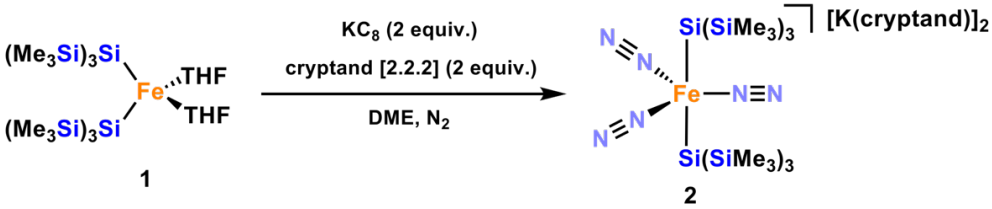
Synthesis of tris(dinitrogen) iron(0) complexes stabilized by organosilicon ligands

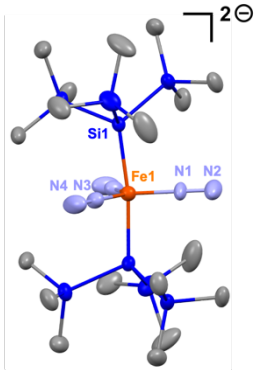
R. Ishii,[a] Y. Sunada[a] [b]

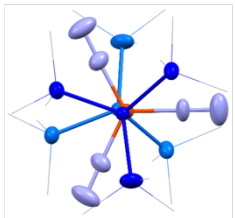
[a] *Department of Applied Chemistry, School of Engineering, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505 Japan.*
[b] *Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505 Japan.*

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 σ-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 KC_8 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 N≡N stretching vibration appeared at 1882 cm^{-1}, suggesting that dinitrogen molecules are strongly activated. The reactivity of complex **2** were also investigated.



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





Top view of complex 2

Selected bond distances (Å) and angles (deg): Fe1–Si1 = 2.3788(8), Fe1–N1 = 1.793(3), Fe1–N3 = 1.791(2), N1–N2 = 1.129(5), N3–N4 = 1.146(4), Si1–Fe1–Si1 = 172.30(4).

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

References

[1] S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2004,** *126*, 13794–13807.

[2] Y. Lee, N. P. Mankad, J. C. Peters, *Nat. Chem.* **2010**, *2*, 558–565.