Synthesis of tris(dinitrogen) iron(0) complexes stabilized by organosilicon ligands

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It is known that iron dinitrogen complexes can function as highly active catalysts and often be used as an alternative of noble metal catalysts[1]. Furthermore, conversion reactions of coordinated dinitrogen molecules have also attracted much attentions[2]. Construction of low-valent and electron-rich iron centers could be considered as an efficient way to improve the reactivity of iron dinitrogen complexes. In this study, we focused on the introduction of strong \( \sigma \)-donating organosilicon ligands, and novel iron(0) dinitrogen complexes bearing two silyl ligands were was synthesized. First, complex \( 2 \) was synthesized by two-electron reduction of iron(II) disilyl complex \( 1 \) using \( \text{KCl}_2 \) under a dinitrogen atmosphere (Scheme 1). Molecular structure of \( 2 \) was determined by X-ray diffraction analysis, and the ORTEP drawing of \( 2 \) is depicted in Figure 1. In complex \( 2 \), the iron center adopts a pseudo-trigonal bipyramidal coordination geometry with three dinitrogen ligands. Subsequently, FT-IR spectra were measured to evaluate the degree of activation of dinitrogen molecules in complex \( 2 \). Absorption bands attributed to \( \text{N} \equiv \text{N} \) stretching vibration appeared at \( 1882 \text{ cm}^{-1} \), suggesting that dinitrogen molecules are strongly activated. The reactivity of complex \( 2 \) were also investigated.

\[ \begin{align*}
\text{Me}_3\text{Si}_2\text{Si} & \quad \text{THF} \\
\text{THF} & \quad \text{KCl}_2 (\text{2 equiv.}) \\
\text{cryptand} [2.2.2] (\text{2 equiv.}) & \quad \text{DME, N}_2 \\
\text{Fe} & \quad [\text{K(cryptand)}]_2
\end{align*} \]

Scheme 1. Synthesis of iron(0) dinitrogen complex \( 2 \)

Selected bond distances (\( \text{Å} \)) and angles (deg):

\begin{align*}
\text{Fe}1–\text{Si}1 &= 2.3788(8), \text{Fe}1–\text{N}1 = 1.793(3), \text{Fe}1–\text{N}3 = 1.791(2), \text{N}1–\text{N}2 = 1.129(5), \text{N}3–\text{N}4 = 1.146(4), \\
\text{Si}1–\text{Fe}1–\text{Si}1 &= 172.30(4).
\end{align*}

Figure 1. ORTEP drawing of complex \( 2 \). Hydrogen atoms and counter cations are omitted for clarity.

References