

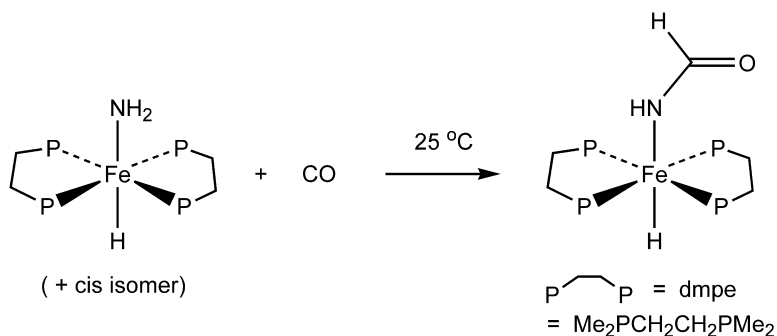
Communication

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## Synthesis of a First-Row Transition Metal Parent Amido Complex and Carbon Monoxide Insertion into the Amide N–H Bond

Daniel J. Fox and Robert G. Bergman\*

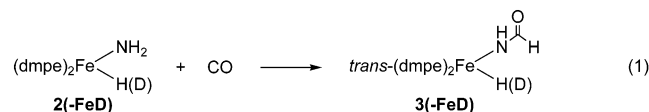
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Late transition metal complexes containing nondative metal–nitrogen and –oxygen single bonds play important roles in many biological systems and have been proposed as intermediates in numerous industrial processes.<sup>1–3</sup> Work in our laboratories has focused on the development of methods for the generation of these types of complexes and the study of their reactivity.<sup>4,5</sup> Recently, the parent amido ruthenium complex *trans*-(dmpe)<sub>2</sub>Ru(H)(NH<sub>2</sub>) (**1**, dmpe = 1,2-bis(dimethylphosphino)ethane) was synthesized, and its reactivity was studied extensively.<sup>6–8</sup> We now report the successful expansion of these efforts within group 8 to include the analogous iron amido complex, (dmpe)<sub>2</sub>Fe(H)(NH<sub>2</sub>) (**2**).<sup>9</sup> To our knowledge, this complex represents the first example of a first-row transition metal parent amido complex. This Communication describes the synthesis and structural characterization of amido complex **2** and an unusual reaction of this material in which carbon monoxide behaves as an apparent electrophile.

Treatment of *trans*-(dmpe)<sub>2</sub>Fe(H)(Cl)<sup>10</sup> with NaNH<sub>2</sub> in a THF/NH<sub>3(l)</sub> solvent mixture results in the formation of complex **2** in 63% isolated yield as an orange crystalline solid (Scheme 1). An X-ray diffraction study revealed that amido complex **2** crystallizes from pentane at –35 °C only as the *trans* isomer. Bond lengths and angles are similar to those reported for complex **1**, and the high quality of the X-ray structure provides evidence that the amide nitrogen is pyramidal.<sup>11</sup> In solution, however, complex **2** is observed by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} spectroscopy to be an equilibrium mixture of *trans* and *cis* isomers in a 4:1 ratio.<sup>12</sup>

Like its ruthenium analogue, amido complex **2** exhibits exceptional basicity. Complex **2** deprotonates weak carbon acids and undergoes H/D exchange with extremely weak acids such as toluene-*d*<sub>8</sub>.<sup>13</sup> Additionally, reaction of **2** with 1 atm of carbon monoxide in toluene results not in the expected Fe–N insertion, but instead in net insertion of CO into the N–H bond of the amide ligand to form *trans*-(dmpe)<sub>2</sub>Fe(H)(NHCHO) (**3**, eq 1) in 60% isolated yield as a yellow crystalline solid. An X-ray diffraction



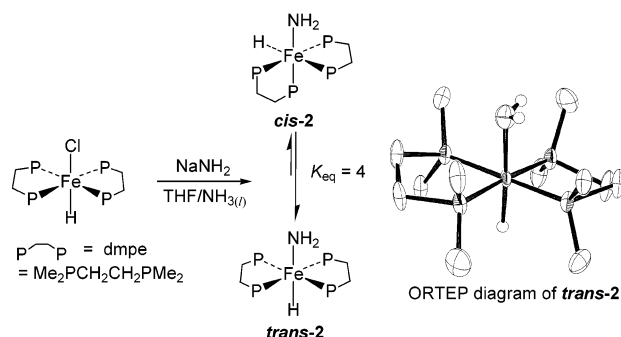
study on crystals of complex **3** grown from toluene at –35 °C confirmed its structure (Figure 1). To our knowledge, this represents the first preferential insertion of CO into a transition metal amide N–H bond rather than the M–N bond.<sup>15–20</sup> Mechanistic studies of this transformation have therefore been pursued.

Three possible mechanisms have been considered to explain the unusual CO insertion. The first involves direct attack of the amide nitrogen on the carbon of free CO to form a zwitterionic intermediate that gives the observed product (**3**) after proton transfer (Scheme 2). Because CO is a poor electrophile, we have also considered a second mechanism for CO insertion, which is illustrated in Scheme

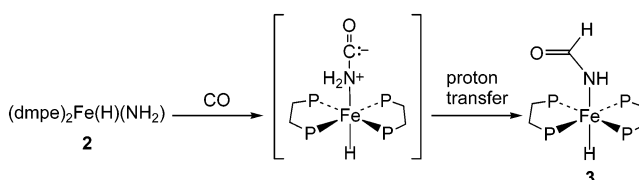


Figure 1. ORTEP diagram of *trans*-(dmpe)<sub>2</sub>Fe(H)(NHCHO) (**3**).<sup>14</sup>

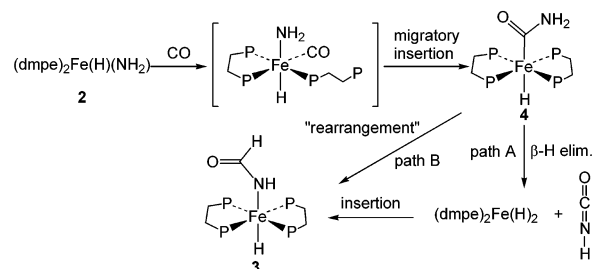
### Scheme 1



### Scheme 2

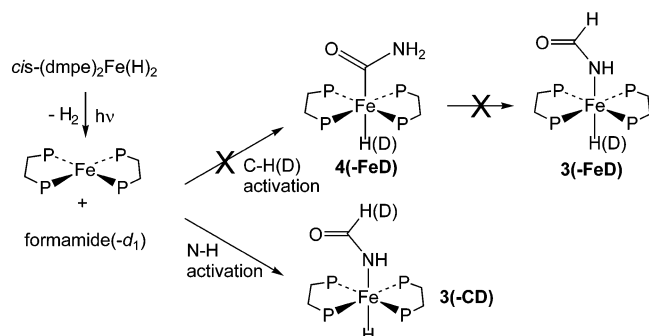


### Scheme 3

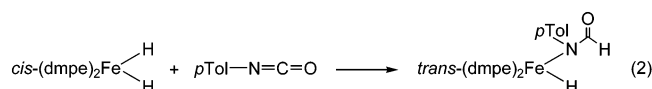


3, path A. This mechanism is initiated by dissociation of one arm of a dmpe ligand from the iron center in **2** and coordination of CO. Migratory insertion of CO into the M–N bond would yield the intermediate *trans*-(dmpe)<sub>2</sub>Fe(H)(C(O)NH<sub>2</sub>) (**4**).<sup>17,21,22</sup>  $\beta$ -Hydride elimination of isocyanic acid, followed by insertion into the iron hydride bond, would give complex **3**. This mechanism is supported by experimental results obtained both in our laboratory<sup>23</sup> and by Field and co-workers<sup>24</sup> involving the insertion of several heterocumulenes into *cis*-(dmpe)<sub>2</sub>Fe(H)<sub>2</sub> to form products similar to **3** (an

Scheme 4



example from our laboratory is shown in eq 2). However, deuterium-labeling experiments do not support the formation of isocyanic acid in the CO insertion reaction. Reaction of CO with (dmpe)<sub>2</sub>Fe(D)(NH<sub>2</sub>) (**2-FeD**) results solely in the formation of *trans*-(dmpe)<sub>2</sub>Fe(D)(NHCHO) (**3-FeD**, eq 1). Path A of Scheme 3 would result in the scrambling of the deuterium label into the carbonyl C-H bond of the product. This mechanism as illustrated can therefore be discounted.<sup>25</sup>



Although the intermediacy of the iron dihydride complex could be ruled out, we considered the possibility that M-N insertion product **4** is formed during the course of the reaction, followed by rearrangement to the observed N-bound product **3** (Scheme 3, path B). Photolysis of *cis*-(dmpe)<sub>2</sub>Fe(H)<sub>2</sub> forms the unsaturated iron(0) complex (dmpe)<sub>2</sub>Fe, which undergoes both C-H and N-H bond activation with a variety of substrates.<sup>26–28</sup> We reasoned that reaction of formamide with the iron(0) complex could indicate whether complex **4** was a likely intermediate. However, when *cis*-(dmpe)<sub>2</sub>Fe(H)<sub>2</sub> is irradiated (500 W mercury lamp, through Pyrex) in the presence of formamide in THF-*d*<sub>8</sub>, N-H activation product **3** is observed, while C-H activation product **4** is not detected (Scheme 4). Photolysis of *cis*-(dmpe)<sub>2</sub>Fe(H)<sub>2</sub> in the presence of formamide-*d*<sub>1</sub> results in the formation of complex **3-CD** (Scheme 4) as observed by <sup>1</sup>H, <sup>2</sup>H{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. While this experiment did not provide an independent route to intermediate **4**, the absence of **3-FeD** excludes the possibility of C-H (or C-D) activation in the photolysis reactions.

Finally, we considered the possible intermediacy of (dmpe)<sub>2</sub>Fe(CO), formed by reductive elimination of NH<sub>3</sub> from the amide starting material. The metal in this complex could serve to activate the bound CO toward attack at its carbon by the amide ligand of a second molecule of complex **2**, leading to the observed product. This mechanism was tested by treatment of **2** with CO in the presence of 1 equiv of (dmpe)<sub>2</sub>Fe(<sup>13</sup>CO). We observed no incorporation of <sup>13</sup>C into product **3**, indicating that this bimetallic mechanism is not operative. Considering the above observations as a whole, we conclude that our experimental evidence most strongly supports the simple nucleophilic attack mechanism illustrated in Scheme 2, although we cannot unilaterally rule out the mechanism shown in Scheme 3, path B.

In summary, we have synthesized the first example of a first-row transition metal parent amido complex. Additionally, we have uncovered a new mode of reactivity: an unusual net insertion of

CO into a metal amide N-H bond is observed according to a reaction mechanism that appears to involve direct nucleophilic attack of the amide group on the CO carbon. Further studies of the reactivity of **2** are underway.

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**Supporting Information Available:** Synthesis and characterization of all compounds, reaction details, and crystallographic data for *trans*-**2** and **3** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The hydride and the amide hydrogens were located in a difference Fourier map and included in refined coordinates.
- The ratio of the *trans* isomer to the *cis* isomer at equilibrium does not vary appreciably between -54.0 and 54.1 °C.
- However, complex **2** is less basic than complex **1**. See the Supporting Information for details of these experiments.
- The formamide moiety is disordered and occupies two sites related by approximately 180° rotation about the iron-nitrogen coordination axis. The nitrogen atom was refined with full occupancy, and the carbon and oxygen atoms of the formamide moiety (C1, C2, O1, O2) were refined with half occupancy. C2, O2, and selected hydrogen atoms have been removed for clarity.
- Ruthenium amido complex **1** was found to insert CO to yield both the C-bound product, *trans*-(dmpe)<sub>2</sub>Ru(H)(C(O)NH<sub>2</sub>), and the N-bound product, *trans*-(dmpe)<sub>2</sub>Ru(H)(NHCHO): Fulton, J. R.; Bergman, R. G., unpublished results.
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