*Articles*

# Synthesis of an Iron Parent Amido Complex and a Comparison of Its Reactivity with the Ruthenium Analog

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The iron amido complex $(dmpe)_2Fe(H)(NH_2)$ (**2**; dmpe = 1,2-bis(dimethylphosphino)ethane) has been prepared from the hydrido chloride complex using sodium amide in a liquid ammonia/THF solvent mixture. The complex is a mixture of trans and cis isomers in solution, although it crystallizes as the trans isomer exclusively. Complex **2** is a strong base, although somewhat weaker than the ruthenium amido complex *trans*-$(dmpe)_2Ru(H)(NH_2)$ (**1**). Amido complex **2** deprotonates several weak acids, and some of these deprotonations result in displacement of ammonia, while others do not. The basicity of complex **2** is further demonstrated with systems in which acidic substrates are reversibly deprotonated. Complex **2** undergoes H/D exchange with toluene-$d_8$, and it catalyzes H/D exchange between toluene-$d_8$ and several other extremely weak acids. An investigation into the mechanism of the H/D exchange and isomerization reactions of *trans*-9,10-diisopropyl-9,10-dihydroanthracene (*trans*-**4**) using **1**, **2**, and *cis*-$(PMe_3)_4Ru(H)(NH_2)$ (**5**) as catalysts demonstrates that the H/D exchange reactions proceed through formation of ion pairs, although it is surprising that displacement of ammonia is never observed. Amido complexes **1** and **2**, as well as the hydroxo complex *trans*-$(dmpe)_2Ru(H)(OH)$, are also good nucleophiles. For example, they ring-open 1,3-di-*tert*-butylaziridinone in a nucleophilic manner to form *trans*-$(dmpe)_2M(H)(XC(O)CH(t\text{-}Bu)NH(t\text{-}Bu))$ (M = Fe, X = NH; M = Ru, X = NH, O). A second example is an unusual insertion of carbon monoxide into the N−H bond of **2** to form the carboxamide complex *trans*-$(dmpe)_2Fe(H)(NHCHO)$ (**6**). Although CO is a poor electrophile, mechanistic experiments suggest that this reaction proceeds through direct attack of the amide nitrogen on the CO carbon.

## Introduction

Late-transition-metal complexes containing nondative metal−nitrogen and −oxygen single bonds have been shown to play important roles in many biological systems[1,2] and have been proposed as intermediates in numerous synthetic[3−7] and industrial processes.[5,8] The direct study of the metal−heteroatom complexes has represented a particular challenge in many of these cases, leading many groups to develop techniques for the synthesis and study of these species.[8−17] Roundhill and co-workers have demonstrated the nucleophilic and insertion chemistry of $CpRu(dcpe)(NH_2)$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) with various electrophiles.[13] Recent examples that most closely relate to our work, from the laboratories of Gunnoe and co-workers, demonstrate the strong basicity of several $TpRu(L)_2NHR$ complexes[15,16] and the nucleophilicity of (dtbpe)Cu(NHPh) (dtbpe = 1,2-bis(di-*tert*-butylphosphino)-

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ethane).$^{17}$ Through the study of late-transition-metal–heteroatom complexes, we hope to further our fundamental understanding of the factors that control their overall reactivity and the mechanisms of this reactivity. As the knowledge base of these key factors develops, a concomitant improvement of processes that proceed through similar transition-metal–heteroatom species should be achieved.

We have developed techniques for the synthesis of metal alkoxo, aryloxo, hydroxo, and amido complexes using several different metal centers (Re, Ru, Rh, Ir, Ni). In the process, we have observed many different types of reactivities involving these species including, but not limited to, insertions, deprotonations, and nucleophilic displacements/ring openings.$^{18}$

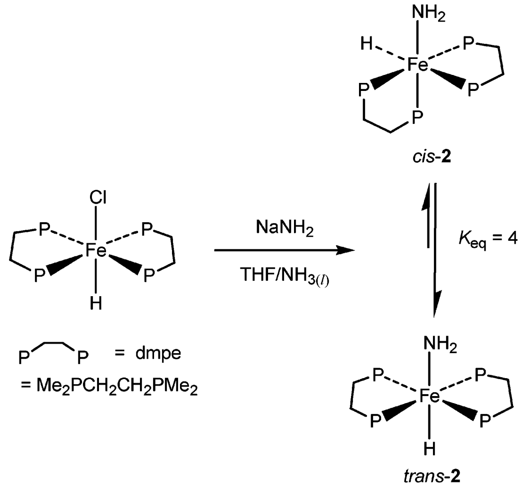
Most recently, the work in our laboratories involving transition-metal–heteroatom complexes has involved the study of a ruthenium complex with a parent (i.e. unsubstituted) amido ligand, *trans*-(dmpe)$_2$Ru(H)(NH$_2$) (**1**; dmpe = 1,2-bis(dimethylphosphino)ethane).$^{19-21}$ Complex **1** is the first structurally characterized monomeric late-transition-metal parent amido complex. The reactivity of amido complex **1** is dominated by its exceptionally high basicity;$^{20,21}$ it was found to deprotonate weak carbon acids such as fluorene and phenylacetylene and even undergo H/D exchange with extremely weak acids such as toluene and propene.$^{20}$ The p$K_a$ of a representative conjugate acid of **1**, [*trans*-(dmpe)$_2$Ru(H)(NH$_3$)][Ph$_3$C], was determined to be between 23 and 24.$^{21}$

We pursued an expanded scope of this metal–amido chemistry by the study of the first-row analog (dmpe)$_2$Fe(H)(NH$_2$) (**2**). The work presented in this paper concerns the synthesis and reactivity of **2**, which was synthesized using the techniques previously developed for the ruthenium amido complex **1**.$^{22}$ The basic and nucleophilic properties of **2** were explored, including an investigation into the mechanism of H/D exchange. Additionally, the mechanism of an unusual process involving carbon monoxide insertion into the N–H bond of complex **2** rather than the M–N bond was studied.

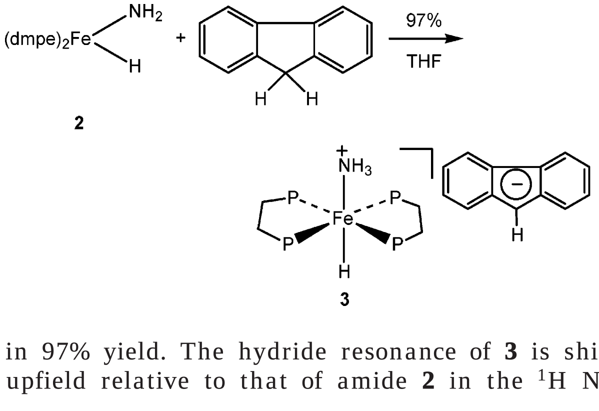
## Results and Discussion

**Synthesis of (dmpe)$_2$Fe(H)(NH$_2$) (2).** The iron hydrido chloride complex *trans*-(dmpe)$_2$Fe(H)(Cl) was synthesized as reported by Field and co-workers$^{23}$ from *cis*-(dmpe)$_2$Fe(H)$_2$. Although the dihydride complex was reported previously,$^{24}$ we developed a new synthesis that entailed the reduction of *trans*-(dmpe)$_2$Fe(Cl)$_2$ by sodium in liquid ammonia. This synthetic method was found to produce the dihydride complex in greater yield than that obtained by reduction of the dichloride complex by lithium aluminum hydride$^{24}$ and with shorter reaction time than that required for reduction by sodium in the presence of H$_2$$^{25}$ with extraction and filtration as the only necessary purification. The iron parent amido complex (dmpe)$_2$Fe(H)(NH$_2$) (**2**) was synthesized by treatment of *trans*-(dmpe)$_2$Fe(H)(Cl) with NaNH$_2$ in a THF/NH$_3$(l) solvent mixture$^{22}$ and was isolated in 63% yield as an orange crystalline solid (Scheme 1). As we have noted in a previous communication,$^{22}$ a significant difference between the iron amido complex **2** and the ruthenium amido complex **1** is that, in solution, complex **2** is a rapidly isomerizing equilibrium mixture of cis and trans isomers, while complex **1** is the pure trans species. We presume that the isomerization of **2** proceeds through a dechelation of one of the dmpe ligands, followed by a Berry pseudorotation$^{26,27}$ and rechelation of the ligand.

**Scheme 1**



**Deprotonation Reactions.** The amido complex **2** was found to deprotonate several weak carbon acids irreversibly. In some of these systems, the only observed product was the ion pair. Reaction of **2** with fluorene in THF resulted in an immediate color change to a brighter orange than that of the starting amide solution, and a small quantity of the ion pair precipitated as an orange crystalline solid. Removal of THF under reduced pressure after stirring for 3 h resulted in clean formation of [*trans*-(dmpe)$_2$Fe(H)(NH$_3$)][Fl] (**3**, Fl = fluorenide; eq 1)



(1)

in 97% yield. The hydride resonance of **3** is shifted upfield relative to that of amide **2** in the $^1$H NMR

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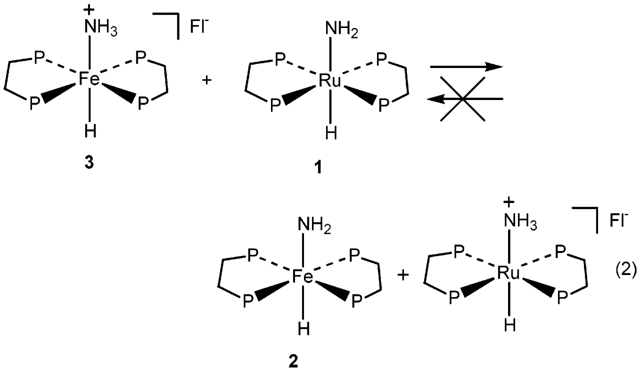
spectrum (−29.61 ppm), and the selectively decoupled $^{31}P$ spectrum shows a doublet at 74.0 ppm.[28]

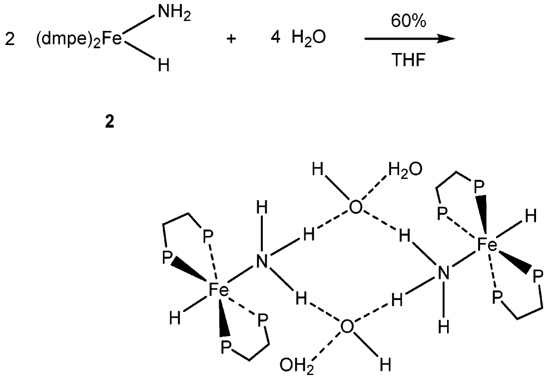
Having determined that iron amido complex **2** is strongly basic, we wished to determine its basicity relative to ruthenium amido complex **1**. Addition of **1** to ion pair **3** resulted in clean formation of **2** and [*trans*-$(dmpe)_2Ru(H)(NH_3)$][Fl]. As expected from the previous result, addition of **2** to [*trans*-$(dmpe)_2Ru(H)(NH_3)$][Fl] did not result in proton transfer, demonstrating that the ruthenium amido complex is the stronger base (eq 2). The difference in basicity between the ruthenium and iron amido complexes is most likely due to the fact that ruthenium is more electron rich than iron, as demonstrated by the lower frequency of the carbonyl stretch in $CpRu(CO)_2CH_3$ relative to $CpFe(CO)_2CH_3$.[29,30] We assume that this increased electronic density is transmitted to the attached nitrogen atom (and lone pair) through the Fe−N single bond.



**3** **1** **2**

(2)

Our group had found that addition of water to ruthenium amido complex **1** resulted in formation of *trans*-$(dmpe)_2Ru(H)(OH)$ through loss of ammonia.[31] However, when water was added to the iron amido complex **2** in THF-$d_8$, no loss of ammonia was observed by $^1H$ NMR spectroscopy. Upon addition of water to a stirred solution of **2** in THF, the solution became yellow-orange. A yellow crystalline solid, insoluble in pentane, was isolated (60% yield) and recrystallized from THF at −35 °C to give material whose chemical composition was found by combustion analysis and NMR spectroscopy to be consistent with [*trans*-$(dmpe)_2Fe(H)(NH_3)]_2$-$[OH]_2 \cdot H_2O$. The complex displayed a hydride resonance at −28.17 ppm in the $^1H$ NMR spectrum and a doublet at 70.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum. An X-ray diffraction study revealed a dimeric structure consisting of two *trans*-$(dmpe)_2Fe(H)(NH_3)$ moieties bridged by hydroxide anions through hydrogen bonding of each hydroxy oxygen atom to two ammonia hydrogen atoms; each hydroxide anion was also hydrogen bonded to a water molecule (eq 3, Figure 1). This dimeric structure is similar to that of the ion pair that was formed upon addition of *p*-cresol to the ruthenium amido complex **1**.[21] Presumably, the stability of the hydrogen-bound hydroxide-bridged dimer prohibits displacement of ammonia from the iron center. Efforts to produce the iron hydroxide complex from the hydroxide-bridged dimer by thermolysis were unsuccessful.

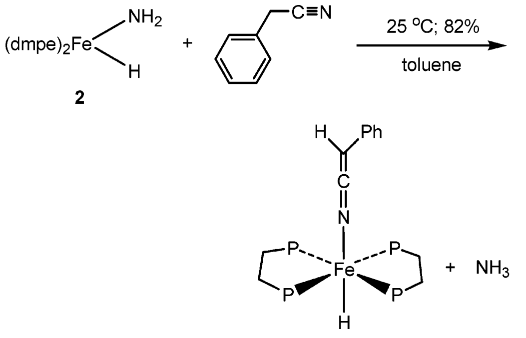


**2**

(3)

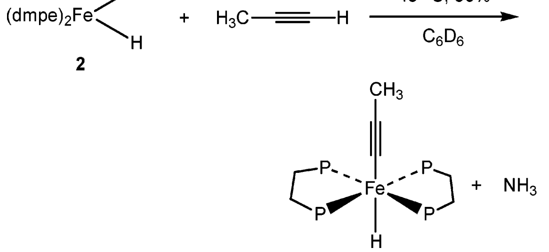
The reactions of iron amido complex **2** with fluorene and water showed that some anions are not capable of displacing ammonia from the *tran*s-$(dmpe)_2Fe(H)(NH_3)$ cation. Similar behavior was observed with the *trans*-$(dmpe)_2Ru(H)(NH_3)$ cation using some of the same anions, although the behavior of the hydroxide anion is an exception.[21] In the case of hydroxide, the hydrogen bonding present in the dimeric ion pair is probably responsible for the lack of displacement, while the fluorenide anion is too large to bind well to the iron center.

As with ruthenium amido complex **1**, there are cases in which displacement of ammonia does occur. The keteniminate complex *trans*-$(dmpe)_2Fe(H)(NCC(H)Ph)$ was formed in 82% yield upon deprotonation of phenylacetonitrile by amido complex **2** and displacement of ammonia by the keteniminate anion (eq 4). This complex is characterized by a quintet hydride resonance at −27.28 ppm in the $^1H$ NMR spectrum and a keteniminate stretch at 2111 $cm^{-1}$ in the IR spectrum.[21] Reaction of **2** with terminal alkynes also resulted in displacement of ammonia and formation of the corresponding alkynyl complexes. For example, addition of propyne to **2** in benzene-$d_6$ solution resulted in formation of the iron methylacetylide complex *trans*-$(dmpe)_2Fe(H)(CCMe)$ in 50% yield (eq 5), in addition to smaller quantities of two



**2**

(4)



**2**

(5)

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[28] The range of the proton decoupler is such that $^1H$ resonances upfield of −20 ppm are not decoupled.

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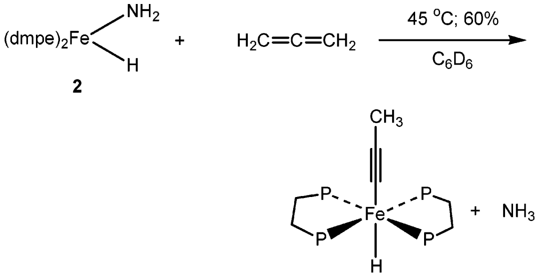
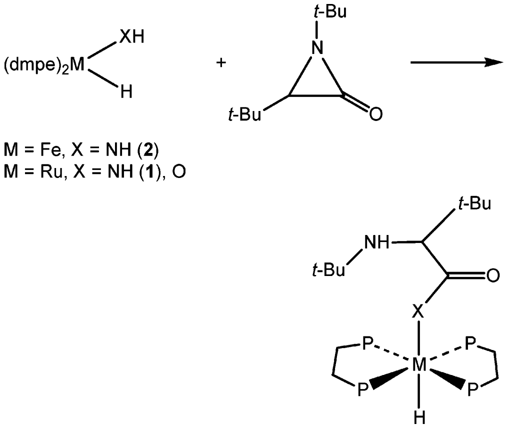
unidentified products.[32] Furthermore, complex **2** also caused isomerization of allene, such that the alkynyl complex *trans*-(dmpe)$_2$Fe(H)(CCMe) was formed in 60% yield, along with a smaller quantity of an unidentified product (eq 6). These products are analogous to those formed by similar reactions with ruthenium amido complex **1**.[21]



(6)

**Nucleophilic Reactivity of Parent Amido Complexes.** In addition to acting as bases, the amido complexes were observed to act as nucleophiles toward strained-ring systems. For example, addition of **2** to 1,3-di-*tert*-butylaziridinone[33] at 25 °C resulted in immediate formation of the ring-opened product *trans*-(dmpe)$_2$Fe(H)(NHC(O)CH(*t*-Bu)NH(*t*-Bu)) as a yellow crystalline solid in 74% yield (eq 7). The product displays a hydride quintet at −28.41 ppm in the $^1$H NMR spectrum and a complex multiplet at 71.2 ppm in the $^{31}$P{$^1$H} NMR spectrum. The complex splitting pattern in the $^{31}$P NMR spectrum is likely the result of hindered rotation of the large carboxamide ligand. Additionally, the C=O stretch in the IR spectrum of the product is significantly red-shifted relative to the C=O stretch in 1,3-di-*tert*-butylaziridinone (to 1580 cm$^{-1}$ from 1850 cm$^{-1}$), indicative of aziridinone ring opening. The observed final product was the result of nucleophilic attack on the carbonyl carbon, followed by ring opening by the breaking of the C−N bond and proton transfer to the *tert*-butyl-substituted nitrogen.



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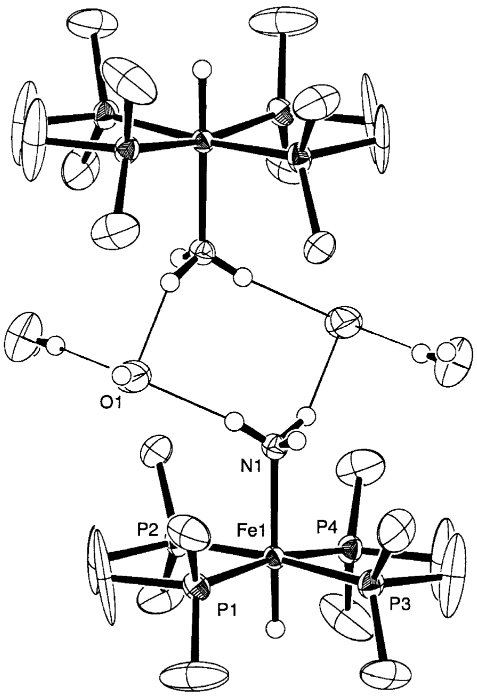
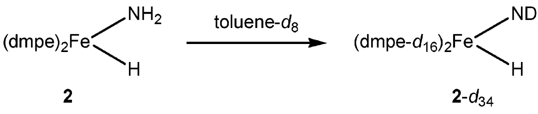


**Figure 1.** ORTEP diagram of [*trans-(dmpe)*$_2$Fe(H)(NH$_3$)]$_2$[OH]$_2$·2H$_2$O. The hydrogen atoms on the dmpe ligands have been removed for clarity. The hydride, ammonia, hydroxide, and water hydrogen atoms were located from a difference Fourier map, and their positions were refined. The structure shows the hydrogen bonds to two symmetry-related hydroxide anions (N1−O1 = 2.95 Å, N1−O1′ = 2.88 Å). Selected bond lengths (Å) and angles (deg): Fe1−N1, 2.103(5); Fe1−H33, 1.37(5); N1−Fe1−H33, 178(2); H−N1−H(average), 103. Thermal ellipsoids are shown at the 50% probability level.

Analogous reactions occurred upon addition of 1,3-di-*tert*-butylaziridinone to both the ruthenium amido complex **1** and the ruthenium hydroxo complex *trans*-(dmpe)$_2$Ru(H)(OH). With these systems, *trans*-(dmpe)$_2$Ru(H)(NHC(O)CH(*t*-Bu)NH(*t*-Bu) (61%, $\nu_{CO}$ 1582 cm$^{-1}$) and *trans*-(dmpe)$_2$Ru(H)(OC(O)CH(*t*-Bu)NH(*t*-Bu) (77%, $\nu_{CO}$ 1588 cm$^{-1}$) were isolated, respectively (eq 7). The product derived from the ruthenium amide displays a hydride quintet at −18.79 ppm in the $^1$H NMR spectrum and a multiplet at 43.8 ppm in the $^{31}$P{$^1$H} spectrum, while the hydroxide-derived product displays a hydride quintet at −23.28 ppm in the $^1$H NMR spectrum and a multiplet at 43.6 ppm in the $^{31}$P{$^1$H} spectrum. An X-ray diffraction study performed on a crystal of the ruthenium amide derived complex confirmed the connectivity of the complex, although the resolution of the structure was poor due to crystal decomposition. Reaction of the ruthenium hydroxide complex with 1,3-di-*tert*-butylaziridinone is slower than with the amido complexes, as complete conversion required 12 h.

**H/D Exchange Reactions.** The high basicity of iron amido complex **2** can also be demonstrated with substrates that **2** deprotonates reversibly. Dissolution of **2** in toluene-$d_8$ resulted in H/D exchange between the toluene methyl group and the amide hydrogens; this process also resulted in exchange into all of the bound dmpe hydrogen positions to form (dmpe-$d_{16}$)$_2$Fe(H)(ND$_2$) (**2**-$d_{34}$, eq 8). In the polydeuterated complex, only the hydride resonances (both trans and cis) remained inert to exchange. The $^2$H{$^1$H} NMR spectrum contained aliphatic resonances corresponding to the dmpe ligands



(8)

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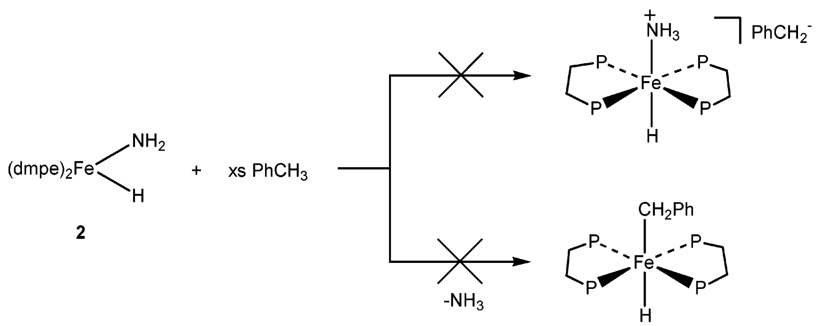
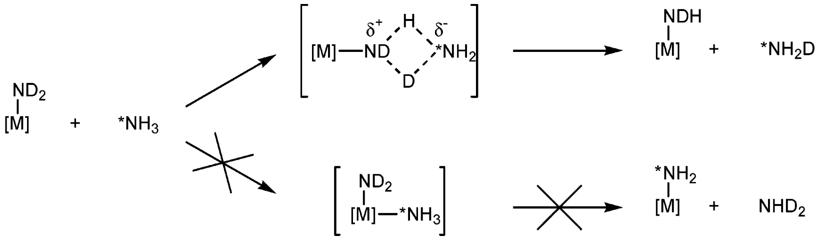
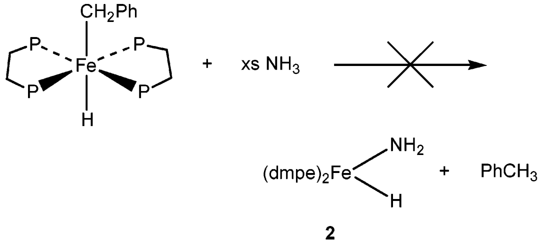
**Scheme 2**



**Scheme 3**

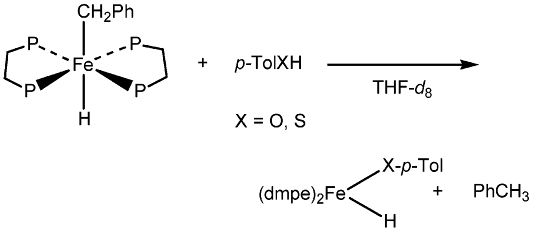


and also displayed a broad N−D resonance at −4.6 ppm; no iron-bound deuteride was observed. Although exchange was observed with toluene, neither the ion pair [*trans*-(dmpe)$_2$Fe(H)(NH$_3$)][CH$_2$Ph] nor the ammonia displacement product *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) was observed (Scheme 2). However, treatment of *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) with excess ammonia did not result in the formation of **2** (eq 9). Therefore, we cannot



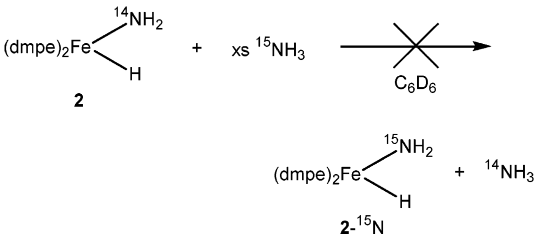
(9)

draw conclusions about the thermodynamics of the process, but a large kinetic barrier for the transformation must exist that prevents displacement in either direction. Treatment of *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) with *p*-cresol and *p*-thiocresol did result in formation of the cresolate and thiocresolate complexes, respectively (eq 10).



(10)

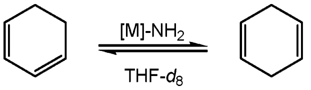
Amido complex **2** is also a catalyst for the transfer of deuterium from toluene-$d_8$ to dihydrogen, ammonia, cycloheptatriene, 9,10-dihydroanthracene, 9,10-disubstituted 9,10-dihydroanthracenes (exchange into 9,10-positions), cyanocyclopropane, and the aliphatic proton of triphenylmethane. However, unlike the ruthenium amido complex **1**, complex **2** does not catalyze H/D exchange between toluene-$d_8$ and propene.[21] This observation is consistent with our conclusion derived from proton-transfer studies that the iron amido complex is less basic than its ruthenium analog (vide supra). Although **2** is a catalyst for H/D exchange between toluene-$d_8$ and ammonia, treatment of **2** with $^{15}$N-labeled ammonia did not result in incorporation of $^{15}$N into **2** (eq 11). This result indicated that deuterium



(11)

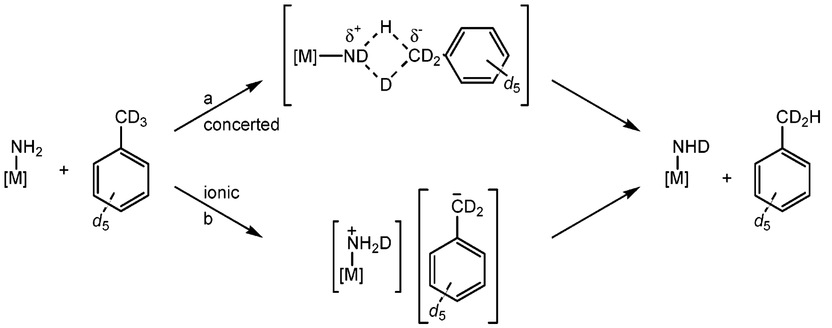
exchange into ammonia was achieved through an acid/base mechanism rather than associative exchange of the nitrogen ligand (Scheme 3). Although exchange of deuterium into the complex's dmpe ligands was observed, the amido complex **2** did not catalyze H/D exchange between toluene-$d_8$ and free dmpe or the dmpe ligands of *trans*-(dmpe)$_2$Fe(H)(Cl), indicating that the exchange of deuterium into the dmpe ligands of **2** probably occurred in an intramolecular fashion.

**Catalytic Isomerization Reactions.** Displacement of ammonia was not observed in any H/D exchange reactions of very weak acids, consistent with two possible mechanisms: (a) exchange occurred via a concerted mechanism and ion pairs were not formed or (b) ion pairs were formed, but the anion that was generated failed to displace the ammonia from the metal center (Scheme 4). We observed that our amido complexes catalyzed (also without displacement) the isomerization of 1,3-cyclohexadiene to an equilibrium mixture of 1,4- and 1,3-cyclohexadiene (eq 12) and the H/D exchange

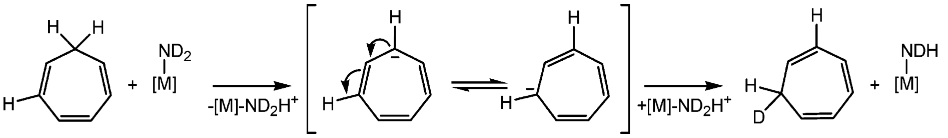


(12)

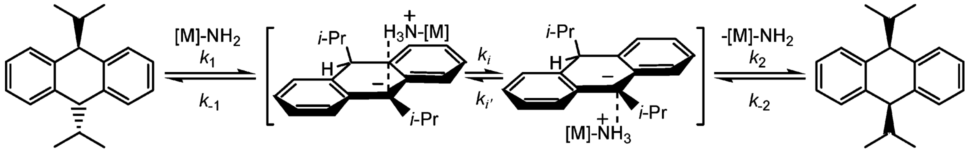
**Scheme 4**



**Scheme 5**



**Scheme 6**



*trans*-**4** *cis*-**4**

between toluene-$d_8$ and cyclohexadiene, 9,10-dihydroanthracene, and cycloheptatriene. Deuterium incorporation into all hydrogen positions of cycloheptatriene also implied that an isomerization had taken place (Scheme 5; presumably the isomerization of 1,3-cyclohexadiene occurs in a similar manner).

The observation of these rearrangements suggests that formation of an ion pair with some mobility of the two ions is the more likely mechanistic pathway. We reasoned that if the H/D exchange reactions occurred via a concerted (or very tight ion pair) mechanism (Scheme 4, path a), isomerization of 9,10-disubstituted-9,10-dihydroanthracenes might not be expected to occur, while ion pair formation (Scheme 4, path b) could be expected to lead to isomerization to the thermodynamically favored isomer.[34] *trans*-9,10-Diisopropyl-9,10-dihydroanthracene (*trans*-**4**) was prepared according to literature procedures,[35] and the trans geometry was confirmed by comparison to previously reported NMR data.[36] When a catalytic quantity of amido complex (**1**, **2**, or *cis*-$(PMe_3)_4Ru(H)(NH_2)$ (**5**)) was added to *trans*-**4** in benzene-$d_6$ solution, isomerization to the thermodynamically favored *cis*-**4** was observed (Scheme 6).[34] The isomerization of *trans*-**4** to the cis isomer necessitates removal of a proton from one face of the molecule and reprotonation on the opposite face. We surmised that comparison of the isomerization rate with the rate of H/D exchange could give an indication as to how closely the mechanisms of the two processes were related. Additionally, it could be possible to determine if H/D exchange was faster in one isomer than in the other.

**Table 1. Conversion and H/D Exchange Data for Reactions with *trans*-4 and *cis*-4**

| entry | catalyst | substrate | $k$ ($M^{-1}$ $s^{-1}$) | conversn, % | amt of H, % | |
|---|---|---|---|---|---|---|
| | | | | | cis | trans |
| 1 | 60% **5** | *trans*-**4** | $2.18 \times 10^{-3}$ | | | |
| 2 | 60% **5** | *trans*-**4**-$d_2$ | $7.2 \times 10^{-4}$ | 21 | 47 | 6.5 |
| | | | | 62 | 54 | 7.7 |
| | | | | 87 | 56 | 10 |
| 3 | 5% **1** | *trans*-**4**-$d_2$ | | 62 | 43 | 9.9 |
| | | | | 100 | 37 | |
| | | *cis*-**4**-$d_2$ | | | 18 (20 h) | |
| 4 | 5% **2**-$d_{34}$ | *trans*-**4** | | 20 | 91 | 94 |
| | | | | 65 | 87 | 90 |
| | | | | 90 | 86 | 75 |
| | | | | 100 | 79 | |
| 5 | 10% *t*-BuNHLi,[a] 45 °C | *trans*-**4**-$d_2$ | | 51 | 46 | 1.0 |
| | | *cis*-**4**-$d_2$ | | | 6 (15 h) | |

[a] 2 equiv of *t*-$BuNH_2$ was added as a hydrogen source.

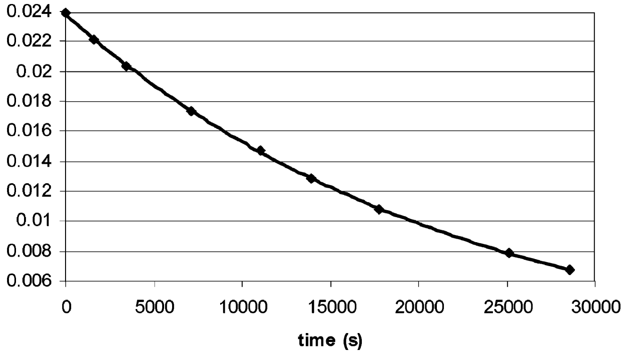


**Figure 2.** Kinetic plot showing first-order decay of *trans*-**4** using **5** as catalyst. Initial concentrations: 25 mM *trans*-**4**, 21 mM **5**, 25 °C.

Isomerization of *trans*-**4** to the cis isomer using **5** as catalyst in benzene-$d_6$ was found to be first order in both catalyst and substrate with an average rate constant of $k = (2.18 \pm 0.11) \times 10^{-3}$ $M^{-1}$ $s^{-1}$ (Figure 2, Table 1). When the isomerization was performed using *trans*-**4**-$d_2$ (deuterated in the 9- and 10-positions) as the substrate and 5 mol % of the bis-dmpe ruthenium amido

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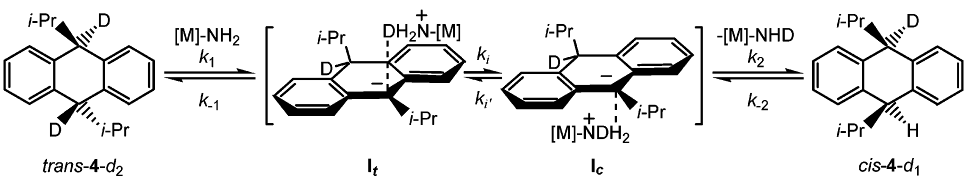
[34] Harvey, R. G.; Cho, H. *J. Am. Chem. Soc.* **1974**, *96*, 2434.
[35] Harvey, R. G.; Davis, C. C. *J. Org. Chem.* **1969**, *34*, 3607.
[36] Zieger, H. E.; Schaeffer, D. J.; Padronaggio, R. M. *Tetrahedron Lett.* **1969**, *10*, 5027.

**Scheme 7**

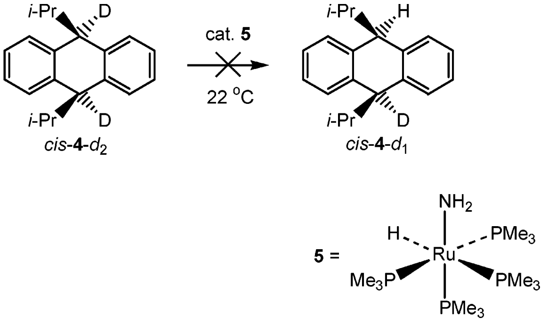


complex **1** as catalyst and hydrogen source[37] in benzene-$d_6$, observation of the reaction solution by $^1$H NMR spectroscopy after 62% conversion showed that H/D exchange had occurred to vastly different extents in the trans substrate and cis product (Table 1). Integration of the benzylic resonances relative to the methine resonances indicated that, in the cis product at this percent conversion, the benzylic position contained 43% hydrogen and the remaining trans starting material contained only 9.9% hydrogen. These observations are most easily rationalized by assuming that the ion pair $I_t$ is formed initially (Scheme 7). This species is potentially capable of either transferring H or D back to the carbanion or rearranging to the diastereomeric trans ion pair $I_c$. We assume that a primary isotope effect would encourage transfer of H preferentially to D in both intermediates. It is notable that the product contains 43% H, close to the 50% that would be expected if the initial ion pair were formed and isomerized and then the carbanion reprotonated by exclusive $H^+$ rather than $D^+$ back transfer from the countercation. Since so little H is found in the trans starting material at this substantial extent of reaction, and the amount of H incorporated into the cis product is much larger, the thermodynamic preference that favors the cis over the trans hydrocarbon in this system is felt in the rate constants that control the relative rates of isomerization and H/D exchange.

There are two possible ways of explaining this behavior. The first assumes that the initially formed ion pair $I_t$ rearranges to its stereoisomer $I_c$, and this undergoes proton transfer to give the rearranged product *cis*-**4**, relatively rapidly compared to the rate of reconversion of $I_t$ to the starting hydrocarbon *trans*-**4** (i.e., non-Curtin–Hammett conditions). In this case, there could be a strong driving force for rearrangement of the trans ion pair $I_t$ to the cis ion pair $I_c$ (i.e., rearrangement to the opposite face of the carbanion is more rapid than reverse proton transfer in the initial intermediate, a situation illustrated in the free energy diagram in Figure 3a). Once formed, the isotope effect requires the cis ion pair to transfer $H^+$ predominantly over $D^+$ to the carbanion. However, although many proton transfers are very fast, transfers to delocalized carbanions are an exception and often tend to be unusually slow, due to the necessity of electron reorganization in the reprotonation transition state. Therefore, molecular tumbling in the ion pair might be faster than reprotonation, and in this case Curtin–Hammett constraints might apply. In this scenario, the ratio of back proton transfer (as monitored approximately by H/D exchange in the trans starting material) to formation of cis product would be determined only by the relative free energies of the reprotonation transition states. It is conceivable that the transition state leading to the cis product might be the lower energy, reflecting the greater thermodynamic stability of this diastereomer (Figure 3b).

Whatever the situation is with respect to the relative rates in Scheme 7, these isomerization and exchange results are reminiscent of classical experiments carried out by Cram and co-workers in their stereochemical studies of carbanion rearrangements that proceed via organic ion pairs.[38,39] Therefore, they support the ion pair mechanism for H/D exchange in weak carbon acids. After 7 half-lives (1.5 h), 37% H/D exchange was observed in the cis product, indicating that H/D exchange apparently did not progress after the isomerization was complete (Table 1). Although it seemed unlikely, there remained the possibility that H/D exchange simply occurred at a faster rate in *cis*-**4** than in *trans*-**4**. Therefore, *cis*-**4**-$d_2$ was synthesized by addition of *trans*-**4** to a DMSO-$d_6$ solution containing 5 mol % NaH.[40] When *cis*-**4**-$d_2$ was exposed to 5 mol % **1**, only 18% H/D exchange was observed after 20 h, indicating that H/D exchange does not occur rapidly with *cis*-**4**-$d_2$ (Table 1). That is, $\Delta G_c^\ddagger$ is large, reflecting the greater thermodynamic stability of *cis*-**4** over *trans*-**4**.

To monitor the reaction progress more carefully, we used ruthenium amido complex **5** as catalyst because it catalyzed the isomerization of *trans*-**4** more slowly than the bis-dmpe amido complex. Under identical conditions, *trans*-**4**-$d_2$ and *cis*-**4**-$d_2$ were subjected to 60 mol % **5** in THF-$d_8$ at 22 °C. *trans*-**4**-$d_2$ was isomerized by **5** with $k = (7.2 \pm 0.4) \times 10^{-4}$ M$^{-1}$ s$^{-1}$. The cis product contained 50% hydrogen in the benzylic position, but no H/D exchange was observed when *cis*-**4**-$d_2$ was used as the substrate (eq 13, Table 1), observations analogous to those described above using **1** as the catalyst. These results indicated that, in the isomerization reactions, the H/D exchange that was observed was not the result of exchange with the cis product but occurred along with the isomerization process.



(13)

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[37] The catalyst contains 34 exchangeable hydrogen atoms in each molecule.

[38] Cram, D. J.; Gosser, L. *J. Am. Chem. Soc.* **1963**, *85*, 3890.

[39] Cram, D. J.; Gosser, L. *J. Am. Chem. Soc.* **1964**, *86*, 2950.

[40] Gleiter, R.; Weigl, H.; Haberhauer, G. *Eur. J. Org. Chem.* **1998**, 1447.

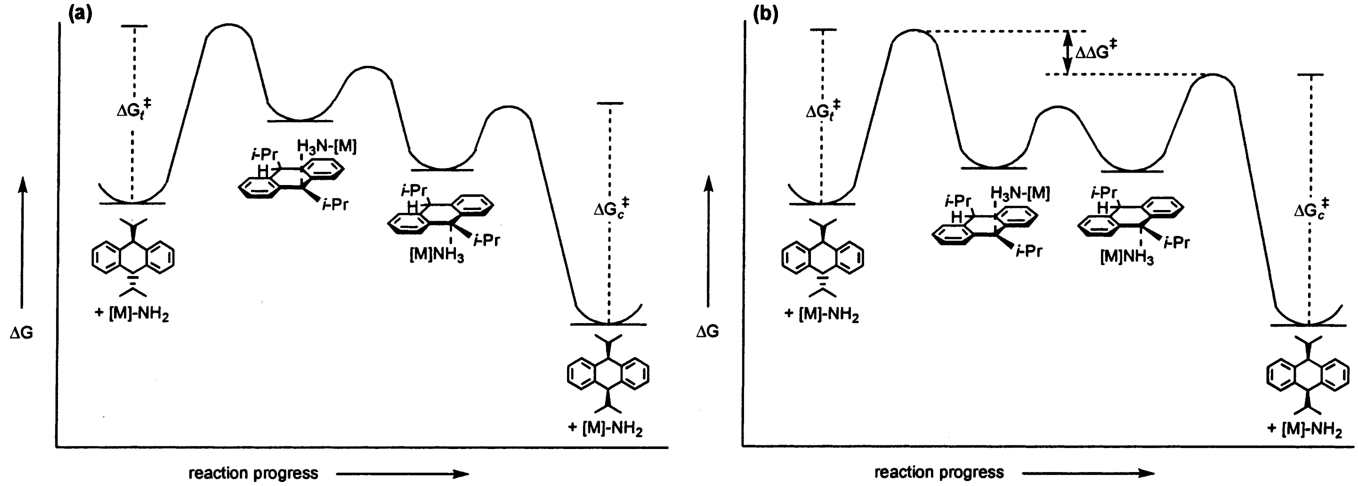
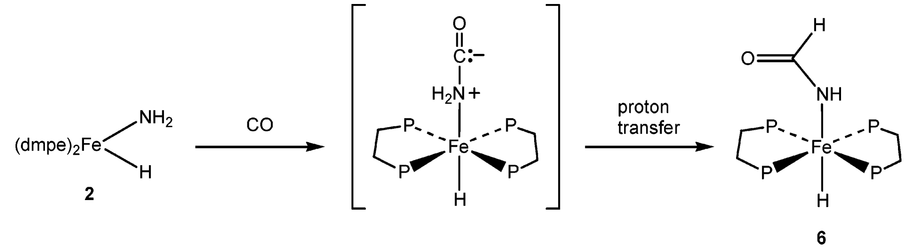


**Figure 3.** Reaction coordinate diagrams representing the isomerization of *trans*-**4** to *cis*-**4** using a parent amido complex as catalyst: (a) non-Curtin–Hammett conditions; (b) Curtin–Hammett conditions.

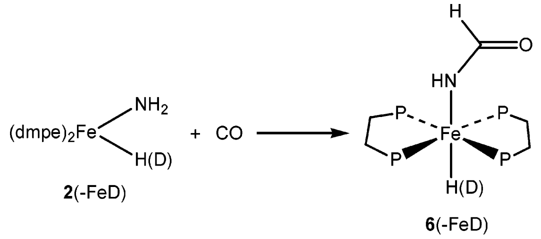
**Scheme 8**



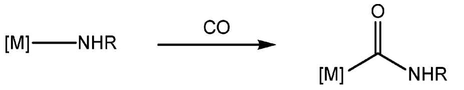
We also wished to determine if more traditional anionic bases catalyzed the isomerization and H/D exchange reactions in the same way as those catalyzed by our amide bases. Isomerization of *trans*-**4**-$d_2$ with 10% *t*-BuNHLi and 2.0 equiv of *t*-BuNH$_2$ as a source of hydrogen at 45 °C yielded results similar to those observed with the neutral amide bases. After 51% conversion, the benzylic position of the cis product contained 46% H, while the starting trans substrate contained only 1% H (Table 1). Under the same conditions starting with *cis*-**4**-$d_2$, only 6% H was observed in the benzylic position of the substrate after the same amount of time required for 51% conversion of the trans substrate. These experiments indicate that the results observed with the neutral amido bases are not unique to those species and provide strong support for the ion pair mechanism, which has been firmly established for organic exchange reactions.[38,39]

To determine whether isotope effects had an influence on the H/D exchange results, the isomerization of *trans*-**4** was carried out using 5% (dmpe-$d_{16}$)$_2$Fe(H)(ND$_2$) (**2**-$d_{34}$) as the catalyst and deuterium source. The isomerization reaction was observed over the course of 21 h (100% conversion). The amount of hydrogen in the product varied from 91% after 10 min (20% conversion) to 79% after 21 h (100% conversion), while it varied from 94% at 10 min to 75% at 3 h (90% conversion) in the starting material (Table 1). This result indicated that deuterium was less likely to be returned to the substrate than hydrogen and agreed with the observation in the isomerization of *trans*-**4**-$d_2$ that hydrogen incorporation in the cis product was approximately 50%. When a deuterium was removed in order for isomerization to take place, it was most often a hydrogen that was returned to the molecule rather than a deuterium.

**Insertion of Carbon Monoxide into the Amide N–H Bond.** As reported previously,[22] reaction of the iron amido complex **2** with 1 atm of CO in toluene resulted in net insertion of CO into the N–H bond of the amide ligand to form *trans*-(dmpe)$_2$Fe(H)(NHCHO) (**6**, eq 14) in 60% isolated yield as a yellow crystalline solid. To our knowledge, this represents the first preferential insertion of CO into a late-transition-metal amide N–H bond rather than the M–N bond. Carbon monoxide reacts with several late-transition-metal amido complexes through insertion into the M–N bond (eq 15); no instances of N–H insertion had been reported previously.[10,12,13,41,42] The M–N insertion reactions are proposed to proceed via coordination of CO to the metal



(14)



(15)

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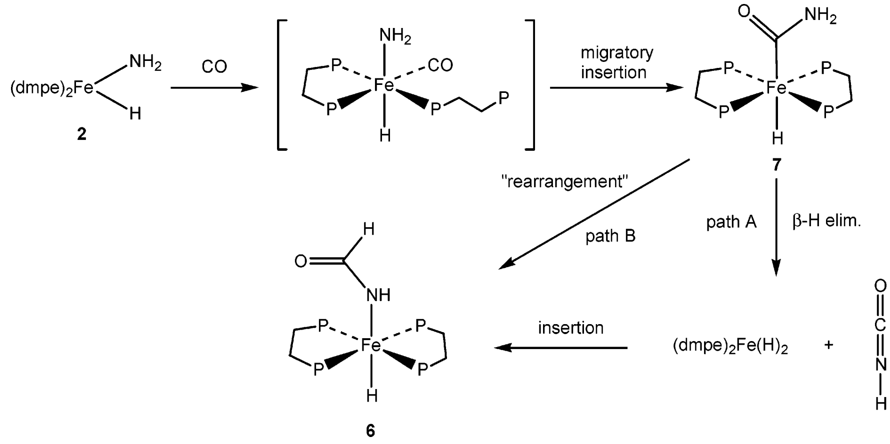
[41] The ruthenium amido complex **1** was found to insert CO to yield both the C-bound product, *trans*-(dmpe)$_2$Ru(H)(C(O)NH$_2$), and the N-bound product, *trans*-(dmpe)$_2$Ru(H)(NHCHO): Fulton, J. R.; Bergman, R. G. Unpublished results.

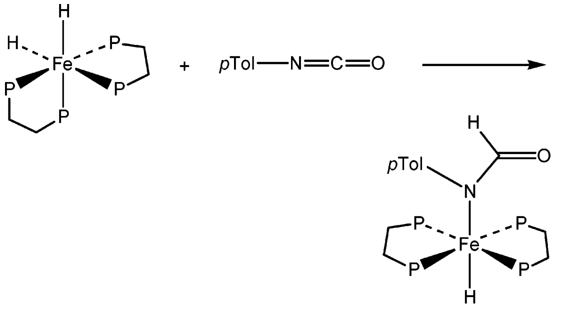
[42] Holland, P. L.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1092.

**Scheme 9**



center, followed by migratory insertion of CO to yield the observed product.

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 (**6**) after proton transfer (Scheme 8).[43] Because CO is a poor electrophile, we have also considered a second mechanism for CO insertion, illustrated in Scheme 9, 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*-$(dmpe)_2Fe(H)(C(O)NH_2)$ (**7**).[11,42,44] A similar mechanism is observed with lithium amide and lithium alkyl species, which are carbonylated by CO through a nucleophilic mechanism.[43] $\beta$-Hydride elimination of isocyanic acid, followed by insertion into the iron−hydride bond, would give rise to complex **6**. The above mechanism is supported by experimental results obtained both in our laboratory and by Field and coworkers[45] involving the insertion of several heterocumulenes into *cis*-$(dmpe)_2Fe(H)_2$ to form products similar to **6** (an example from our laboratory is shown in eq 16).



(16)

However, deuterium-labeling experiments do not support the formation of isocyanic acid in the CO insertion reaction. The iron deuterio amide complex $(dmpe)_2Fe(D)(NH_2)$ (**2**-FeD) was treated with CO as indicated above for the proton-containing analog. This reaction resulted in exclusive formation of *trans*-$(dmpe)_2Fe(D)(NHCHO)$ (**6**-FeD, eq 14). Path A of Scheme 9 as written would result in scrambling of the deuterium label into the carbonyl C−H bond of the product. Additionally, reaction of **2** with 1 atm of CO in the presence of 1 equiv of *cis*-$(dmpe)_2Fe(D)_2$ resulted in no deuterium incorporation into product **6**. We therefore eliminated this mechanism, as illustrated, on the basis of the two labeling experiments.[46]

Although the intermediacy of the iron dihydride complex could be ruled out, we considered the possibility that the M−N insertion product **7** is formed during the course of the reaction, followed by rearrangement to the observed N-bound product **6** (Scheme 9, path B). Photolysis of *cis*-$(dmpe)_2Fe(H)_2$ forms the unsaturated iron(0) complex $(dmpe)_2Fe$, which undergoes both C−H and N−H bond activation with a variety of substrates.[6,47,48] We reasoned that reaction of formamide with the iron(0) complex could lead to **7**, allowing us to test whether this complex was a likely intermediate. However, when *cis*-$(dmpe)_2Fe(H)_2$ was irradiated (500 W mercury lamp, through Pyrex) in the presence of formamide in THF-$d_8$, the N−H activation product **6** was observed while C−H activation product **7** was not detected (Scheme 10). Photolysis of *cis*-$(dmpe)_2Fe(H)_2$ in the presence of formamide-*d* resulted in the formation of the complex **6**-CD (Scheme 10), as observed by $^1H$, $^2H\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. While this experiment did not provide an independent route to intermediate **7**, the absence of **6**-FeD excluded the possibility of C−H (or C−D) activation in the photolysis reactions.

Finally, we considered the possible intermediacy of $(dmpe)_2Fe(CO)$, formed by reductive elimination of $NH_3$ from the amide starting material and coordination of CO. 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

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(43) Alkali-metal salts of strongly basic nitrogen and carbon anions are known to attack CO. See, for example: (a) Rautenstrauch, V.; Joyeux, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 85. (b) Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Sbarbati, N. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118.

(44) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 1987.

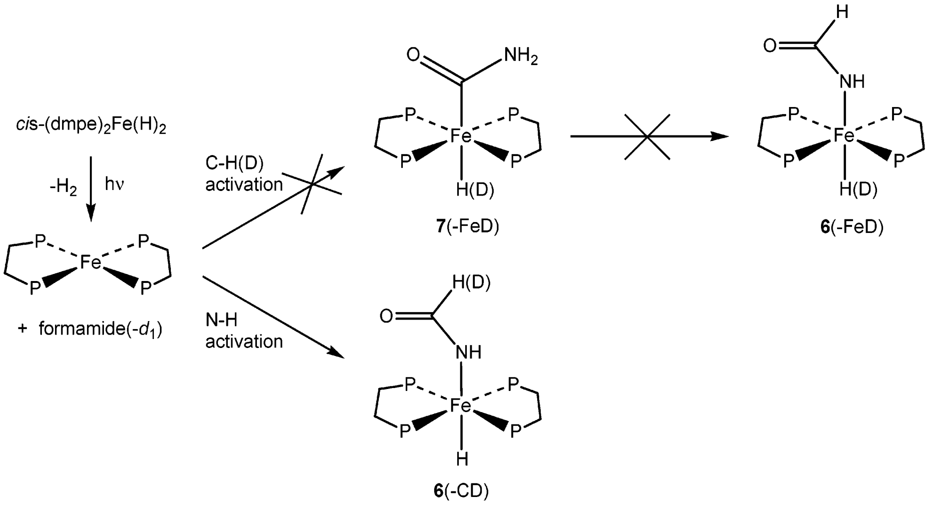
(45) Field, L. D.; Lawrenz, E. T.; Shaw, W. J.; Turner, P. *Inorg. Chem.* **2000**, *39*, 5632.

(46) It is possible that $\beta$-hydride elimination, if it occurs by dechelation of the dmpe ligand, would form a species with coordinated HNCO. If this is the case, and the hydrides maintained their inequivalence, scrambling of the deuterium label might not be observed.

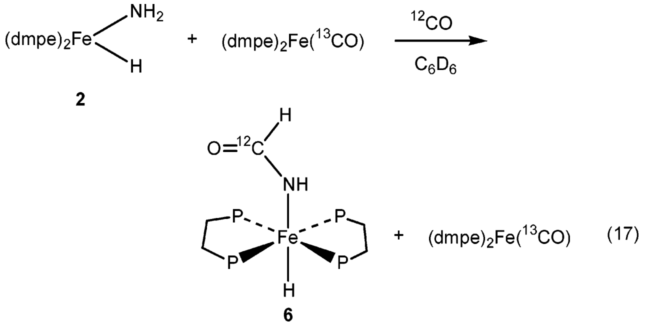
(47) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433.

(48) Buys, I. E.; Field, L. D.; Hambley, T. W.; McQueen, A. E. D. *J. Chem. Soc., Chem. Commun.* **1994**, 557.

### Scheme 10



$(dmpe)_2Fe(^{13}CO)$. We failed to observe incorporation of $^{13}C$ into product **6**, indicating that this mechanism was not operative (eq 17). Considering the above observations as a whole, we conclude that our experimental evidence most strongly supports the simple nucleophilic attack mechanism illustrated in Scheme 8, although the mechanism shown in Scheme 9, path B, cannot be ruled out conclusively.



## Conclusion

A technique developed for the synthesis of ruthenium amido complex **1** was shown to be applicable to the synthesis of its iron amido analog **2**. Complex **2** was found to be a strong base, although it is less basic than **1**. The difference in basicity between **1** and **2** may be understood in terms of the greater electron richness of ruthenium relative to iron. Deprotonation of terminal alkynes and phenylacetonitrile led to ammonia displacement products, while the deprotonation of fluorene and water did not lead to displacement of ammonia. The mechanism of H/D exchange reactions between parent amido complexes **1**, **2**, and **5** with very weak acids was investigated by qualitatively comparing the relative rates of H/D exchange and trans to cis isomerization of *trans*-**4** using the amido complexes as catalysts. These experiments indicate that an ion pair is formed and that *trans*-**4** (due to its higher free energy of formation) is more acidic than *cis*-**4**. Although our evidence suggests that (presumably very tight) ion pair formation occurs during the course of the H/D exchange, displacement of ammonia was never observed, even in systems where the counteranion that is presumably formed is not large. It is not clear why ion pair formation in some systems leads to displacement of ammonia (acetylides, keteniminates) while others do not lead to displacement (fluorenide, hydroxide, benzyl). However, both the size of the anion and the degree of hydrogen bonding in the ion pair may play important roles in controlling this selectivity.

The nucleophilic reactivity of amido complexes **1** and **2** (and *trans*-$(dmpe)_2Ru(H)(OH)$) was also demonstrated by the nucleophilic ring opening of 1,3-di-*tert*-butylaziridinone. The mechanism of an unusual transformation involving net insertion of CO into the N−H bond of amido complex **1** was investigated; the mechanism of this reaction appears to involve direct nucleophilic attack of the amide group at the CO carbon.

## Experimental Section

**General Comments.** All manipulations were carried out under an inert atmosphere or by using standard Schlenk or vacuum-line techniques unless noted otherwise. The $^{1}H$, $^{13}C\{^{1}H\}$, $^{2}H\{^{1}H\}$, $^{31}P\{^{1}H\}$, and $^{15}N\{^{1}H\}$ NMR spectra were obtained on Bruker 300, 400, and 500 MHz Fourier transform spectrometers with commercial Bruker AM or AV series interfaces. IR spectra were obtained using a Mattson Instruments Galaxy 3000 Fourier transform spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility, on a Perkin-Elmer 2400 Series II CHNO/S analyzer.

Reagents were purchased from commercial vendors, checked for purity, and used without further purification unless otherwise noted. Liquids were degassed using three freeze−pump−thaw cycles and dried over 4 Å activated molecular sieves or passed through an activated alumina column. Solids were stored in an inert-atmosphere glovebox. Toluene, benzene, and pentane (UV grade, alkene free) were passed through a column of activated alumina (A1, 12 × 32, Purifry Co.) under nitrogen pressure and sparged with nitrogen prior to use.[49] Tetrahydrofuran and diethyl ether were distilled from purple sodium/benzophenone ketyl under nitrogen. Benzene-$d_6$ and toluene-$d_8$ were degassed by three freeze−pump−thaw cycles, placed over 4 Å activated molecular sieves, and filtered through glass-fiber filter paper prior to use. THF-$d_8$ was vacuum-transferred from purple sodium/benzophenone ketyl and stored under an inert atmosphere. Addition of known quantities of condensable gases was achieved using a known

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[49] Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*, 64.

volume bulb attached to a high-vacuum line equipped with a digital MKS Baratron gauge.

UV irradiation was performed using a 500 W medium-pressure Hanovia mercury vapor lamp housed in a water-cooled quartz immersion well. During irradiation, samples were immersed in spectral grade ethylene glycol maintained by a Neslab Endocal circulating refrigeration bath at 20 °C.

The following compounds were synthesized according to literature procedures: *trans*-(dmpe)$_2$Fe(Cl)$_2$,[50] *trans*-(dmpe)$_2$Fe(H)(Cl),[23] *cis*-(dmpe)$_2$Fe(H)$_2$,[22] (dmpe)$_2$Fe(H)(NH$_2$) (**2**),[22] *trans*-(dmpe)$_2$Ru(H)(NH$_2$) (**1**),[19] *cis*-(PMe$_3$)$_2$Ru(H)(NH$_2$) (**5**),[51] 9,10-dihydroanthracene-*d*$_4$,[40] 1,3-di-*tert*-butylaziridinone,[33] *trans*-(dmpe)$_2$Fe(H)(NHCHO) (**6**),[22] and *trans*-(dmpe)$_2$Fe(H)(N(*p*-Tol)CHO).[22] Details of some of the experiments discussed in the text have also been described previously.[22]

**(dmpe)$_2$Fe(H)($^{15}$NH$_2$) (2-$^{15}$*N*).** To a heavy-walled glass vessel with a fused Teflon stopcock were added a stir bar, THF (2 mL), (dmpe)$_2$Fe(H)(Cl) (200 mg, 0.51 mmol), and NaNH$_2$ (33 mg, 0.82 mmol). The vessel was sealed and degassed on a vacuum line using three freeze−pump−thaw cycles, after which equal quantities of NH$_3$ and $^{15}$NH$_3$ were condensed into the vessel (the total solution volume after warming to 25 °C was 4 mL). The reaction vessel was warmed to 25 °C behind a blast shield, and the mixture was stirred at this temperature for 4 h. The ammonia was allowed to boil off under N$_2$, and the remaining volatile materials were removed in vacuo to give an orange solid. The solid was extracted with pentane (40 mL), and the extracts were filtered through Celite on a glass frit. The resulting bright orange solution was concentrated to yield **2**-$^{15}$*N* (50% $^{15}$N label) as an orange, powdery solid (186 mg, 98%). The $^1$H and $^{31}$P{$^1$H} NMR spectra of **2**-$^{15}$*N* were identical with those obtained for **2**. It is not clear why no splitting due to the $^{15}$N label is observed. $^{15}$N{$^1$H} NMR (C$_6$D$_6$; 50.5 MHz): $\delta$ −456.3, −457.4 (mixture of trans and cis isomers; the downfield peak is of greater intensity).

**[*trans*-(dmpe)$_2$Fe(H)(NH$_3$)][C$_{13}$H$_9$] (3).** A THF solution (3 mL) of fluorene (45 mg, 0.27 mmol) was added dropwise to an equal volume of a THF solution of **2** (100 mg, 0.27 mmol). Within 5 s, precipitation of a bright orange, powdery solid was observed. The mixture was stirred at 25 °C for 3 h. The volatile materials were removed in vacuo to leave 140 mg (97%) of **3** as a bright orange crystalline solid. $^1$H NMR (THF-*d*$_8$; 400 MHz): $\delta$ 7.82 (d, 2H, $J$ = 7.6 Hz, Ar *H*), 7.24 (d, 2H, $J$ = 8.3 Hz Ar *H*), 6.76 (t, 2H, $J$ = 7.0 Hz, Ar *H*), 6.39 (t, 2H, $J$ = 7.3 Hz, Ar *H*), 5.90 (s, 1H, Ar *H*), 1.42 (br m, 8H, PC*H*$_2$), 1.13 (s, 12H, PC*H*$_3$), 0.92 (s, 12H, PC*H*$_3$), −1.61 (br s, 3H, N*H*$_3$), −29.61 (quintet, 1H, $J_{HP}$ = 48.8 Hz, Fe*H*). $^{13}$C{$^1$H} NMR (THF-*d*$_8$; 100.4 MHz): $\delta$ 138.2 (s, *C*, aryl), 119.4 (s, *C*H, aryl), 119.2 (s, *C*H, aryl), 118.7 (s, *C*, aryl), 117.0 (s, *C*H, aryl), 109.0 (s, *C*H, aryl), 83.6 (s, *C*H, aryl), 31.8 (m, P*C*H$_2$), 23.2 (m, P*C*H$_3$), 13.8 (m, P*C*H$_3$). $^{31}$P{$^1$H} NMR (THF-*d*$_8$; 162 MHz): $\delta$ 74.0 (d, $J_{PH}$ = 45.4 Hz). IR (Nujol): 1816 (m), 1600 (w), 1568 (w), 1509 (m), 1377 (m), 1301 (s), 1220 (m), 1197 (w), 1154 (w), 1140 (w), 1063 (w), 936 (s), 838 (m), 715 (s), 636 (m), 571 (m) cm$^{-1}$. Anal. Calcd for C$_{25}$H$_{45}$NP$_4$Fe: C, 55.67; H, 8.41; N, 2.60. Found: C, 55.63; H, 8.37; N, 2.49.

**Deprotonation of 3 by 1.** The iron amido complex **2** (10 mg, 0.027 mmol), fluorene (4.5 mg, 0.027 mmol), and THF-*d*$_8$ (0.3 mL) were added to an NMR tube. Some orange precipitate was observed upon mixing. After formation of **3** was confirmed by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy (data same as above), the NMR tube was opened in the glovebox and the ruthenium amido complex **1** (11 mg, 0.027 mmol) was added as a solution in THF-*d*$_8$ (0.2 mL). The solution became a darker orange color and the orange precipitate of **3** that had formed redissolved. Formation of complex **2** and [*trans*-(dmpe)$_2$Ru(H)(NH$_3$)][C$_{13}$H$_9$][21] was confirmed by $^1$H NMR spectroscopy (hydride quintets at −27.35 and −19.97 ppm, respectively) and $^{31}$P{$^1$H} NMR spectroscopy (doublet at 76.0 and singlet at 46.0 ppm, respectively).

**Addition of 2 to [*trans*-(dmpe)$_2$Ru(H)(NH$_3$)][C$_{13}$H$_9$].** The ruthenium amido complex **1** (11 mg, 0.027 mmol), fluorene (4.5 mg, 0.027 mmol), and THF-*d*$_8$ (0.3 mL) were added to an NMR tube. After formation of [*trans*-(dmpe)$_2$Ru(H)(NH$_3$)][C$_{13}$H$_9$] was confirmed by NMR spectroscopy (hydride at −19.78 ppm in the $^1$H NMR spectrum and singlet at 40.8 ppm in the $^{31}$P{$^1$H} NMR spectrum),[21] the iron amido complex **2** (10 mg, 0.027 mmol) was added to an NMR tube containing [*trans*-(dmpe)$_2$Ru(H)(NH$_3$)][C$_{13}$H$_9$] as a THF-*d*$_8$ solution (0.2 mL). The $^1$H and $^{31}$P{$^1$H} NMR spectra were consistent with those reported above (hydride resonances at −19.41 and −26.65 ppm; $^{31}$P{$^1$H} resonances at 73.3 and 43.1 ppm), indicating that complex **2** did not deprotonate [*trans*-(dmpe)$_2$Ru(H)(NH$_3$)][C$_{13}$H$_9$].

**Reaction of 2 with Water.** Water was degassed by bubbling N$_2$ through it for 1 h. A portion of the water (14.5 $\mu$L, 0.80 mmol) was then added via syringe to 1 mL of THF, which was added to a stirred solution of **2** (100 mg, 0.27 mmol) in THF (4 mL). The reaction mixture was stirred at 25 °C for 3 h, and the solvent was removed in vacuo to leave a yellow-orange solid. The solid was extracted with pentane to give an orange solution and leave behind a yellow solid (65 mg, 60%). The pentane solution was found by NMR spectroscopy to contain starting material and decomposition products. The yellow solid was dissolved in THF and filtered through a glass fiber filter and crystallized from THF at −35 °C to give a product whose combustion and NMR analysis data were consistent with [(dmpe)$_2$Fe(H)(NH$_2$)]$_2$·3H$_2$O. An X-ray crystallographic study revealed a dimeric structure: [*trans*-(dmpe)$_2$Fe(H)(NH$_3$)]$_2$[OH]$_2$·2H$_2$O (Figure 1). Note that the material used for NMR and combustion analysis was dried in vacuo, while the material used for X-ray diffraction analysis was not dried. This difference in the purification method accounts for the different molecular formulas found. $^1$H NMR (THF-*d*$_8$; 400 MHz): $\delta$ 2.23 (br s, 10H, O*H*/N*H*), 2.15 (br m, 8H, PC*H*$_2$), 1.58 (br m, 8H, PC*H*$_2$), 1.52 (s, 24H, PC*H*$_3$), 1.27 (s, 24H, PC*H*$_3$), −28.17 (quintet, 2H, $J_{HP}$ = 47.2 Hz, Fe*H*). $^{13}$C{$^1$H} NMR (THF-*d*$_8$; 100.4 MHz): $\delta$ 32.5 (quintet, $J_{CP}$ = 14.1 Hz, P*C*H$_2$), 24.4 (m, P*C*H$_3$), 15.2 (br m, P*C*H$_3$). $^{31}$P{$^1$H} NMR (THF-*d*$_8$; 162 MHz): $\delta$ 70.5 (d, $J_{PH}$ = 43.7 Hz). IR (Nujol): 1781 (m), 1647 (w), 1281 (w), 936 (s), 889 (m), 838 (w), 800 (w), 698 (m), 643 (m) cm$^{-1}$. Anal. Calcd for C$_{24}$H$_{76}$N$_2$O$_3$P$_8$Fe$_2$: C, 36.02; H, 9.57; N, 3.50. Found: C, 36.10; H, 9.65; N, 3.46.

***trans*-(dmpe)$_2$Fe(H)(NCC(H)Ph).** Phenylacetonitrile (31 $\mu$L, 0.27 mmol) was added dropwise via syringe to a stirred solution of **2** (100 mg, 0.27 mmol) in toluene (5 mL) in a 20 mL vial. The solution was stirred at 25 °C for 5 h, during which time a yellow precipitate formed. The volatile materials were removed in vacuo to leave *trans*-(dmpe)$_2$Fe(H)(NCC(H)Ph) as a canary yellow, powdery solid (100 mg, 82%). The product was crystallized from toluene at −35 °C to give analytically pure material. $^1$H NMR (C$_6$D$_6$; 400 MHz): $\delta$ 7.31 (t, 2H, $J$ = 7.5 Hz, Ar *H*), 7.08 (d, 2H, $J$ = 7.4 Hz, Ar *H*), 6.67 (t, 1H, $J$ = 7.1 Hz, Ar *H*), 3.49 (s, 1H, NCC(*H*)Ph), 1.47 (br m, 8H, PC*H*$_2$), 1.21 (s, 12H, PC*H*$_3$), 0.94 (s, 12H, PC*H*$_3$), −27.28 (quintet, 1H, $J_{HP}$ = 48.0 Hz, Fe*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$; 100.4 MHz): $\delta$ 129.2 (s, *C*, aryl), 128.7 (s, *C*H, aryl), 128.5 (s, *C*H, aryl), 128.3 (s, *C*H, aryl), 118.6 (s, N*C*C(H)Ph), 113.2 (s, NC*C*(H)Ph), 32.0 (quintet, $J_{CP}$ = 13.4 Hz, P*C*H$_2$), 22.4 (br m, P*C*H$_3$), 15.5 (br m, P*C*H$_3$). $^{31}$P{$^1$H} NMR (C$_6$D$_6$; 162 MHz): $\delta$ 72.0 (d, $J_{PH}$ = 42.0 Hz). IR (Nujol): 2111 (s), 1920 (m), 1806 (m), 1749 (m), 1588 (s), 1419 (m), 1291 (m), 1226 (w), 1171 (s), 1119 (w), 1091 (w), 1062 (w), 981 (m), 929 (s), 888 (m), 731 (s), 700 (s) cm$^{-1}$. Anal. Calcd for C$_{20}$H$_{39}$NP$_4$Fe: C, 50.76; H, 8.31; N, 2.96. Found: C, 50.59; H, 8.44; N, 3.34.

**Reaction of 2 with Propyne.** A solution of **2** (10 mg, 0.027 mmol) and hexamethylbenzene internal standard (1.4 mg, 0.0090 mmol) in benzene-*d*$_6$ (0.3 mL) was added to an NMR tube, and the tube was fitted with a Cajon adaptor. The tube

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was degassed using three freeze−pump−thaw cycles, and propyne (0.054 mmol) was added by vacuum transfer. The tube was heated to 45 °C for 3 days. The NMR spectra indicated formation of *trans*-(dmpe)$_2$Fe(H)(CCCH$_3$) as the major product (60%, hydride at −18.71 ppm, $^{31}$P resonance at 75.5 ppm).[32] An equivalent quantity of NH$_3$ was also observed. Two other species with hydride resonances at −20.26 (12%) and −32.00 ppm (20%) were also observed. Attempts to isolate *trans*-(dmpe)$_2$Fe(H)(CCCH$_3$) were not successful.

**Reaction of 2 with Allene.** A solution of **2** (10 mg, 0.027 mmol) and hexamethylbenzene internal standard (1.4 mg, 0.0090 mmol) in benzene-$d_6$ (0.3 mL) was added to an NMR tube, and the tube was fitted with a Cajon adaptor. The tube was degassed using three freeze−pump−thaw cycles, and allene (0.054 mmol) was added by vacuum transfer. After 3 days at 45 °C, the hydride resonance of *trans*-(dmpe)$_2$Fe(H)(CCCH$_3$) was observed at −18.73 ppm (60% yield) with a corresponding signal in the $^{31}$P{$^1$H} NMR spectrum at 75.5 ppm.[32] A second hydride resonance was observed at −20.26 ppm (12%). Attempts to isolate *trans*-(dmpe)$_2$Fe(H)(CCCH$_3$) were not successful.

***trans*-(dmpe)$_2$Fe(H)(NHC(O)C(H)(*t*-Bu)N(H)(*t*-Bu)).** A pentane solution of **2** (100 mg, 0.27 mmol) was slowly added to a stirred solution of 1,3-di-*tert*-butylaziridinone (45 mg, 0.27 mmol) in pentane (total volume, 10 mL). The solution immediately became cloudy, followed by formation of light orange crystals. The solution remained a dark orange-red. The vial was then cooled to −35 °C for 1 day. Yellow crystals of *trans*-(dmpe)$_2$Fe(H)(NHC(O)C(H)*t*-BuN(H)*t*-Bu) were isolated from the pentane solution (107 mg, 74%). $^1$H NMR (C$_6$D$_6$; 400 MHz): $\delta$ 2.80 (d, 1H, $J$ = 8.0 Hz, N*H*C(CH$_3$)$_3$), 2.44 (d, 1H, $J$ = 7.6 Hz, C*H*C(CH$_3$)$_3$), 2.13 (br m, 2H, PC*H*$_2$), 2.01 (br m, 2H, PC*H*$_2$), 1.63 (br s, 1H, N*H*), 1.55 (br m, 2H, PC*H*$_2$), 1.43 (d, 9H, $J$ = 6.4 Hz, NHC(C*H*$_3$)$_3$), 1.36 (br m, 3H, PC*H*$_2$, N*H*), 1.21 (s, 12H, PC*H*$_3$), 1.20 (s, 12H, PC*H*$_3$), 1.06 (d, $J$ = 8.0 Hz, 9H, CHC(C*H*$_3$)$_3$), −28.41 (quintet, 1H, $J_{\mathrm{HP}}$ = 49.4 Hz, Fe*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$; 100.4 MHz): $\delta$ 181.9 (s, N*C*O), 69.7 (s, CHC(CH$_3$)$_3$), 50.5 (s, NH*C*(CH$_3$)$_3$), 35.6 (s, CH*C*(CH$_3$)$_3$), 32.9 (m, P*C*H$_2$), 31.3 (s, NHC(*C*H$_3$)$_3$), 29.1 (s, CHC(*C*H$_3$)$_3$), 25.7 (br m, P*C*H$_3$), 24.9 (br m, P*C*H$_3$), 18.0 (m, P*C*H$_3$), 17.7 (m, P*C*H$_3$). $^{31}$P{$^1$H} NMR (C$_6$D$_6$; 162 MHz): $\delta$ 71.4 (m). IR (Nujol): 3270 (w), 1794 (s), 1580 (s), 1280 (s), 1262 (s), 1108 (m), 1079 (w), 1033 (w), 922 (s), 838 (m), 796 (m), 697 (s), 643 (s) cm$^{-1}$. Anal. Calcd for C$_{22}$H$_{54}$N$_2$OP$_4$Fe: C, 48.71; H, 10.03; N, 5.16. Found: C, 48.71; H, 9.70; N, 5.13.

***trans*-(dmpe)$_2$Ru(H)(NHC(O)C(H)(*t*-Bu)N(H)(*t*-Bu)).** A pentane solution of **1** (50 mg, 0.12 mmol) was slowly added to a stirred solution of 1,3-di-*tert*-butylaziridinone (20 mg, 0.12 mmol) in pentane (total volume, 10 mL). The solution immediately became cloudy, followed by formation of a white precipitate. The solution remained light yellow. The vial was then cooled to −35 °C for 1 day. Colorless crystals of *trans*-(dmpe)$_2$Ru(H)(NHC(O)C(H)(*t*-Bu)N(H)(*t*-Bu)) were isolated from the pentane solution (43 mg, 61%). $^1$H NMR (C$_6$D$_6$; 400 MHz): $\delta$ 2.81 (d, 1H, $J$ = 8.4 Hz, N*H*C(CH$_3$)$_3$), 2.71 (br s, 1H, N*H*), 2.59 (d, 1H, $J$ = 8.4 Hz, C*H*C(CH$_3$)$_3$), 1.99 (br m, 4H, PC*H*$_2$), 1.79 (br m, 4H, PC*H*$_2$), 1.43 (s, 6H, PC*H*$_3$), 1.35 (s, 6H, PC*H*$_3$), 1.28 (s, 9H, NH(C*H*$_3$)$_3$), 1.25 (s, 9H, CH(C*H*$_3$)$_3$), 1.16 (d, 12H, $J$ = 4.0 Hz, PC*H*$_3$), −18.79 (quintet, 1H, $J_{\mathrm{HP}}$ = 22.0 Hz). $^{13}$C{$^1$H} NMR (C$_6$D$_6$; 100.4 MHz): $\delta$ 172.6 (s, N*C*O), 69.7 (s, *C*HC(CH$_3$)$_3$), 50.6 (s, NH*C*(CH$_3$)$_3$), 35.5 (s, CH*C*(CH$_3$)$_3$), 32.5 (quintet, $J_{\mathrm{CP}}$ = 13.6 Hz, P*C*H$_2$), 32.1 (quintet, $J_{\mathrm{CP}}$ = 13.6 Hz, P*C*H$_2$), 31.3 (s, NHC(*C*H$_3$)$_3$), 29.1 (s, CHC(*C*H$_3$)$_3$), 25.1 (m, P*C*H$_3$), 24.2 (m, P*C*H$_3$), 18.2 (m, P*C*H$_3$), 17.6 (m, P*C*H$_3$). $^{31}$P{$^1$H} NMR (C$_6$D$_6$; 162 MHz): $\delta$ 43.8 (m). IR (Nujol): 3339 (w), 3280 (w), 1868 (s), 1582 (s), 1286 (m), 1237 (m), 1171 (w), 1108 (w), 1032 (w), 933 (s), 887 (m), 840 (m), 797 (m), 760 (w), 723 (s), 699 (s), 645 (m) cm$^{-1}$. Anal. Calcd for C$_{22}$H$_{54}$N$_2$OP$_4$Ru: C, 44.97; H, 9.26; N, 4.77. Found: C, 45.23; H, 9.56; N, 4.56.

***trans*-(dmpe)$_2$Ru(H)(OH).** Water was degassed by bubbling N$_2$ through it for 30 min. A solution of **1** (63 mg, 0.15 mmol) in THF (5 mL) was added to a glass vessel with a fused Teflon stopcock. Degassed water (2.7 $\mu$L, 0.15 mmol) was added to the stirred solution of **1** with a syringe. The solution was stirred for 1 h, and the volatile materials were removed in vacuo. The hydroxide complex was isolated as a cream-colored powdery solid (60 mg, 95%), and crystallization from THF gave clean material whose NMR spectra were identical with those previously reported.[52]

***trans*-(dmpe)$_2$Ru(H)(OC(O)C(H)(*t*-Bu)N(H)(*t*-Bu)).** In an NMR tube, solutions of *trans*-(dmpe)$_2$Ru(H)(OH) (6.1 mg, 0.015 mmol) and 1,3-di-*tert*-butylaziridinone (2.5 mg, 0.015 mmol) in C$_6$D$_6$ (0.3 mL total volume) were mixed. After 20 h, complete conversion to product was observed by $^1$H and $^{31}$P{$^1$H} NMR spectroscopy. The solution was concentrated in vacuo to give 6.6 mg (77%) of *trans*-(dmpe)$_2$Ru(H)(OC(O)C(H)(*t*-Bu)N(H)(*t*-Bu)) as a colorless solid. The product was crystallized from THF layered with pentane at −35 °C to give analytically pure material. $^1$H NMR (C$_6$D$_6$; 400 MHz): $\delta$ 2.83 (d, 1H, $J$ = 8.4 Hz, N*H*C(CH$_3$)$_3$), 2.52 (d, 1H, $J$ = 7.6 Hz, C*H*C(CH$_3$)$_3$), 2.02 (br m, 4H, PC*H*$_2$), 1.85 (br m, 4H, PC*H*$_2$), 1.46 (s, 6H, PC*H*$_3$), 1.41 (s, 6H, PC*H*$_3$), 1.28 (s, 9H, NHC(C*H*$_3$)$_3$), 1.23 (s, 9H, CC(C*H*$_3$)$_3$), 1.13 (s, 6H, PC*H*$_3$), 1.09 (s, 6H, PC*H*$_3$), −23.28 (quintet, 1H, $J_{\mathrm{HP}}$ = 21.9 Hz, Ru *H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$; 100.4 MHz): $\delta$ 179.6 (s, N*C*O), 67.2 (s, *C*HC(CH$_3$)$_3$), 50.6 (s, NH*C*(CH$_3$)$_3$), 35.3 (s, CH*C*(CH$_3$)$_3$), 31.9 (m, P*C*H$_2$), 31.2 (s, NHC(*C*H$_3$)$_3$), 29.2 (s, CHC(*C*H$_3$)$_3$), 24.1 (quintet, $J_{\mathrm{CP}}$ = 13.1 Hz, P*C*H$_3$), 23.1 (quintet, $J_{\mathrm{CP}}$ = 13.1 Hz, P*C*H$_3$), 18.0 (quintet, $J_{\mathrm{CP}}$ = 9.5 Hz, P*C*H$_3$), 17.2 (quintet, $J_{\mathrm{CP}}$ = 9.5 Hz, P*C*H$_3$). $^{31}$P{$^1$H} NMR (C$_6$D$_6$; 162 MHz): $\delta$ 43.6 (m). IR (benzene-$d_6$): 2967 (s), 2903 (s), 1922 (m), 1839 (w), 1588 (s), 1473 (w), 1356 (m), 1278 (w), 1231 (w), 937 (s), 888 (m), 728 (m), 644 (m) cm$^{-1}$. Anal. Calcd for C$_{22}$H$_{53}$NO$_2$P$_4$Ru: C, 44.89; H, 9.08; N, 2.38. Found: C, 44.41; H, 9.07; N, 2.24.

**H/D Exchange between 2 and Toluene-$d_8$.** Complex **2** (10 mg, 0.027 mg) was dissolved in toluene-$d_8$ (0.3 mL) in a J. Young NMR tube. Integration relative to the residual aryl solvent peaks revealed that the intensity of the toluene methyl peak increased, while the NH$_2$ and dmpe resonances of **2** decreased in intensity; the hydride resonances of **2** remained unchanged. After 3 days at 25 °C, the NH$_2$ and dmpe resonances of **2** were no longer observed. The $^2$H{$^1$H} spectrum after removal of the deuterated solvent in vacuo and dissolution of the remaining orange solid in benzene-$h_6$ revealed deuterium signals corresponding to the dmpe and NH$_2$ ligands of **2**; no resonance in the hydride region was observed.

***trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph).** A 1.0 M diethyl ether solution of benzylmagnesium chloride (0.61 mL, 0.61 mmol) was added to a stirred solution of *trans*-(dmpe)$_2$Fe(H)(Cl) (200 mg, 0.51 mmol) in THF (5 mL). The orange solution was stirred for 3 h, and the solvent was removed in vacuo. The orange solid was extracted with pentane (10 mL) and filtered through a glass fiber filter. The pentane was removed at reduced pressure to give an orange solid. The product was crystallized from diethyl ether at −35 °C to give a clean product (73 mg, 32%). $^1$H NMR (C$_6$D$_6$; 400 MHz): $\delta$ 7.12−7.02 (m, 4H, Ar *H*), 6.88 (t, 1H, $J$ = 7.0 Hz, Ar *H*), 1.63 (br m, 4H, PC*H*$_2$), 1.38 (br m, 4H, PC*H*$_2$), 1.19 (s, 12H, PC*H*$_3$), 1.10 (s, 12H, PC*H*$_3$), 1.07 (quintet, 2H, $J_{\mathrm{HP}}$ = 6.0 Hz, FeC*H*$_2$Ph), −23.3 (quintet, 1H, $J_{\mathrm{HP}}$ = 48.00 Hz, Fe*H*). $^{13}$C{$^1$H} NMR (C$_6$D$_6$; 100.4 MHz): $\delta$ 165.4 (quintet, $J_{\mathrm{CP}}$ = 3.0 Hz, *C*, aryl), 128.1 (s, *C*H, aryl), 127.0 (s, *C*H, aryl), 118.6 (s, *C*H, aryl), 32.4 (quintet, $J_{\mathrm{CP}}$ = 13.5 Hz, P*C*H$_2$), 28.1 (quintet, $J_{\mathrm{CP}}$ = 6.4 Hz, P*C*H$_3$), 16.2 (s, quintet, $J_{\mathrm{CP}}$ = 2.9 Hz, P*C*H$_3$), 8.8 (quintet, $J_{\mathrm{CP}}$ = 10.5 Hz, Fe*C*H$_2$Ph). $^{31}$P{$^1$H} NMR (C$_6$D$_6$; 162 MHz): $\delta$ 73.3 (s). IR (Nujol): 1738 (s), 1588 (m), 1422 (m), 1272 (m), 1206 (m), 1172 (w), 1015 (w), 982 (w), 927 (s), 884 (m), 832 (w), 788 (w), 748 (w), 691 (s), 637 (m) cm$^{-1}$. Anal. Calcd for C$_{19}$H$_{40}$P$_4$Fe: C, 50.91; H, 8.99. Found: C, 51.07; H, 9.24.

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**Thermolysis of *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) in the Presence of NH$_3$.** A solution of *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) (10 mg, 0.022 mmol) in 0.3 mL of THF-$d_8$ was added to a J. Young NMR tube. The tube was degassed using three freeze−pump−thaw cycles, and 1 atm of NH$_3$ was added. The reaction mixture was stable indefinitely at 25 °C. After 5 h at 45 °C, toluene was observed in the $^1$H NMR spectrum, but no evidence for formation of **2** was apparent. Further heating at 45 °C resulted in further decomposition of the benzyl complex.

**Dissolution of *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) in Liquid NH$_3$.** A stirbar and *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) (18 mg, 0.040 mmol) were added to a heavy-walled glass vessel with a fused Teflon stopcock. The vessel was evacuated and frozen at −196 °C, and NH$_3$ was condensed into it such that, when it was warmed to ambient temperature behind a blast shield, the total volume of the mixture was 5 mL. The mixture was stirred for 3 h at ambient temperature. The substrate was only slightly soluble in the NH$_3$ solvent, resulting in a reaction mixture with the appearance of orange juice. After 3 h, the NH$_3$ was allowed to boil off under N$_2$. The yellow solid that remained was dissolved in benzene-$d_6$, and NMR spectra indicated that no reaction had occurred.

**Reaction of *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) with *p*-Thiocresol.** THF-$d_8$ solutions of *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) (10 mg, 0.022 mmol) and *p*-thiocresol (2.7 mg, 0.022 mmol) were mixed (total volume 0.3 mL) and added to a J. Young NMR tube. Upon mixing, the solution immediately became a darker orange. NMR analysis indicated clean formation of a mixture of the cis and trans isomers of (dmpe)$_2$Fe(H)(S-*p*-Tol) in a 1:2 ratio with loss of toluene. The identity of the products was confirmed by comparison of the observed Fe*H* resonances with those previously reported for (dmpe)$_2$Fe(H)(SPh).[53]

***trans*-(dmpe)$_2$Fe(H)(O-*p*-Tol).** THF solutions of *trans*-(dmpe)$_2$Fe(H)(CH$_2$Ph) (220 mg, 0.49 mmol) and *p*-cresol (64 mg, 0.59 mmol) were mixed (total volume, 5 mL) in a 20 mL vial. Upon mixing, the solution immediately became a darker orange. After 2 h, the volatile materials were removed in vacuo to give *trans*-(dmpe)$_2$Fe(H)(OTol) as a dark orange crystalline solid (140 mg, 60%). The product was crystallized from toluene at −35 °C to give 77 mg (33%) of analytically pure material. $^1$H NMR (THF-$d_8$; 400 MHz): $\delta$ 7.04 (d, 2H, $J = 8.3$ Hz, Ar *H*), 6.15 (d, 2H, $J = 7.6$ Hz, Ar *H*), 2.36 (s, 3H, ArC*H*$_3$), 1.96 (br m, 4H, PC*H*$_2$), 1.46 (br m, 4H, PC*H*$_2$), 1.31 (s, 12H, PC*H*$_3$), 1.05 (s, 12H, PC*H*$_3$), −35.02 (quintet, 1H, $J_{HP} = 49.8$ Hz, Fe*H*). $^{13}$C{$^1$H} NMR (THF-$d_8$; 100.4 MHz): $\delta$ 171.8 (s, *C*O, aryl), 129.8 (s, *C*H, aryl), 120.3 (s, *C*H, aryl), 117.2 (s, *C*CH$_3$, aryl), 32.3 (quintet, $J_{CP} = 13.2$ Hz, P*C*H$_2$), 23.6 (quintet, $J_{CP} = 6.6$ Hz, P*C*H$_3$), 21.3 (s, Ar*C*H$_3$), 15.8 (br m, P*C*H$_3$). $^{31}$P{$^1$H} NMR (THF-$d_8$; 162 MHz): $\delta$ 70.9 (dd, $J = 32.4$, 13.0 Hz). IR (Nujol; cm$^{-1}$): 1789 (s), 1601 (s), 1503 (s), 1378 (w), 1334 (s), 1291 (s), 1155 (m), 1094 (m), 1067 (w), 990 (w), 884 (m), 816 (m), 696 (s), 642 (s). Anal. Calcd for C$_{19}$H$_{40}$OP$_4$Fe: C, 49.15; H, 8.68. Found: C, 49.36; H, 8.96.

**H/D Exchange between 2 and H$_2$ in Toluene-$d_8$.** A solution of **2** (10 mg, 0.027 mmol) in toluene-$d_8$ (0.3 mL) was added to a J. Young NMR tube. The tube was degassed using three freeze−pump−thaw cycles, and H$_2$ (1 atm) was added to the tube. The resonances corresponding to the dmpe and NH$_2$ ligands of **2**, and of H$_2$, were observed to decrease in intensity relative to the residual aryl resonances of the solvent.

**H/D Exchange between 2 and Ammonia in Toluene-$d_8$.** A solution of **2** (10 mg, 0.027 mmol) in toluene-$d_8$ (0.3 mL) was added to a J. Young NMR tube. The tube was degassed using three freeze−pump−thaw cycles, and NH$_3$ (0.054 mmol) was added to the tube by vacuum transfer. The resonances corresponding to the dmpe and NH$_2$ ligands of **2**, and of ammonia, were observed to decrease in intensity relative to the residual aryl resonances of the solvent.

**Addition of $^{15}$NH$_3$ to 2.** A solution of **2** (10 mg, 0.027 mmol) in benzene-$d_6$ (0.3 mL) was added to a J. Young NMR tube. The tube was degassed using three freeze−pump−thaw cycles, and $^{15}$NH$_3$ (0.054 mmol) was added to the tube by vacuum transfer. Over the course of 3 days, no $^{14}$NH$_3$ was observed by $^1$H NMR spectroscopy and the quantity of $^{15}$NH$_3$ did not decrease, indicating that $^{15}$N was not incorporated into **2**.

**H/D Exchange between 2 and Cycloheptatriene in Toluene-$d_8$.** Solutions of **2** (10 mg, 0.027 mmol) and cycloheptatriene (5.1 $\mu$L, 0.054 mmol) in toluene-$d_8$ (0.3 mL) were added to a J. Young NMR tube. The resonances corresponding to the dmpe and NH$_2$ ligands of **2**, and all the resonances of cycloheptatriene, were observed to decrease in intensity relative to the residual aryl resonances of the solvent.

**H/D Exchange between 2 and Cyanocyclopropane in Toluene-$d_8$.** Solutions of **2** (10 mg, 0.027 mmol) and cyanocyclopropane (2.0 $\mu$L, 0.027 mmol) in toluene-$d_8$ (0.3 mL) were added to a J. Young NMR tube. Over the course of 46 h, the cyanocyclopropane resonances at 0.30 and 0.00 ppm were observed to decrease in intensity relative to the residual solvent aryl resonances, as did the resonances corresponding to the dmpe and NH$_2$ ligands of **2**. At $t = 10$ min, the ratio of the cyanocyclopropane resonances to the aryl peaks was 21:1, and after 46 h, the ratio was 10:1.

**H/D Exchange between 2 and Ph$_3$CH in Toluene-$d_8$.** Solutions of **2** (10 mg, 0.027 mmol) and triphenylmethane (13 mg, 0.054 mmol) in toluene-$d_8$ (0.3 mL) were added to a J. Young NMR tube. The resonances corresponding to the dmpe and NH$_2$ ligands of **2**, and those of the methine hydrogen of triphenylmethane, were observed to decrease in intensity relative to the residual aryl resonances of the solvent.

**Attempted H/D Exchange between 2 and Propene in Toluene-$d_8$.** A solution of **2** (10 mg, 0.027 mmol) in toluene-$d_8$ (0.3 mL) was added to a J. Young NMR tube. The tube was degassed using three freeze−pump−thaw cycles, and propene (0.054 mmol) was added to the tube by vacuum transfer. While the resonances corresponding to the dmpe and NH$_2$ ligands of **2** were observed to decrease in intensity, no decrease (±5%) in intensity of the propene resonances was observed.

**Attempted H/D Exchange between 2 and *trans*-(dmpe)$_2$Fe(H)(Cl) in Toluene-$d_8$.** Complex **2** (5.0 mg, 0.013 mmol) and *trans*-(dmpe)$_2$Fe(H)(Cl) (5.0 mg, 0.013 mmol) were dissolved in toluene-$d_8$, and the solution was added to an NMR tube that was flame-sealed. Over the course of 2 days, observation of the $^1$H NMR spectrum showed that while the resonances corresponding to the dmpe and NH$_2$ ligands of **2** decreased in intensity relative to the residual aryl resonances of the solvent, the dmpe resonances of *trans*-(dmpe)$_2$Fe(H)(Cl) did not decrease in intensity.

**Isomerization of 1,3-Cyclohexadiene by 2.** Benzene-$d_6$ solutions of **2** (10 mg, 0.027 mmol) and 1,3-cyclohexadiene (5.1 $\mu$L, 0.076 mmol) were mixed (total volume 0.3 mL) and added to a J. Young NMR tube. After 1 day, 1,3-cyclohexadiene and 1,4-cyclohexadiene were observed in an equilibrium ratio of 2:1.[54] Complex **2** remained unreacted.

***trans*-9,10-Diisopropyl-9,10-dihydroanthracene (*trans*-4).** The compound was synthesized using a procedure similar to that reported by Harvey and Davis for the synthesis of other 9,10-dialkyl-9,10-dihydroanthracenes.[35] To a solution of 9,10-dihydroanthracene (2.0 g, 11 mmol) in diethyl ether (50 mL) and liquid ammonia (50 mL) at −35 °C was added 18 mL of a 1.5 M solution of *n*-butyllithium in hexane (27 mmol). The bright red-orange solution was stirred for 30 min at −35 °C, and 2-bromopropane (4.2 mL, 44 mmol) was added via syringe, resulting in the solution becoming first yellow and then colorless after 10 min. After the mixture was stirred for 30 min at −35 °C, water (15 mL) was added and the ammonia was allowed to evaporate. Diethyl ether (75 mL) was added, and the organic solution was washed with brine (3 × 20 mL)

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[53] Boyd, S. E.; Field, L. D.; Hambley, T. W.; Young, D. J. *Inorg. Chem.* **1990**, *29*, 1496.

[54] Taskinen, E.; Nummelin, K. *J. Org. Chem.* **1985**, *50*, 4844.

and dried with $MgSO_4$. Evaporation of the diethyl ether on a rotary evaporator led to formation of a thick yellow oil. After 2 days, clear, colorless crystals formed in the oil. These were isolated and recrystallized from diethyl ether to give 432 mg (15% yield) of *trans*-**4** as white crystals. $^1H$ NMR ($C_6D_6$; 400 MHz): $\delta$ 7.27 (m, 4H, aryl), 7.14 (m, 4H, aryl), 3.75 (d, 2H, $J$ = 4.8 Hz, benzylic C*H*), 2.25 (m, 2H, C*H*($CH_3$)$_2$), 0.91 (d, 12H, $J$ = 7.2 Hz, CH(C*H*$_3$)$_2$). Lit.[36] $^1H$ NMR (no solvent indicated): 7.25 (m), 3.78 ($J$ = 5.0 Hz), 0.97 ($J$ = 6.8 Hz).

**Isomerization of *trans*-4 by 5.** In a typical experiment, benzene-$d_6$ stock solutions of **5** and substrate were mixed such that 0.018 mmol of **5** and 0.025 mmol of *trans*-**4** were used. The resulting solution was diluted to 1.0 mL and transferred to an NMR tube that was subsequently flame-sealed. The progress of the reaction was monitored by $^1H$ NMR spectroscopy at regular intervals. The isomerization was repeated eight times, and the isomerization was found to be first order in both catalyst and substrate with $k = (2.18 \pm 0.11) \times 10^{-3}\ M^{-1}\ s^{-1}$.

***trans*-9,10-Diisopropyl-9,10-dihydroanthracene-$d_2$ (*trans*-4-$d_2$).** The deuterio analog was synthesized using the method described above with 9,10-dihydroanthracene-$d_4$[40] (1.4 g, 7.6 mmol) as the substrate, 18 mmol of *n*-butyllithium, and 2.0 mL (30 mmol) of 2-bromopropane. The product was purified by column chromatography (100% hexanes; silica gel) followed by recrystallization from pentane to give 240 mg (20%) of clean *trans*-**4**-$d_2$. The $^1H$ NMR spectrum was identical with that of the nondeuterated analog, except that the benzylic resonance was not observed (>95% deuteration).

**Isomerization of *trans*-4-$d_2$ by 1.** A benzene-$d_6$ solution of **1** (1.0 mg, 0.0024 mmol) was added to a benzene-$d_6$ solution of *trans*-**4**-$d_2$ (13 mg, 0.048 mmol), and the resulting solution (0.3 mL total volume) was added to an NMR tube that was subsequently flame-sealed. The $^1H$ NMR spectrum after 10 min revealed that conversion to the cis product was 64% complete. Additionally, the spectrum revealed that while the remaining trans starting material contained only 10% $^1H$ in the benzylic position, the cis product contained 43% $^1H$ in the benzylic position. After 1.5 h, conversion to product was complete and the product contained 40% $^1H$ in the benzylic position.

**Isomerization of *trans*-4-$d_2$ by 5.** A THF-$d_8$ solution of *trans*-**4**-$d_2$ (7.5 mg, 0.028 mmol) was added to a 1.0 mL volumetric flask. A THF-$d_8$ solution of **5** (6.9 mg, 0.016 mmol) was then added to the same flask, and the solution was diluted to 1.0 mL and transferred to an NMR tube that was subsequently flame-sealed. The progress of the isomerization and H/D exchange was observed by $^1H$ NMR spectroscopy at regular intervals. First-order decay of *trans*-**4** was observed for the isomerization with $k = (7.2 \pm 0.4) \times 10^{-4}\ M^{-1}\ s^{-1}$; the cis product contained 50% hydrogen in the benzylic position.

***cis*-9,10-Diisopropyl-9,10-dihydroanthracene-$d_2$ (*cis*-4-$d_2$).** The procedure of Gleiter et al. for the deuteration of 9,10-dihydroanthracene was used[40] with *trans*-**4** as substrate. A 20 mL DMSO-$d_6$ solution of NaH (5.6 mg, 0.23 mmol) was heated in a glass vessel with a fused Teflon stopcock at 90 °C for 1 h. *trans*-**4** (155 mg, 0.59 mmol) was added, and the (now pink) solution was stirred at 80 °C for 1 h. The reaction mixture was quenched by addition of $D_2O$ (75 $\mu$L, 4.0 mmol), and the solution turned orange. After the mixture was stirred for 10 min, $H_2O$ (20 mL) was added, leading to the precipitation of the product as a white powdery solid. The product was collected by filtration and washed with 5 mL of $H_2O$. Analysis of the crude product by $^1H$ NMR spectroscopy revealed 95% deuteration in the benzylic position. Purification by column chromatography (100% hexanes; silica gel) gave a white crystalline solid (100 mg, 64%) that was observed to be clean *cis*-**4**-$d_2$ by $^1H$ NMR spectroscopy with 95% deuteration. $^1H$ NMR ($C_6D_6$; 400 MHz): $\delta$ 7.12 (m, 8H, aryl), 3.27 (d, 0.1H, $J$ = 10.0 Hz, benzylic C*H*), 1.76 (septet, 2H, $J$ = 8.8 Hz, C*H*($CH_3$)$_2$), 0.97 (d, 12H, $J$ = 8.8 Hz, CH(C*H*$_3$)$_2$). Lit.[36] $^1H$ NMR (no solvent indicated): 7.20 (m), 3.27 ($J$ = 9.5 Hz), 1.00 ($J$ = 6.2 Hz).

**H/D Exchange between *cis*-4-$d_2$ and 1.** A THF-$d_8$ solution of **1** (1.0 mg, 0.0024 mmol) was added to a THF-$d_8$ solution of *cis*-**4**-$d_2$ (13 mg, 0.048 mmol), and the resulting solution (0.3 mL total volume) was added to an NMR tube. The $^1H$ NMR spectra after 10 min and 1 and 20 h revealed $^1H$ incorporation into the benzylic position of the substrate of 6.6%, 10%, and 18%, respectively.

**Isomerization of *trans*-4-$d_2$ by *t*-BuNHLi/*t*-BuNH$_2$.** Solutions of *trans*-**4**-$d_2$ (10 mg, 0.038 mmol) and *t*-BuNHLi (0.3 mg, 0.004 mmol) in THF-$d_8$ (0.3 mL total volume) were mixed and added to an NMR tube. *t*-BuNH$_2$ (7.9 $\mu$L, 0.075 mmol) was added to the tube with a syringe. The tube was then flame-sealed. The tube was heated to 45 °C, and the reaction progress was monitored by $^1H$ NMR spectroscopy at regular intervals. After 15 h, 51% conversion was observed, with 46% H in the benzylic position of the product and 1% H in the benzylic position of the substrate.

**H/D Exchange between *cis*-4-$d_2$ and *t*-BuNH$_2$ Catalyzed by *t*-BuNHLi.** Solutions of *cis*-**4**-$d_2$ (10 mg, 0.038 mmol) and *t*-BuNHLi (0.3 mg, 0.004 mmol) in THF-$d_8$ (0.3 mL total volume) were mixed and added to an NMR tube. *t*-BuNH$_2$ (7.9 $\mu$L, 0.075 mmol) was added to the tube with a syringe. The tube was then flame-sealed. The tube was heated to 45 °C, and the reaction progress was monitored by $^1H$ NMR spectroscopy at regular intervals. After 15 h, 6% H was observed in the benzylic position of the substrate.

**Isomerization of *trans*-4 by 2-$d_{34}$.** Solutions of **2**-$d_{34}$ (0.8 mg, 0.002 mmol) and *trans*-**4** (10 mg, 0.038 mmol) in THF-$d_8$ (0.3 mL) were mixed and added to an NMR tube. The relative quantities of *cis*-**4** and *trans*-**4**, and the amount of H in the benzylic position of each, were observed at 10 min and 1, 3, and 21 h by $^1H$ NMR spectroscopy (Table 1).

***trans*-(dmpe)$_2$Fe(H)($^{15}$NHCHO) (6-$^{15}N$).** CO (1 atm) was added to a degassed J. Young NMR tube containing a benzene-$d_6$ solution (0.3 mL) of **2**-$^{15}N$ (10 mg, 0.027 mmol). The tube was shaken for 4 h at 25 °C. The $^1H$ and $^{31}P\{^1H\}$ NMR spectra of **6**-$^{15}N$ (50% $^{15}N$ label) were identical with those obtained for **6**. $^{15}N\{^1H\}$ NMR ($C_6D_6$; 50.5 MHz): $\delta$ −24.1 (s).

***cis*-(dmpe)$_2$Fe(D)$_2$.** *trans*-(dmpe)$_2$Fe(Cl)$_2$ (1.0 g, 2.3 mmol), sodium (2.0 g, 87 mmol, cut finely), and THF (40 mL) were added to a 1 L glass vessel with a fused Teflon stopcock. The mixture was degassed using three freeze−pump−thaw cycles, and $D_2$ (2.5 atm) was added. The reaction mixture was stirred at ambient temperature until the sodium became a single large clump (1 week). The volatile materials were removed at reduced pressure, the purple-brown residue was extracted with benzene and toluene (70 mL each), and the extracts were filtered through Celite on a glass frit. The solvent was removed in vacuo to give a yellow-orange solid (0.82 g, 97%). $^1H$ NMR ($C_6D_6$; 400 MHz): $\delta$ 1.58 (br s, 10H, PC*H*$_2$/PC*H*$_3$), 1.35 (br m, 4H, PC*H*$_2$), 1.27 (s, 12H, PC*H*$_3$), 1.08 (d, 6H, $J_{HP}$ = 4.4 Hz, PC*H*$_3$). $^2H\{^1H\}$ NMR ($C_6D_6$; 61.6 MHz): $\delta$ −13.9 (br m) $^{31}P\{^1H\}$ NMR ($C_6D_6$; 162 MHz): $\delta$ 77.7 (undecet, $J$ = 9.1 Hz), 67.8 (t, $J$ = 26.7 Hz).

**Reaction of 2 with CO in the Presence of *cis*-(dmpe)$_2$Fe(D)$_2$.** Solutions of **2** (10 mg, 0.027 mmol) and *cis*-(dmpe)$_2$Fe(D)$_2$ (19 mg, 0.054 mmol) in benzene-$d_6$ and benzene-$h_6$ (each 0.3 mL) were added to two J. Young NMR tubes. The tubes were degassed using three freeze−pump−thaw cycles, and 1 atm of CO was added to each. The tubes were shaken for 12 h, and NMR spectroscopy ($^1H$, $^2H\{^1H\}$, and $^{31}P\{^1H\}$) indicated that **8** was formed with no incorporation of deuterium; *cis*-(dmpe)$_2$Fe(D)$_2$ remained unreacted.

**Reaction of 2 with CO in the Presence of (dmpe)$_2$Fe($^{13}$CO).** A benzene-$d_6$ (0.3 mL) solution of *cis*-(dmpe)$_2$Fe(H)$_2$ (10 mg, 0.028 mmol) was added to a J. Young NMR tube. The tube was degassed using three freeze−pump−thaw cycles, and 1 atm of $^{13}$CO was added. The tube was irradiated for 3.5 h, at which time NMR spectroscopy indicated complete conversion to (dmpe)$_2$Fe($^{13}$CO) ($^{13}$C{$^1$H} quintet at $\delta$ 222.9 ppm, $^{31}$P{$^1$H} doublet at 64.8 ppm). The tube was again degassed, and **2** (10 mg, 0.027 mmol) was added to the solution. The tube was degassed, and 1 atm of unlabeled CO was added to the tube. After the tube was shaken for 3.5 h, the $^{13}$C label was not observed in insertion product **6** by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy, and no loss of the label was observed in (dmpe)$_2$Fe($^{13}$CO).

**X-ray Structure Determination for [*trans*-(dmpe)$_2$Fe(H)(NH$_3$)]$_2$[OH]$_2$·H$_2$O.** The X-ray crystal structure was obtained by Dr. F. J. Hollander and Dr. A. G. Oliver at the UC Berkeley X-ray facility (CHEXRAY). The crystals were mounted on glass fibers using Paratone N hydrocarbon oil. All measurements were made on a SMART CCD area detector with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). The data were collected with a detector position of 60.00 mm. Data were integrated by the program SAINT and were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP.[55] The structure was solved by direct methods and expanded using Fourier techniques.

The coordinated ammonia of the iron complex forms hydrogen bonds to two symmetry-related hydroxide anions (N1−O1 = 2.95 Å; N1−O1′ = 2.88 Å), each of which are also hydrogen bonded to the ammonia of another symmetry-related iron complex and to the water of crystallization (O1−O2 = 2.55 Å). The H-bonding pattern is such that the two iron complexes and two H-bonded hydroxides form a rhomboidal dimer about the inversion center with two waters of crystallization attached to the sides. The hydrogen atoms of the hydride, ammonia, hydroxide, and water of crystallization were located from a difference Fourier map and assigned on the basis of the reasonable hydrogen-bond geometries they displayed. These hydrogens were assigned fixed $B_{\mathrm{iso}}$ values ($B_{\mathrm{iso}}$ = 2.85), and their positions were refined (all other hydrogen atoms were included in calculated positions but were not refined). The data were collected using 10 s frames with an $\omega$ scan of 0.3°. Empirical absorption corrections based on comparison of redundant and equivalent reflections were applied using SADABS[56] ($T_{\max}$ = 0.91, $T_{\min}$ = 0.78). The maximum and minimum peaks on the final difference Fourier map correspond to 0.39 and −0.49 e/Å$^3$, respectively.

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**Supporting Information Available:** Crystallographic data for [*trans*-(dmpe)$_2$Fe(H)(NH$_3$)]$_2$[OH]$_2$·2H$_2$O as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(55) XPREP (v. 5.03), part of the SHELXTL Crystal Structure Determination; Siemens Industrial Automation, Inc., Madison, WI, 1995.

(56) SADABS: Siemens Area Detector Absorption Correction Program: Sheldrick, G. M. Advance copy, private communication, 1996.