



New routes to low-coordinate iron hydride complexes: The binuclear oxidative addition of H₂

Thomas R. Dugan, Patrick L. Holland*

Department of Chemistry, University of Rochester, Rochester, NY 14627, USA

ARTICLE INFO

Article history:

Received 3 February 2009

Received in revised form 3 April 2009

Accepted 3 April 2009

Available online 17 April 2009

Keywords:

Iron

Hydride

Dihydrogen

Oxidative addition

Deuteration

ABSTRACT

The oxidative addition and reductive elimination reactions of H₂ on unsaturated transition-metal complexes are crucial in utilizing this important molecule. Both biological and man-made iron catalysts use iron to perform H₂ transformations, and highly unsaturated iron complexes in unusual geometries (tetrahedral and trigonal planar) are anticipated to give unusual or novel reactions. In this paper, two new synthetic routes to the low-coordinate iron hydride complex [L^{tBu}Fe(μ-H)]₂ are reported. Et₃SiH was used as the hydride source in one route by taking advantage of the silaphilicity of the fluoride ligand in three-coordinate L^{tBu}FeF. The other synthetic method proceeded through the binuclear oxidative addition of H₂ or D₂ to a putative Fe(I) intermediate. Deuteration was verified through reduction of an alkyne and release of the deuterated alkene product. Mössbauer spectra of [L^{tBu}Fe(μ-H)]₂ indicate that the samples are pure, and that the iron(II) centers are high-spin.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The oxidative addition of H₂ to transition metal complexes to form hydride complexes is now a well known reaction [1]. It has been studied in detail in part due to chemists' desire to understand the mechanism of homogeneous catalytic transformations of H₂ such as hydrogenation [2]. The interaction of H₂ with transition metal complexes during oxidative addition is usually thought to proceed through a dihydrogen complex, followed by scission of the H–H bond to give a dihydride complex [3–7].

The standard organometallic description of the first part of this reaction is that the σ orbital of H₂ interacts with an empty d orbital (Fig. 1a) [1,8]. This model has been supported by the spectroscopic and crystallographic characterization of hundreds of dihydrogen complexes, which typically have diamagnetic transition metal sites from strong field ligands [6]. The subsequent H₂ cleavage formally oxidizes the metal by two electrons (Fig. 1b).

The Holland research group has focused its organometallic chemistry efforts on complexes that have a high-spin electronic configuration [9]. We use bulky β-diketiminato ligands that are weak-field π-donors to enforce a low coordination number. High-spin complexes like these with 5 or more d electrons have *no empty d orbitals*, so the model above does not apply unless a spin-state change or other electronic reorganization can occur.

Recent computational and experimental work has been instrumental in demonstrating the importance of spin-state changes in

organometallic chemistry [10–16]. One of our goals with β-diketiminato complexes is to discover new reactions that do not fit the usual organometallic mold and that may involve spin-state changes or use singly-occupied orbitals as acceptors (2-center/3-electron interactions). For example, alkyl complexes L^RFeCH₂CH₂R (L^R = L^{Me} or L^{tBu}, Fig. 2) readily undergo β-hydride elimination upon mild heating [17]. As shown in Scheme 1, the transient hydride complex is trapped by the addition of another alkene. The β-hydride elimination mechanism was confirmed by the use of isotope labeling, activation parameters, and an H/D kinetic isotope effect (KIE) of 2.2 [17]. Therefore, a pathway exists for high-spin complexes to undergo β-hydride elimination in the absence of *completely empty d orbitals*. Based on these ideas, we have also been interested to find examples of oxidative addition and reductive elimination, especially involving the fundamentally interesting molecule H₂.

In previous work, we isolated a dimeric hydride complex, [L^{tBu}Fe(μ-H)]₂, from the reaction of L^{tBu}FeCl with KBt₃H (Scheme 2a) [18]. This was the first iron hydride complex with a coordination number less than five, and the only other one known is its close analogue [L^{Me}Fe(μ-H)]₂ [19]. [L^{tBu}Fe(μ-H)]₂ is curious because the hydride bridges hold the two iron(II) ions exceptionally close to one another (2.624(2) Å) [18]. Despite the dimeric structure in the solid state, in solution the great steric interference between the diketiminato ligands on the two iron atoms leads the molecule to partially dissociate into monomers L^{tBu}FeH, which were observed by ¹H NMR spectroscopy [18]. Both the monomer and dimer show ¹H NMR spectra with broadened resonances over a large chemical shift range, which are characteristic of paramag-

* Corresponding author. Tel./fax: +1 585 273 3092.

E-mail address: holland@chem.rochester.edu (P.L. Holland).

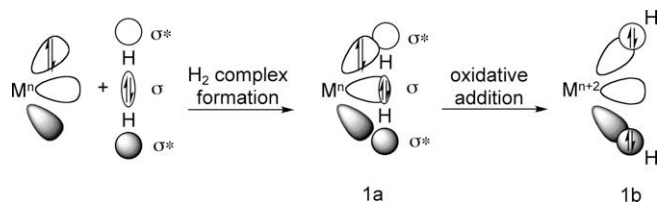


Fig. 1. Interaction of dihydrogen orbitals with metal d orbitals. In the standard model, an empty d orbital lobe forms a σ interaction with the H–H bonding orbital, and two lobes of a filled d orbital donate into the empty σ^* orbital of H_2 .

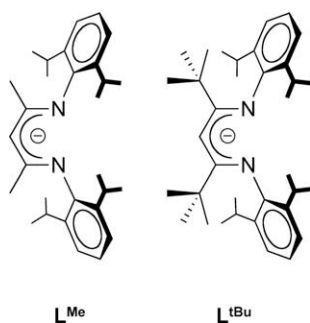


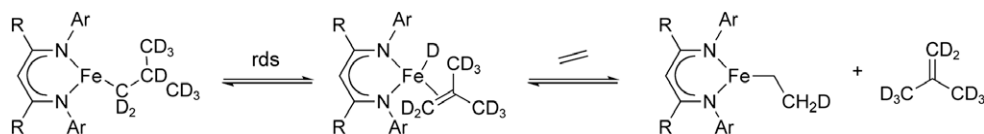
Fig. 2. β -Diketimate ligands L^R , where R indicates the substituent on the 2 and 4 positions of the C_3N_2 backbone.

netic molecules. Therefore, the available data suggested a high-spin electronic configuration for the iron(II) centers in $[L^{tBu}Fe(\mu-H)]_2$, but were not definitive because an excited electronic state might be accessed at room temperature.

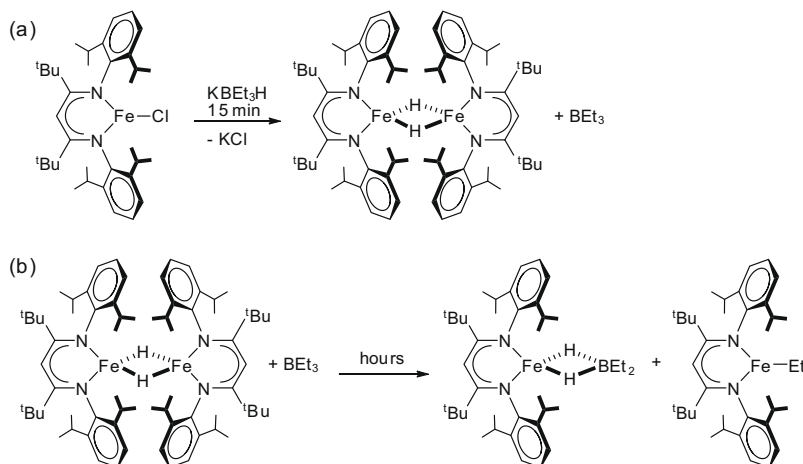
The reactivity of the dimeric hydride complex, $[L^{tBu}Fe(\mu-H)]_2$, has been examined with a range of substrates in solution [18–21]. The most relevant reaction to this work is the addition of

strong field ligands such as CO to the hydride complex, which resulted in reductive elimination of H_2 to form Fe(I) products (Scheme 3) [19]. This observation shows that the reductive elimination of H_2 from $[L^{tBu}Fe(\mu-H)]_2$ is facile in the presence of strong field ligands. However, photolysis was required to eliminate H_2 in the presence of weaker ligands. For example, photolysis of the hydride complex under N_2 atmosphere resulted in loss of H_2 and formation of the dinitrogen complex, $L^{tBu}FeNNFe^{tBu}$ [19]. The intermediate species in this process are unknown, but it is conceivable that a highly unsaturated “ $L^{tBu}Fe$ ” species is formed; then this iron(I) intermediate would be trapped by N_2 . The prospect of trapping this species with H_2 inspired us to evaluate the oxidative addition of H_2 to highly unsaturated iron(I) species in the absence of N_2 .

The hydride complex also reacts with boranes R_3B to give $L^{tBu}Fe(\mu-H)_2BR_2$ and $L^{tBu}FeR$ (Scheme 2b) [21]. While the mechanistic study of this reaction was interesting [21], the reactivity of $[L^{tBu}Fe(\mu-H)]_2$ towards boranes posed a practical problem. The synthesis of $[L^{tBu}Fe(\mu-H)]_2$ utilized $KBET_3H$ as the hydride source, giving BEt_3 as a byproduct. The desired hydride complex was the kinetic product of the reaction (formed within 15 min), but $[L^{tBu}Fe(\mu-H)]_2$ immediately began to react with the BEt_3 byproduct to give the thermodynamic product $L^{tBu}Fe(\mu-H)_2BR_2$ over several hours. Therefore, our samples of crude $[L^{tBu}Fe(\mu-H)]_2$ were invariably contaminated with the dihydridoborate complex, and the separation of the two complexes by crystallization was laborious [19]. Therefore, another motivation for the studies below was the development of a new synthetic route to $[L^{tBu}Fe(\mu-H)]_2$. Since $[L^{tBu}Fe(\mu-H)]_2$ demonstrated the ability to reductively eliminate H_2 , we decided to explore the microscopic reverse, oxidative addition of H_2 to Fe(I), as a possible synthetic route. Here we report two new independent syntheses of $[L^{tBu}Fe(\mu-H)]_2$ and provide further characterization of the complex using Mössbauer spectroscopy.



Scheme 1.



Scheme 2.

Download English Version:

<https://daneshyari.com/en/article/1327334>

Download Persian Version:

<https://daneshyari.com/article/1327334>

[Daneshyari.com](https://daneshyari.com)