* P atoms in **3A** [3,26]. The ^{31}P signals for **3B** at δ 49.3 and 37.1 with much

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