Efficient Hydrogenation of Ketones and Aldehydes Catalyzed by Well-Defined Iron(II) PNP Pincer Complexes: Evidence for an Insertion Mechanism

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Supporting Information

ABSTRACT: We have prepared and structurally characterized a new class of Fe(II) PNP pincer hydride complexes [Fe(PNP-iPr)(H)(CO)(L)]n (L = Br−, CH3CN, pyridine, PMe3, SCN−, CO, BH4−; n = 0, +1) based on the 2,6-diaminopyridine scaffold where the PiPr2 moieties of the PNP ligand are connected to the pyridine ring via NH and/or NMe spacers. Complexes [Fe(PNP-iPr)(H)(CO)(L)]n with labile ligands (L = Br−, CH3CN, BH4−) and NH spacers are efficient catalysts for the hydrogenation of both ketones and aldehydes to alcohols under mild conditions, while those containing inert ligands (L = pyridine, PMe3, SCN−, CO) are catalytically inactive. Interestingly, complex [Fe(PNPMe-iPr)(H)(CO)(Br)], featuring NMe spacers, is an efficient catalyst for the chemoselective hydrogenation of aldehydes. The first type of complexes involves deprotonation of the PNP ligand as well as heterolytic dihydrogen cleavage via metal-alkoxide cooperation, but no reversible aromatization/deprotonation of the PNP ligand. In the case of the N-methylated complex the mechanism remains unclear, but obviously does not allow bifunctional activation of dihydrogen. The experimental results complemented by DFT calculations strongly support an insertion of the C=O bond of the carbonyl compound into the Fe−H bond.

INTRODUCTION

The catalytic reduction of polar multiple bonds via molecular hydrogen plays a significant role in modern synthetic organic chemistry. This reaction is excellently performed by many transition metal complexes containing noble metals such as ruthenium, rhodium, or iridium.1 However, the limited availability of precious metals, their high price, and their toxicity diminish their attractiveness in the long run, and more economical and environmentally friendly alternatives have to be found. In this respect, the preparation of well-defined iron-based catalysts of comparable activity would be desirable.2 Iron is the most abundant transition metal in the earth’s crust and is ubiquitously available. Accordingly, it is not surprising that the field of iron-catalyzed hydrogenations of polar multiple bonds is rapidly evolving, as shown by several recent examples.3−7 It is interesting to note that many of these hydrogenations involve ligand−metal bifunctional catalysis (metal−ligand cooperation),8 that is, the complexes contain electronically coupled hydride and acidic hydrogen atoms as a result of heterolytic dihydrogen cleavage that may be transferred to polar unsaturated substrates in an outer-sphere fashion or may be transferred via hydride migration (inner-sphere mechanism). An effective way of bond activation by metal−ligand cooperation involves aromatization/dearomatization of the ligand in pincer-type complexes. In particular, pincer ligands in which a central pyridine-based backbone is connected with −CH2PR2 and/or −CH2NR2 substituents were shown to exhibit this behavior.9 This has resulted in the development of novel and unprecedented iron catalysis where this type of cooperation plays a key role in the heterolytic cleavage of H2.4 In the case of ketones and aldehydes, most efficient are...
complexes of the types [Fe(PNP)\text{CH$_2$-iPr})\text{(CO)}\text{(H)}\text{(Br)}\] and [Fe(PNP)\text{CH$_2$-iPr})\text{(CO)}\text{(H)}\text{(k$^3$-BH$_4$)}], where the bromide and BH$_4^-$ ligands are labile, facilitating the coordination of the substrates. It has thus been suggested by Milstein that this reaction proceeds via an inner-sphere mechanism involving insertion of the carbonyl compounds into the Fe=$\text{H}$ bond.$^{1a,c}$

We are currently focusing on the synthesis and reactivity of iron complexes containing PNP pincer ligands based on the 2,6-diaminopyridine scaffold. In these ligands the aromatic pyridine ring and the phosphine moieties are connected via NH, N-alkyl, or N-aryl linkers. The advantage of these ligands is that both substituents of the phosphine and amine sites can be systematically varied in a modular fashion, which has a decisive effect on the outcome of reactions.$^{10}$ Recently we prepared the cationic Fe(II) hydride complex cis-[Fe(PNP-iPr)(CO)\text{(H)}\]*, which involved reversible NH activation as well as heterolytic dihydrogen cleavage via metal−PNP ligand cooperation.$^{11}$ This complex turned out to be catalytically inactive for the hydrogenation of ketones and aldehydes, which was attributed to the fact that this complex is substitutionally inert and/or that the basicity of the hydride is too low.

Herein we report the synthesis, characterization, and catalytic activity of a series of neutral iron hydride complexes of the type [Fe(PNP-iPr)(CO)(H)(L)]\] (2a−c) where the P(iPr)$_2$ moieties of the PNP ligand are connected to the pyridine ring via NH and/or NMe spacers (Scheme 1). In addition, the synthesis of a series of neutral and cationic hydride complexes of the type $^{[Fe(PNP-\text{H}_{2},\text{Me})\text{(CO)}(H)(L)]}$\] (3a−g) (n = +1, 0) where L = CH$_3$CN, pyridine, PMe$_3$, k$^2$-N-coordinated SCN$^-$, and k$^1$-coordinated BH$_4^-$ is described. All complexes featuring labile ligands L = Br$^-$, CH$_3$CN, BH$_4^-$ are efficient catalysts for the hydrogenation of ketones and aldehydes to alcohols under mild conditions. Moreover, the N-methylated complex 2b is a chemoselective catalyst for the reduction of aldehydes. The first example of catalytic hydrogenation of aldehyde that is chemoselective against ketone was recently reported by Beller.$^{13}$ However, this reaction required elevated temperatures (120 °C) and a high H$_2$ pressure (20 bar). The experimental results are complemented by DFT calculations.

### RESULTS AND DISCUSSION

The synthesis of complexes [Fe(PNP-iPr)(CO)(H)(Br)]\] (2a−c) was accomplished in 63−67% isolated yields by treatment of anhydrous FeBr$_2$ with 1 equiv of the corresponding PNP-iPr ligands 1a−c in THF in the presence of CO and subsequent addition of 1.1 equiv of Na[BH$_3$Et$_2$] (Scheme 2). This reaction proceeds via the intermediacy of the dibromo complexes [Fe(PNP-iPr)(CO)(Br)$_2$]$,^1c$ which, in principle, can be isolated in pure form as shown previously,$^{13}$ but are labile, slowly losing CO, and were thus directly used without prior isolation. In the case of the symmetrical N-methylated PNP-iPr ligand 1b, two isomers were obtained in a ca. 2.7:1 ratio with the hydride ligand being trans to the bromide and to the CO ligand, respectively, which could not be separated. All hydride complexes are air sensitive both in the solid state and in solution.

Characterization was accomplished by elemental analysis and by $^{1}$H, $^{13}$C($^1$H), and $^{31}$P($^1$H) NMR and IR spectroscopy. The $^{1}$H NMR spectrum confirmed the presence of one hydride ligand, which appeared at $\sim-21.4$, $\sim-21.6$, and $\sim-21.8$ ppm, respectively, as a well-resolved triplet with a $^3$$J_{HH}$ coupling constant of about 57 Hz. Isomer 2b exhibits the hydride resonance at $\sim-1.1$ ppm. In the $^{13}$C($^1$H) NMR spectrum the most noticeable resonance is the low-field resonance of the carbonyl carbon atom trans to the pyridine nitrogen observed at 217.1−222.7 ppm ($J_{CP}$ about 13−23 Hz). The $^{31}$P($^1$H) NMR spectra of complexes 2a and 2b give rise to a singlet at 147.1 and 164.0 ppm, respectively, while in the case of 2c two doublets centered at 165.0 and 147.2 ppm are observed. In the IR spectrum the strong bands for CO stretching frequencies are found in the range 1901 to 1903 cm$^{-1}$.

The solid-state structure of 2a was determined by single-crystal X-ray diffraction. A structural view is depicted in Figure 1 with selected bond distances given in the caption. Complex 2a adopts a distorted octahedral geometry around the metal center with the hydride ligand being in cis position to a CO ligand. The PNP ligand is coordinated to the iron center in a typical tridentate meridional mode, with a P1−Fe1−P2 angle of 164.58(4)$^\circ$. The hydride and the N−H atoms could be unambiguously located in the difference Fourier maps. The Fe−H distance was refined to 1.46(2) Å.

Complexes 2a−c are substitutionally labile. This has been exemplarily studied in more detail with 2a (Scheme 3). Dissolution of 2a in MeOH$^{-}$, resulted in an immediate replacement of the Br$^-$ ligand to give the cationic complex [Fe(PNP-iPr)(CO)(MeOH$^{-}$)]\] (3a), as evident by a new hydride resonance at $\sim-26.6$ ppm and a $^3$$J_{HH}$ signal at 140.6 ppm. Interestingly, in ethanol dissociation of the bromide...
These complexes exhibit the characteristic hydride resonances (indicated by a broad signal at 3.61 ppm (4H). The observation of a broad four-proton resonance in this region of the $^1$H NMR spectrum for a free coordination site (vide infra). The addition of L = CH$_3$CN, pyridine, PMe$_3$, SCN$^-$, CO, and BH$_4^-$ leads to the formation of the corresponding cationic or neutral complexes [Fe(PNP-iPr)(H)(CO)(L)]$^+$ (3b–g) as shown in Scheme 3. Complexes 3b–g could also be isolated in pure form by reacting 2a with the respective ligands CH$_3$CN (neat), pyridine, PMe$_3$, SCN$^-$ (Na$^+$ salt), BH$_4^-$ (Na$^+$ salt), and CO in both the absence and presence of silver salts in 83–97% isolated yields. These complexes exhibit the characteristic hydride resonances at $-18.6$, $-20.1$, $-11.1$, $-19.8$, $-7.5$, and $-18.2$, ppm, respectively. In the case of 3g the BH$_4^-$ ligand gives rise to a broad signal at $-3.61$ ppm (4H). The observation of a broad four-proton resonance in this region of the $^1$H NMR spectrum is typical for $\kappa^4$-coordinated BH$_4^-$ ligands of iron complexes and indicates dynamic behavior of this ligand.4c

Structural views of 3b, 3c, 3d, 3e, and 3g are depicted in Figures 2–6 with selected bond distances given in the captions.

The lability of complexes 2a and 3b–g was also studied by ESI-MS. Solutions of these complexes in CH$_3$CN were subjected to ESI-MS analysis in the positive ion mode (the neutral complexes were investigated in the presence of NaCl to obtain cationic sodiated species). In the case of 3b–g the intact complexes [M]$^+$ (vide infra) were observed as major fragments. We also investigated an EtOH solution of 2a in the presence of KO$_2$Bu in the hopes of detecting the alkoxide complex [Fe(PNP-iPr)(H)(CO)(OEt)]. However, only the fragment at $m/z$ 426.1 was detected as the major species. These observations are in accord with the fact that the ligands Br$^-$, OEt$^-$, BH$_4^-$, and CH$_3$CN trans to the hydride ligand are substitutionally labile, while pyridine, PMe$_3$, SCN$^-$, and CO are substitutionally inert.

The catalytic activity of all hydride complexes was investigated in the hydrogenation of ketones and aldehydes. In preliminary experiments various solvents were tested for the

Scheme 3. Substitution of the Bromide Ligand in 2a by MeOH-$d_4$, CH$_3$CN, Pyridine, PMe$_3$, SCN$^-$, CO, and BH$_4^-$
Figure 4. Structural view of [Fe(PNP-iPr)(H)(CO)(PMe$_3$)]BF$_4$ (3d) showing 50% thermal ellipsoids (most hydrogen atoms and BF$_4^-$ anion omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1–P1 2.1884(7), Fe1–P2 2.1871(7), Fe1–N1 2.018(1), Fe1–N4 1.998(1), Fe1–C18 1.733(2), Fe1–C3 2.2753(5), Fe1–H1 1.46(2), P1–Fe1–P2 154.89(2), N1–Fe1–C18 176.86(7).

Figure 5. Structural view of [Fe(PNP-iPr)(H)(CO)(CH$_2$CN)]$^+$ (3b) and Fe(PNP-iPr)(H)(CO)–(κ$^3$-BH$_4$)$^-$ (3g) showing 50% thermal ellipsoids (most hydrogen atoms and BF$_4^-$ omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1–P1 2.1884(7), Fe1–P2 2.1881(7), Fe1–N1 1.998(2), Fe1–C18 1.733(2), Fe1–H1 1.46(2), Fe1–H1B1 1.67(2), P1–Fe1–P2 159.99(5), N1–Fe1–C18 178.13(9).

Figure 6. Structural view of [Fe(PNP-iPr)(H)(CO)(x$^2$N-SCN)] (3e) showing 50% thermal ellipsoids (most hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe1–P1 2.1884(7), Fe1–P2 2.1871(7), Fe1–N1 2.018(1), Fe1–N4 1.998(1), Fe1–C18 1.738(2), Fe1–H1 1.49(2), P1–Fe1–P2 164.78(1), N1–Fe1–C18 172.84(5).

Table 1. Iron-Catalyzed Hydrogenation of Acetophenone$^a$

| entry | solvent | yield [%]$^b$ | TOF [h$^{-1}$] |
|-------|---------|--------------|---------------|
| 1     | THF     | 36           | 18            |
| 2     | MeOH    | 58           | 29            |
| 3     | iPrOH   | 89           | 45            |
| 4     | tAmylOH | 99           | 50            |

$^a$Reaction conditions: 2a (0.025 mmol, 1.0 mol %), KOtBu (0.05 mmol), substrate (2.5 mmol), solvent (5 mL), H$_2$ (5 bar), 2 h. Yields were determined by $^3$H NMR.

However, in terms of a better reproducibility 0.5 mol % catalyst was used for all subsequent reactions.

In contrast to 2a, under the same reaction conditions, as well as with even 5 mol %, complex 2b, bearing NMe linkers, was completely inactive for the reduction of ketones, while 2c, containing one NH and one NMe linker, was catalytically active but with a significantly lower activity than 2a (28% yield). On the other hand, the catalytic activity of both [Fe(PNP-iPr)(H)(CO)(CH$_2$CN)]$^+$ (3b) and Fe(PNP-iPr)(H)(CO)–(κ$^3$-BH$_4$)$^-$ (3g) was similar to that of 2a (94% yield). The reaction with 3g could be performed even without addition of an external base, although slightly higher temperatures were required to achieve comparable activities (50 °C) since base has to be generated by alcoholysis of free BH$_4^-$.

Similar observations were recently made by Milstein.$^{14}$ In sharp contrast to the substitutionally labile complexes 2a, 3b, and 3g, the inert compounds 3c–f were catalytically inactive.

On the basis of these results, we investigated the scope and limitations of catalyst 2a using various substrates (Table 2). Halogen substituents had no notable influence on the catalytic activity, while the reaction with 4-methoxycacetophenone and 4-nitroacetophenone resulted in significantly lower yields (entries 5 and 6). Likewise, for simple ketones such as cyclohexanone and benzophenone lower activity was observed. In the presence of a nitrile or primary amine substituents on the aromatic system no reaction was observed, presumably due to preferential coordination of these groups to the iron center, thus blocking a vacant coordination site to accommodate an incoming substrate (entries 7 and 8). The same result was found for 4-acetylpyridine. This is in line with the observation that 3c, containing a strongly bound pyridine ligand, is catalytically inactive. The reduction of 2-acetylpyridine was extremely efficient, giving full conversion even after 1 h (TOF = 200 h$^{-1}$, entry 11). In this case, coordination of pyridine is obviously hampered due to the bulky acetyl substituent in the ortho position of the pyridine unit. The reduction of trans-4-phenylbutenone resulted in mixtures, where reduction of the double bond also took place (entry 13). Finally, the hydrogenation of aldehydes was tested with complexes 2a and 2b as catalysts utilizing benzaldehyde, 4-isopropylbenzaldehyde, cyclohexane carboxaldehyde, picolinic acid, and isonicotinic acid (Table 3).

$^6$Yields were determined by $^3$H NMR.

Organometallics
In order to gain a mechanistic understanding of the catalytic hydrogenation of aldehydes and ketones, some stoichiometric reactions of 2a were investigated. Treatment of 2a in THF with KOtBu resulted in an immediate color change from orange to deep red. In the 1H NMR spectrum hydride signals were no longer present, but in the IR spectrum two strong absorptions at 1872 and 1822 cm$^{-1}$ were observed ($\nu_{\text{Fe-H}}$ and $\nu_{\text{CO}}$). This may be tentatively assigned to the formation of $[\text{Fe}(\text{PNP-H-}i\text{-Pr})(\text{H})(\text{CO})]$ (A) as a result of dehydrohalogenation. In this context it is important to note that a series of related iron PNP pincer complexes were prepared and even structurally characterized recently by Schneider$^{15}$ and Jones.\textsuperscript{16} The formation of the Fe(0) dicarbonyl complex $[\text{Fe}(\text{PNP-}i\text{-Pr})(\text{CO})_{2}]$ can be ruled out by comparison with an authentic sample. \textsuperscript{11} Moreover, purging the solution with H$_2$ afforded a mixture of the trans and cis dihydride complexes $[Fe(\text{PNP-}i\text{-Pr})(\text{CO})(\text{H})_{2}]$ (4a,b) (Scheme 4). Such a reaction does not take place with $[\text{Fe}(\text{PNP-}i\text{-Pr})(\text{CO})_{2}]$. The $^1$H NMR spectrum of the mixture at room temperature exhibited a triplet at $-9.02$ ppm for the trans-dihydride 4a and only one broad signal at $-13.4$ ppm for the cis-dihydride 4b due to fast exchange between the two hydrides. Complexes 4a and 4b did not show any significant reactivity toward acetophenone even after 1 day, suggesting that these are not active species in the catalytic reduction of ketones. Our findings are fully consistent with Milstein’s discoveries based on the related iron pincer complex $[\text{Fe-}[\text{PNPCH}_{2}-i\text{-Pr})\text{H}(\text{CO})(\kappa^{1}\text{-BH}_{4})]$,\textsuperscript{4c} but strongly contrast the recently reported computational study by Yang on the iron-catalyzed reduction of acetophenone.\textsuperscript{17} In his calculated mechanism, the reaction proceeds via trans-$[\text{Fe}(\text{PNP-}i\text{-Pr})(\text{CO})_{2}]$ (4a) and involves an outer-sphere hydrogen transfer from this complex to the carbonyl carbon atom of acetophenone in EtOH as solvent. Accordingly, we believe that this mechanism is not operative in our system with respect to ketone reduction, although trans-dihydride iron PNP complexes were shown to be important species in other reactions.\textsuperscript{4b,3,13,15,16,18} The reduction of aldehydes, in

### Table 2. Iron-Catalyzed Hydrogenation of Ketones$^a$

| Entry | Substrate | Product | Yield$^d$ [\%] | TOF [h$^{-1}$] |
|-------|-----------|---------|----------------|---------------|
| 1     | R = H     | 99      | 100            |               |
| 2$^b$ | R = H     | 77      | 770            |               |
| 3     | R = Cl    | 99      | 100            |               |
| 4     | R = Br    | 99      | 100            |               |
| 5     | R = OMe   | 34      | 34             |               |
| 6     | R = NO$_2$| 47      | 47             |               |
| 7     | R = NH$_2$| 30      | 30             |               |
| 8     | R = CN    | 64      | 64             |               |
| 9     |           | 99      | 200            |               |
| 10    |           | 10     | 100            |               |
| 11$^c$|           | 45      |                |               |
| 12    |           | 45      |                |               |
| 13    |           |         |                |               |

$^a$Reaction conditions: 2a (0.0125 mmol), KOtBu (0.025 mmol), substrate (2.5 mmol), EtOH (5 mL), H$_2$ (5 bar), 2 h. $^b$Reaction conditions: 2a (0.0025 mmol), KOtBu (0.005), substrate (2.5 mmol), EtOH (3 mL), 1 h. $^c$Reaction time: 1 h. $^d$Yields were determined by $^1$H NMR.

### Table 3. Iron-Catalyzed Hydrogenation of Aldehydes$^a$

| Entry | Substrate | Product | Yield$^d$ [\%] | TOF [h$^{-1}$] |
|-------|-----------|---------|----------------|---------------|
| 1$^b$ |           | 23      | 23             |               |
| 2     |           | 99      | 120            |               |
| 3     |           | 99      | 120            |               |
| 4$^c$ |           | 99      | 60             |               |
| 5     |           | 99      | 120            |               |
| 6     |           |         |                |               |

$^a$Reaction conditions: 2a or 2b (0.125 mmol), KOtBu (0.25 mmol), substrate (2.5 mmol), EtOH (5 mL), H$_2$ (5 bar), 10 min. $^b$Reaction conditions: 2a (0.0125 mmol), KOtBu (0.025 mmol), substrate (2.5 mmol), EtOH (5 mL), H$_2$ (5 bar), 2 h. $^c$Reaction time: 20 min. $^d$Yields were determined by $^1$H NMR.

### Scheme 4. Dehydrohalogenation of 2a with KOtBu in THF to Give A and Subsequent Addition of H$_2$ to Afford a Mixture of the trans and cis Dihydride Complexes 4a and 4b
particular with 2b, remains mechanistically unclear at this stage, and the involvement of dihydride complexes cannot be ruled out.

In sharp contrast to the above observations in THF, when KOtBu was added to an EtOH solution of 2a in the presence of dihydrogen, no changes in the IR, $^1$H NMR, and $^{31}$P($^1$H) NMR spectra were observed. This again emphasizes the particular role of EtOH as solvent apparently preventing the formation of 4a and 4b.

Preliminary DFT calculations\textsuperscript{19} were carried out to establish a reasonable mechanism using the hydrogenation of acetaldehyde with 2a as model. A summary of these results with the most relevant points along the catalytic cycle is presented in Scheme 5. Loss of a labile bromide ligand and deprotonation of an NH group in the catalytic precursor 2a will produce a five-coordinated complex, [Fe(PNP$^{-}$H-iPr)(H)-(CO)] (A), that is the starting point in the mechanistic investigations and also the reference for all free energy values. The catalytic cycle depicted in Scheme 5 starts with the occupation of the free coordination site in A by the substrate (in B). Then there is nucleophilic attack of the hydride on the carbonyl C atom with formation of the alkoxide complex, C. The reaction proceeds with coordination of dihydrogen (D) and subsequent protonation of the O atom with formation of the alcohol and regeneration of the hydride (E). The cycle is closed by ligand exchange with liberation of one molecule of the product and coordination of another substrate from E back to B. The highest energy barrier along the cycle corresponds to the hydride migration step, and its value (17.1 kcal/mol) indicates a facile reaction. It has to be emphasized that the PNP ligand remains deprotonated and, thus, deprotonated along the entire cycle and means that N–H acidity has no active part in the reaction mechanism that should not be classified as bifunctional catalysis in this case.

It is also interesting to note that deprotonation of the PNP ligand is accompanied by a substantial increase of the ligand charge. In fact, in the N-protonated counterpart of A, [Fe(PNP-iPr)(H)(CO)]\textsuperscript{+}, the PNP ligand is more positive (C\textsubscript{PNP} = 1.03) electron-donating anionic ligand. In fact, the activation barrier for dihydrogen splitting involving protonation of the PNP N atom, corresponding to reversible aromatization/dearomatization of that ligand to afford E', is considerably higher (34.1 kcal/mol) than the one associated with protonation of the O atom of the alkoxide producing the final alcohol product as shown in Scheme 5 (16.0 kcal/mol).

The dihydrogen splitting step was also studied with the inclusion of one explicit solvent molecule (ethanol) in the calculations (Scheme 6). In fact, the ethanol molecule acting as a proton shuttle could alter the most favorable path and change the conclusions above. The results obtained are shown in Scheme 6 and indicate that O-protonation of the alkoxide ligand remains the preferred pathway for the reaction, with a barrier 12.5 kcal/mol lower than the value calculated for protonation of the PNP N atom. The O-protonation step calculated with an explicit solvent molecule (EtOH), represented in Scheme 6, has a free energy barrier 6.3 kcal/mol higher than the same process calculated without the ethanol molecule (cf. Scheme 5) due to the rise in the entropy term originated by the presence of that extra molecule. If one compares energy values, the barrier becomes 5 kcal/mol lower in the case with the extra ethanol molecule. This result confirms that the PNP ligand remains deprotonated and, thus, deprotonated along the entire cycle and means that N–H acidity has no active part in the reaction mechanism that should not be classified as bifunctional catalysis in this case.
than the same ligand in \( \text{A} \) (\( C_{\text{PNP}} = 0.14 \)). Accordingly, the hydride in the cationic complex is also electron poorer than the equivalent ligand in \( \text{A} \), \( C_{\text{PNP}} = -0.14 \) and \(-0.16 \), respectively, indicating that \( \text{A} \) should be a better active species in a reaction where the key step is hydride nucleophilic attack on the substrate carbonyl C atom.

**CONCLUSION**

In conclusion, we have prepared a new class of Fe(II) PNP pincer hydride complexes \( \text{[Fe(PNP-Pr)(CO)(H)(L)]} \), and \( \text{[Fe(PNP-Pr)(CO)(H)(L)]} \) (3a−g) \( (n = 1, 0) \) based on the 2,6-diaminopyridine scaffold where the \( \text{Pr} \) isotopes of the PNP ligand connect to the pyridine ring via NH and/or NMe spacers and where the complexes feature both labile (Br−, CH₃CN, BH₄⁻) and inert (pyridine, PMe₂, SCN⁻, CO) coligands. Complexes with labile ligands are efficient catalysts for the hydrogenation of ketones and aldehydes to alcohols under mild conditions. These reactions take place at room temperature with turnover frequencies up to 770 h⁻¹ using 5 bar hydrogen pressure and seem to involve heterolytic dihydrogen cleavage via metal-alkoxide cooperation, with the PNP ligand not being involved in dihydrogen activation. The PNP ligand remains deprotonated throughout the catalytic cycle, acting as a strongly electron donating anionic ligand. The catalytic reactions do not proceed in aprotic solvents, but require alcoholic solutions, with the catalytic reactions not proceeding in the absence of an electron donating anionic ligand. The catalytic reactions do not proceed via a bifunctional mechanism. Detailed mechanistic studies, in particular the reaction of catalyst 2b where the mechanism remains unclear, as well as catalyst optimizations are currently under way.

**EXPERIMENTAL SECTION**

**General Procedures.** All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques or an MBraun inert-gas glovebox. The solvents were purified according to standard procedures. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. The ligands \( \text{N}_2\text{N}^\prime\text{-bis(bis(isopropylphosphino)-2,6-diaminopyridine} \) (PNP-Pr) (1a), \( \text{N}_2\text{N}^\prime\text{-bis(bis(isopropylphosphino)-2,6-dimethylpyridine} \) (PNPMe₂-Pr) (1b), and \( \text{N}_2\text{N}^\prime\text{-bis(bis(isopropylphosphino)-N-methyl-2,6-diaminopyridine} \) (PNPMe₂-NPPr) (1c) and complex \( \text{[Fe(PNP-(Pr)(CO)(H)(L)]} \) (M) were prepared according to the literature. \( \text{H} \), \( ^{13}\text{C} \), and \( ^{31}\text{P} \) NMR spectra were recorded on Bruker AVANCE-250 and AVANCE-400 spectrometers. \( ^{13}\text{C}(\text{H}) \) NMR spectra were referenced internally to residual protio-solvent and solvent resonances, respectively, and are reported relative to tetramethylsilane (\( \delta = 0 \) ppm). \( ^{31}\text{P}(\text{H}) \) NMR spectra were referenced externally to \( \text{H}_2\text{PO}_4 \) (85%) (\( \delta = 0 \) ppm). All mass spectrometric measurements were performed on an Esquire 3000plus 3D-quadrupole ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany) in positive-ion mode electrospray ionization (ESI-MS). All mass calculations are based on the lowest mass (i.e. most abundant) iron isotope (\( ^{56}\text{Fe-isotope} \)).

**General Procedure for the Hydrogenation Reactions.** All hydrogenation reactions were performed at ambient temperature (25°C) under a hydrogen atmosphere of 5 bar using a 90 mL Fisher-Porter tube, which was flushed several times with hydrogen gas prior to the addition of the reaction solution. For the preparation of the reaction solutions a vial was charged with the specified amount of catalyst, substrate, and TEOH. Subsequently, KOtBu was added and the solution was taken up into a syringe and transferred to the Fisher-Porter tube. After stirring the solution for the stated time, pressure was carefully released, diethyl ether (20 mL) was added, and the reaction was quenched by addition of an aqueous solution of \( \text{H}_2\text{PO}_4 \) (0.5 M, 0.5 mL). The organic phase was separated, washed with brine, and dried over MgSO₄. The solvent was removed under reduced pressure, and the isolated product was characterized by NMR spectroscopy.

**Syntheses.** \( \text{[Fe(PNP-Pr)(H)(CO)(Br)]} \) (2a). Anhydrous FeBr₂ (190 mg, 0.88 mmol) and 1a (300 mg, 0.88 mmol) were dissolved in 12 mL of THF. The immediately formed yellow suspension was stirred for 1 h at room temperature before CO was bubbled through the reaction mixture for 10 min. During this time the color of the suspension changed from yellow to blue. The reaction mixture was cooled to 0°C, and a solution of Na₂[NBEt₃] in toluene (0.97 mL, 1 M, 0.97 mmol) was slowly added. The reaction mixture was stirred for 30 min at 0°C, in which time the color changed from blue to dark red. After an additional 60 min at room temperature the solution was filtered and the solvent was removed under reduced pressure. The dark residue was taken up in THF (3 mL), and the product was precipitated by addition of \( n \)-hexane (15 mL). The precipitate was separated from the supernatant solution, washed with \( n \)-pentane (3 × 10 mL), and dried under vacuum to afford 2a (76 mg, 67%). Anal. Calcd for \( \text{C}_{31}\text{H}_{34}\text{BrFeN}_3\text{O}_2\text{P}: C, 42.87; H, 6.77; N, 8.30. Found: C, 42.71; H, 6.77; N, 8.30.**

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[Fe(PNP)M(Pr)H]Br(CO)Br(OCOMe)(2c). This complex was prepared analogously to 2a using 1c (300 mg, 0.84 mmol), FeBr2 (181 mg, 0.84 mmol), and Na[BFe(tol)2] (0.92 mL, 1 M in toluene, 0.92 mmol) as starting materials. Yield: 275 mg (63%) of an orange powder. Anal. Calc. for C20H37BF4FeN4OP2: C, 43.35; H, 6.73; N, 7.36. Found: C, 43.59; H, 7.19; N, 7.96. 1H NMR (δ, CDCl3): 7.31 (t, J = 7.8 Hz, 1H, py), 6.22 (d, J = 7.8 Hz, 1H, py), 5.91 (d, J = 7.8 Hz, 1H, py), 5.61 (bs, 1H, NMe), 2.80 (m, 1H, CH(CH3)2), 3.07 (d, J = 3.1 Hz, 3H, NCH3), 2.75 (m, 1H, CH(CH3)2), 2.53 (m, 2H, CH2(CH3)), 1.72 (dd, J = 6.9 Hz, J = 17.4, 3H, CH(CH3)2), 1.65 (dd, J = 7.5 Hz, J = 13.6, 3H, CH(CH3)2), 1.52 (dd, J = 7.8 Hz, J = 9.5, 3H, CH(CH3)2), 1.44 (dd, J = 7.1 Hz, J = 10.7, 3H, CH(CH3)2), 1.26 (dd, J = 6.8 Hz, J = 17.0, 3H, CH(CH3)2), 1.18 (dd, J = 6.9 Hz, J = 17.4, 3H, CH(CH3)2), 0.94 (dd, J = 6.7 Hz, J = 14.4, 3H, CH(CH3)2), 0.88 (dd, J = 6.7 Hz, J = 14.4, 3H, CH(CH3)2), 1.26-16.4 (7H, Jpp = 57.2, 1H, FeH). 31P{1H} NMR (δ, CDCl3): 20.22: (s, Br), 162.4 (bs, py2, py3), 161.0 (bs, py2, py3), 138.9 (s, py4), 98.2 (d, Jpp = 68.8 Hz, py4), 95.7 (d, Jpp = 68.8 Hz, py3), 35.5 (d, Jpp = 21.7 Hz, CH(CH3)2), 33.4 (d, Jpp = 12.1 Hz, NCH3). 31P{1H} NMR (δ, CDCl3): 20.22: (s, Br), 162.0 (t, Jcp = 8.4 Hz, CH3), 27.1 (d, Jcp = 24.1 Hz, CH3), 21.1 (s, CH(CH3)2), 20.4 (d, Jcp = 8.8 Hz, CH3), 19.5 (d, Jcp = 8.8 Hz, CH3), 18.7 (d, Jcp = 10.1 Hz, CH3), 18.5 (s, CH(CH3)2), 18.3 (s, CH(CH3)2), 18.0 (d, Jcp = 9.4 Hz, CH3), 17.1 (d, Jcp = 7.9 Hz, CH3). 31P{1H} NMR (δ, CDCl3): 20.22: 160.5 (d, Jep = 145.1 Hz), 147.2 (d, Jep = 145.1 Hz). IR (ATR, cm⁻¹): 1901 (vCO).

[Fe(PNP)-Pr][H]CO(CH3)CN][BF4](3b). To a solution of 2a (150 mg, 0.30 mmol) in CH2O (10 mL) was added NaSCN (27 mg, 0.33 mmol). After stirring for 1 h at room temperature, the solvent was filtered and the solvent was removed under reduced pressure. The product was washed twice with diethyl ether and dried under vacuum to afford an off-white powder. Yield: 136 mg (93%). Anal. Calc. for C20H37BF4FeN4OP2: C, 43.72; H, 7.08; N, 11.57. Found: C, 43.78; H, 7.13; N, 11.42. 1H NMR (δ, DMSO-d6): 8.26 (s, 2H, NH), 7.26 (t, J = 7.9 Hz, 1H, py), 6.13 (d, J = 7.9 Hz, 2H, py), 2.48 (m, 2H, CH(CH3)2), 2.41 (m, 2H, CH(CH3)2), 1.44 (m, 6H, CH(CH3)2), 1.38 (m, 6H, CH(CH3)2), 1.12 (m, 6H, CH(CH3)2), 0.95 (m, 6H, CH(CH3)2), −19.84 (m, 6H, CH(CH3)2). 13C{1H} NMR (δ, DMSO-d6): 22.07 (t, Jcp = 24.1 Hz, CO), 161.0 (t, Jcp = 9.6 Hz, py), 138.7 (s, py5), 137.4 (d, Jcp = 5.4 Hz, SCN), 96.6 (s, py1), 9.5 (t, Jcp = 10.6 Hz, CH3), 27.8 (t, Jcp = 14.9 Hz, CH3), 18.8 (s, CH(CH3)2), 17.9 (s, CH(CH3)2), 17.8 (s, CH(CH3)2), 17.4 (s, CH(CH3)2), 31P{1H} NMR (δ, CDCl3): 20.22: 146.6. IR (ATR, cm⁻¹): 2074 (v(CS)), 1921 (v(CO)). ESI-MS (m/z, EtOH): pos. ion: 502.2 [M + Na]⁺, 426.1 [M – SCN]⁻, 398.2 [M – CO]⁻.

Method A. To a suspension of Fe(PNP)[CO][Br2] (200 mg, 0.40 mmol) in THF (24 mL) was added sodium borohydride (76 mg, 2.00 mmol). After stirring for 5 min at room temperature, the solution was filtered and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (10 mL), the resulting solution was filtered, and the solvent was removed under reduced pressure. The product was precipitated by addition of n-pentane. The bright yellow powder was washed twice with n-pentane and dried under vacuum. Yield: 132 mg (75%).

Method B. To a suspension of Fe(PNP-Pr)[CO][Br2] (200 mg, 0.40 mmol) in EtOH (10 mL) was added sodium borohydride (65 mg, 1.71 mmol). An immediate gas evolution took place, and the initially blue suspension turned into a dark orange solution within 5 min. After stirring the reaction mixture for 30 min, all volatiles were removed under reduced pressure. The residue was dissolved in dichloromethane (10 mL), the resulting solution was filtered, and the solvent was removed under reduced pressure. The product was precipitated by addition of n-pentane. The bright yellow powder was washed twice with n-pentane and dried under vacuum. Yield: 132 mg (75%).
(t, J_{CF} = 10.6 Hz, CH(CH_{3})_{2}) 27.8 (t, J_{CF} = 13.2 Hz, CH(CH_{3})_{2}), 19.5 (t, J_{CF} = 3.8 Hz, CH(CH_{3})_{2}) 18.6 (t, J_{CF} = 4.6 Hz, CH(CH_{3})_{2}), 18.4 (s, CH(CH_{3})_{2}), 17.4 (s, CH(CH_{3})_{2}), the CO resonance could not be observed. $^{31}$P(1H) NMR ($\delta$, CD_{2}Cl_{2}, 20 °C): 151.2. IR (ATR, cm$^{-1}$): 1911 (υ(CO)). ESI-MS (m/z, EtOH); pos. ion: 426.1 [M – BH_{4}]^{+}, 398.1 [M – BH_{2} – CO]^{+}.

**X-ray Structure Determination.** X-ray diffraction data of 2a-CD_{2}Cl_{2}, 3b, 3c, 3d, and 3e were collected at T = 100 K (3f: T = 200 K due to a phase transition at lower temperatures) in a dry stream of nitrogen on Bruker Kappa APEX II diffractometers using graphite-monochromatized Mo Kα radiation ($\lambda = 0.7103 73$ Å) and fine sliced $\varphi$- and $\omega$-scans. Data of 3d were collected at T = 185 K on a Bruker SMART APEX diffractometer using $\omega$-scans. Data were reduced to intensity values with SAINT, and an absorption correction was applied with the multiscan approach implemented in SADABS.25 The structures were solved by charge flipping using SUPERFLIP24 and refined against $F$ with JANA2006.26 Non-hydrogen atoms were refined anisotropically. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. H atoms connected to N, B, and Fe atoms were located in difference Fourier maps. The Fe–H distances were restrained. The N–H distances were restrained in 2a-CD_{2}Cl_{2} and 3d, whereas the N–H atoms in the remaining models were freely refined. In 3f, the B–H distances were restrained to 1.000(1) Å. Molecular graphics were generated with the program MERCURY.26 Crystal data and experimental details are given in Tables S1 and S2.

**Computational Details.** All calculations were performed using the Gaussian 09 software package27 on the Phoenix Linux Cluster of the Vienna University of Technology. The optimized geometries were obtained with the B3LYP functional.28 That functional includes a mixture of Hartree–Fock exchange29 with DFT19 exchange–correlation, given by Becke’s three-parameter functional with the Lee, Yang, and Parr correlation functional, which includes both local and nonlocal terms. The basis set used for the geometry optimizations (basis b1) consisted of the Stuttgart/Dresden ECP (SDD) basis set30 to describe the electrons of iron and a standard 6-31G(dp) basis set31 for all other atoms. Transition-state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQNM) developed by Schlegel et al.,32 following extensive searches of the potential energy surface. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles. Atomic charges were obtained by means of a natural population analysis (NPA).33 The electronic energies ($E_{el}$) obtained at the B3LYP/b1 level of theory were converted to free energy at 298.15 K and 1 atm ($G_{el}$) by using zero-point energy and thermal energy corrections based on structural and vibration frequency data calculated at the same level.

Single-point energy calculations were performed using the M06 functional and a standard 6-31+1G(d,p) basis set34 on the geometries optimized at the B3LYP/b1 level. The M06 functional is a hybrid meta-GGA functional developed by Truhlar and Zhao,35 and it was shown to perform very well for the kinetics of transition metal molecules, providing a good description of weak and long-range interactions.36 Solvent effects (ethanol) were considered in the M06/6-311+1G(dp)//B3LYP/b1 energy calculations using the polarizable continuum model (PCM) initially devised by Tomasi and co-workers37 with radii and nonelectrostatic terms of the SMD solvation model, developed by Truhler et al.38 The free energy values presented ($G_{el}^{\text{soln}}$) were derived from the electronic energy values obtained at the M06/6-311+1G(dp)//B3LYP/b1 level, including solvent effects ($E_{el}^{\text{soln}}$), according to the following expression: $G_{el}^{\text{soln}} = E_{el}^{\text{soln}} + G_{el}$.

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