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Synthesis, Characterization, and Reactivity of a *High-Spin* Iron(II) Hydrido Complex Supported by a PNP Pincer Ligand and Its Application as a Homogenous Catalyst for the Hydrogenation of Alkenes

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S Supporting Information

ABSTRACT: This study focused on the synthesis and characterization of a range of low-valent, high-spin iron(II) complexes supported by a carbazole-based PNP pincer-type ligand. The addition of the lithiated ligand (PNP)Li to FeCl₂(THF)₁₅ yielded the chlorido complex (PNP)FeCl (1), which could be readily converted to the four-coordinate iron(II) alkyl complexes (PNP)FeR $[R = CH_2SiMe_3 (3a), Me_3 (3a)]$ (3b), CH₂Ph (3c)]. These iron(II) complexes were fully characterized by X-ray analysis and a comprehensive, density-functional-theory-assisted study with complete assignment of their paramagnetic ¹H and ¹³C NMR spectra. Treatment of 1 with KHBEt₃ or the addition of molecular hydrogen to (PNP)FeR afforded a



high-spin iron(II) PNP hydrido complex, which was identified as the dimer $[(PNP)Fe(\mu-H)]_2$ (4) with two bridging hydrido ligands between the iron centers. Exposing complexes 1 and 4 to carbon monoxide led to the corresponding six-coordinate, diamagnetic complexes (PNP)Fe(CO)₂Cl (2) and (PNP)Fe(CO)₂H (5), of which 2 was present as cis/trans isomers. Furthermore, 4 was found to be an active catalyst for the hydrogenation of alkenes.

INTRODUCTION

Replacement of noble metals by the readily available, cheap, and generally less toxic¹ 3d metals in catalysis is currently one of the fastest expanding research fields in chemistry.² Especially iron, which has long been regarded as a "sleeping beauty",^{2a} has experienced a renaissance with regard to its application in homogeneous catalysis during the past decade.^{2a,f,3} One of the most relevant reactions to both industry and academia is the homogeneous hydrogenation of olefins because of its excellent atom economy and its mild, environmentally friendly reaction conditions.^{4,5} In recent years, progress was made in the field of iron-catalyzed olefin hydrogenation by the establishment of various effective homogeneous catalysts. Successful examples range from iron pentacarbonyl⁶ to tris(phosphino)borate complexes developed by Peters et al.7 to tridentate pyridinediimine-supported iron(0) complexes by Chirik et al.^{2f,8} to the aminophosphine-supported catalysts established by Jones and co-workers.⁹ The mechanistic proposals for most of these reactions involved the generation of a reactive paramagnetic iron hydrido species as a part of the catalytic cycle.^{2f,7b,10} Furthermore, these high-spin iron species were not only postulated as key intermediates in catalytic hydrogenations but also for other reductions such as hydrosilylations^{3d,11} and hydroborations,^{12,13} as well as biological systems such as the iron–molybdenum nitrogenase¹⁴ and iron–sulfur hydrogenase.^{15,16} Given their ubiquity, it is surprising that only very few fully characterized paramagnetic, *high-spin* iron hydrido complexes are known to date.^{17–20} This is due to their reactivity, which makes the isolation and detection of these

compounds a challenging target of research.¹⁶ The groups of Nishibayashi and Tonzetich recently demonstrated that lowvalent iron(II) hydrido complexes can be stabilized by a PNP pincer ligand with a pyrrole backbone.^{20,21} In 2013, our group described the synthesis of a carbazole-based PNP ligand scaffold,²² which was shown to be capable of inducing interesting reactivity within different transition metals throughout the periodic table.²³



Herein, we report the synthesis of a high-spin ferrous hydrido complex supported by the PNP pincer ligand (PNP)H and its reactivity toward the catalytic hydrogenation of olefins.

RESULTS AND DISCUSSION

Synthesis and Characterization of Iron(II) PNP Chlorido, Carbonyl, and Alkyl Complexes. The chlorido complex (PNP)FeCl (1) was readily prepared by the addition of the lithiated ligand (PNP)Li^{23a} to a suspension of

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 $FeCl_2(THF)_{1.5}$ in tetrahydrofuran (THF) and isolated in good yield (Scheme 1).





Single crystals suitable for X-ray diffraction were obtained from a saturated solution of 1 in *n*-hexane at -40 °C. The solidstate molecular structure of 1 (Figure 1) revealed that the



Figure 1. Molecular structure of **1** with displacement ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity. The data summarized represent one of the two independent molecules found in the asymmetric unit cell. Selected bond angles [deg] and distances [Å]: Fe1–N1 1.980(3), Fe1–Cl1 2.2456(9), Fe1–P1 2.4033(10), Fe1–P2 2.3895(9); Cl1–Fe1–P1 110.80(4), Cl1–Fe1–P2 125.98(4), P1–Fe1–P2 125.98(4), N1–Fe1–Cl1 125.03(8), N1–Fe1–P1 93.17(7), N1–Fe1–P2 93.02(7).

coordination sphere of the four-coordinate iron(II) center is best described as distorted tetrahedral (geometry factor $\tau_4 =$ 0.77, where $\tau_4 =$ 1.0 represents an ideal tetrahedral structure and $\tau_4 =$ 0.0 represents an ideal square-planar structure).²⁴ The PNP ligand coordinates in a tridentate fashion with both phosphane "arms" bound to the metal center. The Fe–P [2.4033(19) and 2.3895(9) Å, respectively] and Fe–N [1.980(3) Å] bond lengths are in accordance with those of comparable compounds in the literature.^{20,21,23d} Distortion of the coordination geometry can be ascribed to the rigidity of the carbazole backbone, which forces the phosphanes to coordinate at a rather acute angle. The pincer donor atoms describe a P1– N1–P2 bite angle of $84.03(6)^\circ$, while the chlorido ligand is located at an angle of α (N1–Fe1–Cl1) = $125.03(8)^\circ$ with an Fe–Cl bond length of 2.2456(9) Å. Very recently, the Nishibayashi group reported the synthesis of several iron(II) *high-spin* complexes stabilized by a similar carbazolide-based PNP pincer ligand.^{23d}

The solution magnetic moment of 1 with a formal electron count of 14e⁻ was determined by the Evans method²⁵ to be 4.8 $\mu_{\rm B}$ in a toluene- d_8 solution at room temperature. This is in good correspondence with the *spin-only* value of a S = 2 spin system ($\mu_{\rm SO,S=2} = 4.9 \ \mu_{\rm B}$). Complex 1 gives rise to a ¹H NMR spectrum with 11 signals of chemical shifts in the range of +300 to -10 ppm, which is consistent with a molecule with C_s symmetry in solution (Figure 2). These large shifts are significantly greater than commonly seen in *high-spin* iron complexes^{20,21,26} and indicate a high delocalization of unpaired spin density over the ligand atoms, resulting in a large Fermi contact shift.²⁷ *High-spin* ferrous complexes tend to lead to rather sharp signals compared to other paramagnetic 3d metals because of the rapid electron-spin relaxation of their unpaired electrons [which, in turn, renders the observation of electron paramagnetic resonance (EPR) spectra challenging].^{27,28}

Figure 2 shows that the methyl groups of the isopropyl substituents appeared as four broad singlets with a relative intensity corresponding six hydrogen atoms between +20 and -6 ppm, while the methyl protons of the *tert*-butyl groups gave rise to one sharp singlet with a relative intensity of 18H at 2.2 ppm. The six residual resonances, all with a relative intensity of two, could not be assigned based on intensity arguments. However, the spatial proximity of a nucleus to the paramagnetic center leads to the broadening of respective signals as a result of the growing domination of the dipolar relaxation. This dipolar relaxation is proportional to r^{-6} , where *r* is the spatial distance to the paramagnetic center.²⁹ The line widths of the signals at 51.3 and 7.7 ppm ($\nu_{1/2}$ = 32.0 and 51.5 Hz, respectively) were significantly smaller than the others, which allowed a reasonable assignment to the carbazole resonances $H^{4/5}$ and $H^{2/7}$. This assignment was also supported by a ${}^{13}C-{}^{1}H$ correlation experiment, in which these protons showed cross-peaks with the respective carbazole carbon atoms (vide infra).

A total of 15 resonances over the range of +1150 to -40 ppm were observed in the ¹³C NMR spectrum of **1**, which is in accordance with the postulated molecular structure in solution. While the methyl carbon atoms of the *tert*-butyl groups were readily assigned to the signal at 107 ppm by their relative



Figure 2. ¹H NMR spectrum of 1 (600.13 MHz, toluene-d₈, 295 K). Solvent resonances are indicated by asterisk symbols.

intensity of six, identification of the other signals remained more challenging.

The density of the unpaired spin at a certain nucleus can be calculated by density functional theory (DFT) methods, which allows the determination of the Fermi contact shift of the respective nucleus.²⁹ However, this method is only viable for the prediction of NMR shifts dominated by the Fermi contact shift. The latter is the case for paramagnetic ¹³C NMR spectra of many 3d metal complexes, which can be more reliably assigned based on this approach than the corresponding ¹H NMR spectra. For a full assignment of the observed signals, the spin densities $\rho_{\alpha\beta}$ were evaluated at the B3LYP³⁰ level of theory, using the TZVP³¹ basis set for the iron atom only and the 6-311G(d,p)³² basis set for all other atoms. As illustrated in Figure 3, the calculated values correlate well with the observed ¹³C resonances of complex 1.



Figure 3. Plot of the correlation between the experimental (295 K, 150.92 MHz, toluene- d_8) and calculated [B3LYP/6-311(d_p) + TZVP (only for iron)] ¹³C NMR resonances of complex 1. The red dotted line represents the best linear fit: slope m = 1.119; offset b = -31.88; coefficient of determination $R^2 = 0.9838$. Uncertain assignments are indicated by semicolons, and solvent resonances are indicated by asterisks.

The highest value for the spin density was predicted for the methine carbon C^{16} , which appeared as a singlet with a chemical shift of 1123 ppm, while the resonances at 961 and 809 ppm could be assigned to the bridging carbazole carbon atoms $C^{8a/9a}$ and $C^{4a/4b}$, respectively. The good accordance with the predicted values also allowed the assignment of the carbazole carbon atoms $C^{1/8}$ to the signal at 387 ppm, as well as of the carbazole carbon atoms $C^{1/8}$ to the signal at 387 ppm, as well as two doublets at a chemical shift of 11 and -26 ppm, respectively (${}^{1}J_{CH} = 151.1$ Hz). Additionally, the methylene carbon atom C^{12} corresponded to the most high-field-shifted signal at -51 ppm, and the methyl carbon atom C^{14} could be assigned to the singlet at 330 ppm. However, because of the close proximity of the remaining signals and the rather large deviation of the predicted values, a clear differentiation between the carbon atoms $C^{3/6}$, C^{10} , C^{13} , C^{15} , C^{17} , and C^{18} was not possible.

The use of calculated local spin densities to corroborate the assignment of the remaining ¹H resonances of **1** is more problematic because of a greater significance of the pseudocontact shift for the rather small shifts observed in ¹H NMR spectra in comparison with ¹³C NMR spectra.²⁹

However, the trend reflected by the predicted spin densities is in line with the rather widely dispersed ¹H NMR spectrum of complex **1** and, together with the HETCOR experiments, allowed a reasonable assignment of the remaining proton resonances. The furthest shifted signal at 290.9 ppm could therefore be assigned to the methine proton of one of the isopropyl substituents, while the resonance of the other methine proton was observed at 46.7 ppm. The diastereotopic methylene protons appeared as two signals with a chemical shift of 172.9 and 144.0 ppm, respectively.

The addition of 5 bar of carbon monoxide (CO) to complex 1 resulted in an immediate change of color from bright to dark red. The ¹H NMR spectrum of the reaction mixture showed a clean conversion to a newly formed diamagnetic species with seven resonances, indicating a molecule with $C_{2\nu}$ symmetry in solution. This high symmetry is consistent with the stereoisomer 2-trans, in which two carbonyl ligands are oriented trans to each other. The ${}^{31}P{}^{1}H$ NMR spectrum of complex 2-trans showed a single resonance at 46.1 ppm. However, if kept under an atmosphere of CO for 18 h, the formation of a new diamagnetic species was observed. The transformation was monitored via ${}^{31}P{}^{1}H$ NMR spectroscopy, where the new species appeared as a broad singlet at 50.4 ppm. Furthermore, the resonance pattern in the ¹H NMR spectrum suggested that the resulting complex exhibited C_s symmetry in solution. We reasoned that an equilibrium between 2-trans and the related isomer 2-cis, where both carbonyl ligands are located cis to each other, was present in solution. Furthermore, this hypothesis was also supported by the IR spectrum, in which a set of two CO bands emerged at 2015 and 1960 cm⁻¹ next to the CO vibrational band at 1977 cm⁻¹ attributed to 2-trans (Scheme 2). Removal of the CO atmosphere in vacuo revealed





Scheme 3. Synthetic Routes to the *High-Spin* Ferrous Alkyl Complexes 3a-3c



a mixture of complexes **1**, **2-cis**, and **2-trans**, of which over time only traces of the carbonyl complexes were detected. The inseparable nature of the mixture of all three complexes precluded the complete characterization of complexes **2-cis** and **2-trans**.

The reaction of complex 1 with various alkylating agents resulted in the formation of ferrous alkyl complexes (PNP)FeR [$R = CH_2SiMe_3$ (3a), Me (3b), Bn (3c)] in good yield (Scheme 3). Additionally, treatment of the protio ligand (PNP)

H with the ferrous alkyl precursor $(\text{tmeda})\text{Fe}(\text{CH}_2\text{SiMe}_3)_2^{33}$ and subsequent workup led to the isolation of analytically pure **3a**.

The molecular structures of $(PNP)FeCH_2SiMe_3$ (3a; Figure 4) and (PNP)FeBn (3c, see the Supporting Information) were



Figure 4. Molecular structure of 3a with displacement ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [deg]: Fe-N1 2.0195(17), Fe-P1 2.4492(6), Fe-P2 2.4387(6), Fe-C36 2.064(2); P2-Fe-P1 119.45(2), N1-Fe-P1 89.86(5), N1-Fe-P2 91.24(5), N1-Fe-C36 133.51(8), C36-Fe-P1 104.46(6), C36-Fe-P2 117.16(7), P1-N1-P2 83.00(4).

confirmed by X-ray diffraction, featuring the expected "pincer" coordination mode of the PNP ligand in the distorted tetrahedral coordination sphere ($\tau_4 = 0.80$ for 3a). The alkyl carbon of 3a, with an Fe–C bond length of 2.064(2) Å, is located at an angle of α (N1–Fe1–C36) = 133.51(8)°. Additionally, distortion of the coordination geometry is also reflected in a small deviation of the methylene linker atoms of the aromatic carbazole plane and the PNP bite angle of 83.00(4)°. The observed structural metrics are in accordance with a recently published PNP-supported iron(II) alkyl complex by Nishibayashi et al.^{23d}

The alkyl complexes 3a-3c were paramagnetic with a solution magnetic moment of 4.9 μ_B for complex 3a (4.9 μ_B for 3b and 4.8 μ_B for 3c) as determined by Evans' method, consistent with a *high-spin* state for all three compounds. Complex 3a gave rise to a ¹H NMR spectrum with 11 paramagnetically shifted resonances over the range of +240 to -20 ppm, suggesting the same C_s -symmetric structure in solution as that observed in the solid state. The ¹³C NMR spectrum of 3a displayed 16 sharp signals distributed over the range of +1200 to -200 ppm. All protons and carbons were therefore detected, except the ones of the directly coordinated methylene group.^{29,34} Computation of the local spin densities in complex 3a again allowed the assignment of most signals (see the Supporting Information).

Synthesis and Characterization of a High-Spin Iron(II) PNP Hydrido Complex. The reaction of 1 with KHBEt₃ resulted in formation of the dinuclear hydrido complex $[(PNP)Fe(\mu-H)]_2$ (4; Scheme 4). Additionally, 4 could be synthesized by hydrogenation of the alkyl complexes 3a-3c. It is interesting to note that the reaction time of the hydrogenation critically depended on the nature of the alkyl substituent in the precursor complex (vide infra).

Single crystals suitable for X-ray diffraction were obtained from a saturated solution of 4 in *n*-pentane at -40 °C. The

Scheme 4. Synthesis of 4 via Salt Metathesis and Hydrogenation



molecular structure (Figure 5) revealed that 4 is present as a dimer in the solid state with two bridging hydrido ligands



Figure 5. Molecular structure of **4** with displacement ellipsoids drawn at 50% probability. Carbon-bound hydrogen atoms are omitted for clarity. Disordered *tert*-butyl groups are not shown. Selected bond distances [Å] and angles [deg]: Fe1–Fe2 2.5880(7), Fe1–N1 1.989(3), Fe1–P1 2.4063(10), Fe1–P2 2.3777(10), Fe1–H1A 1.65(2), Fe1–H1B 1.63(2); N1–Fe1–P2 88.46(8), N1–Fe1–P1 92.20(8), N1–Fe1–Fe2 116.96(8), Fe1–H1A–Fe2 101(1), Fe1–H1B–Fe2 106(1), N1–Fe1–Fe2–N41 88.81(12). See the Supporting Information for both monomer bond metrics.

between the metal centers. The coordination sphere of each iron atom is best described as highly distorted square-pyramidal (geometry index $\tau_5 = 0.30$, with $\tau_5 = 0.00$ for an ideal squarepyramidal structure and $\tau_5 = 1.00$ for an ideal trigonalbipyramidal structure),³⁵ with the iron centers being displaced from the "pincer" planes defined by the PNP donor atoms by 1.2153(16) and 1.0252(10) Å, respectively. The Fe-Fe distance in complex 4 is 2.5880(7) Å, which lies within the range reported for covalent Fe-Fe bonds.³⁶ However, a more definitive assessment is precluded by the bridging hydrides, which have been shown to induce a significant decrease in the distance within comparable dimeric iron hydrido com-plexes.^{17,18,20} Because of the high quality of the crystals, both hydrido ligands were directly located and refined. The ironhydride bonds exhibit bond lengths of d(Fe1-H1A) = 1.65(2)Å and d(Fe1-H1B) = 1.63(2) Å and angles of $\alpha(Fe1-H1A-H1B) = 1.63(2)$ Fe2) = $101(1)^{\circ}$ and α (Fe1-H1B-Fe2) = $106(1)^{\circ}$. Moreover, it is interesting to note that both molecular fragments are twisted by a torsion angle of $\alpha(N1-Fe1-Fe2-N41) =$ $88.81(12)^{\circ}$ with respect to each other. This can be explained by the high steric demand of the isopropyl substituents. As a result, the planes defined by the PNP donor atoms are also twisted by an angle of $35.38(8)^{\circ}$. In contrast to the dimeric

PNP-supported ferrous hydrido complex reported by Tonzetich et al.,²⁰ both phosphorus donor atoms of the PNP ligand coordinate to the same iron center.

The magnetic momentum of compound 4 was determined to be 3.4 $\mu_{\rm B}$ in a benzene solution at 295 K for each iron center by the method of Evans. This reduced magnetic susceptibility indicated a significant antiferromagnetic coupling, as observed for other dimeric ferrous complexes.^{17,18,20} This observation, in accordance with the complex ¹H NMR spectrum, suggested that the dimeric structure is also present in solution.

The treatment of complex 4 with excess CO (Scheme 5) resulted in an immediate change of color from brown to deep





purple. The ¹H NMR spectrum of the reaction mixture was consistent with a diamagnetic molecule of C_s symmetry, as represented by the carbonyl complex 5 in Scheme 5. The hydrido ligand of 5 appeared as a triplet at -6.32 ppm with a coupling constant of ${}^{2}J_{HP}$ = 53.0 Hz. This multiplicity is not observed in the phosphorus-decoupled ¹H{³¹P} NMR spectrum, in which a singlet was detected for the hydrido ligand. The postulated cis configuration was also supported by a ¹³C NMR spectrum, in which complex 5 gives rise to two carbonyl resonances at 217.3 and 211.7 ppm. Although numerous attempts to crystallize 5 were made, no single crystals suitable for X-ray diffraction spectroscopy were obtained. However, crystallization of the reaction products from a saturated solution of *n*-pentane at -40 °C yielded dark-purple crystals of a minor byproduct, which was identified as the iron(I) species 6 (see the Supporting Information). Attempts to synthesize 6 via the reduction of complex 1 under a CO atmosphere remained unsuccessful. The formation of a similar iron(I) species after the addition of CO to a related ferrous high-spin complex has been reported by the Holland group.³ Furthermore, Tonzetich et al. and Walter et al. recently reported the synthesis of related iron(I) complexes supported by a pyrrolyl-based PNP pincer ligand.^{20,38}

Iron-Catalyzed Homogenous Hydrogenation of Olefins. Facile conversion of the alkyl complexes 3a-3c to the hydrido complex 4 by treatment with molecular hydrogen (H₂) motivated us to investigate the potential of 4 as a hydrogenation catalyst for alkenes. The best precatalyst for that reaction was determined to be the methyl complex 3b because of its fast conversion to 4 in comparison with the other alkyl precursors (Table 1).

The tested hydrogenations of alkenes were performed at 23 °C with 1 mol % precatalyst under a pressure of 8 bar of H_2 , free of base, and in the absence of oxygen and water. The progress of hydrogenation catalysis was monitored via ¹H NMR spectroscopy. Under the given reaction conditions (8 bar of H_2), styrene was hydrogenated to ethylbenzene within 6 h after the addition of hydrogen (Table 2, entry 1). Stoichiometric conversion of complex 4 with styrene resulted in the rapid

Table 1. Conversion of 3 to 4 via Hydrogenation^a

	$(PNP)FeR \xrightarrow{H_2} 4$	
compound	R	t
3a	CH ₂ SiMe ₃	24 h
3b	Me	30 min
3c	CH_2Ph	35 min

^{*a*}Conditions: 0.4 mL of C_6D_6 ; 16.4 μ mol of (PNP)FeR; $p(H_2) = 8$ bar; T = 293 K; conversion of >95% was observed via ¹H NMR spectroscopy.

formation of a novel paramagnetic species, which resisted further identification.

Table	e 2.	Iron-Cata	lyzed	Hyc	lrogenation	of Alkenes ^a
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		R = (R" + R' R"" +	$H_2 \xrightarrow{[Fe]} C_6 D_6$	R R" R' R""		
	entry	substrate	product	time [h]	^b conv. [%]	
-	1			6	100	
	2	F	F	4	100	
	3	N	N	2	100	
	4	Ph	Ph	30	100	
	5	Ph	Ph	72	34	
	6		\bigcirc	4	100	
	7	\sim	$\sim \sim$	20	100	
	8	\sim	$\sim \sim$	25	100	
	9	\succ	\succ	72	_	

^{*a*}Conditions: 0.4 mL of C_6D_6 ; catalyst load of **3b** = 1 mol %; $p(H_2) = 8$ bar; T = 293 K; catalytic reactions were performed in a J. Young tube with a large head space. ^{*b*}Conversion was monitored by ¹H NMR spectroscopy.

A first investigation into the substrate scope of the reaction was carried out (Table 2) to evaluate the influence of structural and electronic variations within the substrate on the reaction rate. Hydrogenation of 2-vinylpyridine with only 2 h of reaction time proceeded at a much faster rate than that of styrene. This observation could be ascribed to the polarizing character of the nitrogen atom in the pyridine moiety but may also indicate a preferred coordination to the catalytic site. α -Methylstyrene, norbornene, and secondary aliphatic alkenes such as 2-pentene and 2-hexene were hydrogenated to complete conversion. On the other hand, hydrogenation of *trans*-stilbene only proceeded to 34% conversion, while decomposition of the catalyst was observed. Finally, hydrogenation of a tetrasubstituted alkene, such as 2,3-dimethylbut-2-ene, did not produce the related alkane. Interestingly, the related primary olefins, 1-pentene and 1hexene, underwent rapid isomerization to the corresponding secondary olefins after the addition of hydrogen. Investigations concerning this isomerization are underway. The mechanism of this reaction is the subject of current research within our group, but all observations to date indicate a molecular catalytic transformation rather than the formation of colloidal species. We note that mercury poisoning did not affect the hydrogenation, although the formation of iron nanoparticles is not necessarily precluded by a negative result of this test.³⁹

CONCLUSION

In this work, we have demonstrated the results of an investigation into the coordination chemistry of a carbazolidebased PNP pincer ligand with iron. A PNP ferrous chlorido complex was shown to be capable of serving as a precursor for the more reactive iron(II) alkyl complexes. Calculated spin densities were employed in order to assign the paramagnetic NMR spectra of these compounds. The ferrous alkyl complex could be transformed into a high-spin iron(II) hydrido complex by hydrogenation. X-ray crystallography revealed that the ferrous hydrido complex is a dimer with two bridging hydrido ligands between the iron(II) centers. Additionally, treatment of the paramagnetic compounds with CO resulted in the formation of diamagnetic dicarbonyl analogues. The respective chlorido complexes appeared to exist in an equilibrium between cis and trans isomers. Furthermore, the ferrous hydrido complex was shown to be an effective catalyst for the hydrogenation of various olefins. Investigations concerning the mechanism of this reaction are currently underway.

EXPERIMENTAL SECTION

All experiments were carried out in oven-dried glassware under an inert gas atmosphere by using standard glovebox or Schlenk techniques. Argon 5.0 from Messer Group GmbH was used as the inert gas and dried over Granusic phosphorus pentoxide granulate prior to use. All solvents were purchased anhydrous from Sigma-Aldrich and either collected from a solvent purification system (M. Braun SPS 800) after being dried over activated alumina columns or dried and degassed using standard methods and stored in glass ampules under an argon atmosphere.⁴⁰ Deuterated solvents were purchased from Deutero GmbH, dried over sodium (benzene- d_6 and toluene- d_8), vacuum-distilled, degassed by at least three successive freeze-pump-thaw cycles, and stored over molecular sieves in Teflon valve ampules under argon. Samples for NMR spectroscopy were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. NMR spectra were recorded on Bruker NMR spectrometers (Avance II 400 MHz and Avance III 600 MHz). ¹H and ¹³C NMR spectra were referenced to residual solvent peaks $[C_6D_{61}, 7.16 \text{ ppm}]^{(1)}$ and 128.06 ppm (^{13}C) ; toluene- $d_{81}, 2.08 \text{ ppm}$ (¹H) and 20.43 ppm (¹³C)]. ³¹P NMR spectra were recorded broadband proton-decoupled and referenced to external P(OMe)₃ (141.0 ppm with respect to 85% H₃PO₄ at 0.0 ppm). The specific assignment of the signals was corroborated using ¹H COSY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC spectra relative to external tetramethylsilane. The appearance of the signals was described using the following abbreviations: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (multiplet), b (broad signal). IR spectra were recorded on a Varian 3100 Fourier transform infrared spectrometer. All samples were prepared as a Nujol mull under an atmosphere of argon and pressed between sodium chloride plates before being measured. Continuous-wave X-band (ca. 9 GHz) EPR spectra were acquired using a Bruker Biospin Elexsys E500 spectrometer. The magnetic field and microwave frequency were calibrated with a Bruker ER 041XK Teslameter and a Bruker microwave-frequency counter. Elemental analysis (carbon, hydrogen, and nitrogen) was carried out at

the Microanalysis Laboratory of the Faculty of Chemistry and Earth Sciences at the University of Heidelberg with an Elementar Vario MICRO cube machine. Single-crystal X-ray diffraction measurements were performed on an Agilent SuperNova-E charge-coupled device or a Bruker AXS Smart 1000 diffractometer at the X-ray crystallography laboratory of the Department of Inorganic Chemistry at the University of Heidelberg. All measurements were performed at low temperature with either Mo K α (λ 0.71073 Å) or Cu K α (λ 1.5428 Å) radiation. Compounds (PNP)H,^{23a} (PNP)Li,^{23a} FeCl₂(THF)_{1,5},⁴¹ and (tmeda)-Fe(CH₂SiMe₃)₂³³ were prepared according to the literature. All other reagents were purchased from commercial sources, degassed, and used without further purification unless otherwise stated.

Synthesis of (PNP)FeCl (1). To a suspension of FeCl₂(THF)₁₅ (454.0 mg, 1.95 mmol, 1.05 equiv) in THF (20 mL) was added a solution of (PNP)Li (1.01 g, 1.85 mmol, 1.0 equiv) in THF (3 mL). The resulting dark-red reaction mixture was allowed to stir at room temperature overnight. The solvent was removed in vacuo, and the residue was taken up in toluene (5 mL) and filtered through a pad of Celite. All volatiles were removed in vacuo, and the crude product was washed with *n*-pentane to yield 1 as a red solid (915 mg, 1.45 mmol, 78% yield). Single crystals of 1 suitable for X-ray crystallography were obtained as dark-red crystals by recrystallization from *n*-hexane at -40 °C. ¹H NMR (600.13 MHz, toluene- d_8 , 295 K): δ 290.9 (s, 2H, CH(CH₃)₂), 172.9 (s, 2H, CHHP), 144.0 (s, 2H, CHHP), 51.3 (s, 2H, H_{Carb4/5}), 46.7 (s, 2H, CH(CH₃)₂), 19.9 (bs, 6H, CH(CH₃)₂), 11.4 (bs, 6H, $CH(CH_3)_2$), 7.7 (s, 2H, $H_{Carb2/7}$), 2.2 (s, 18H, $C(CH_3)_3$, 0.7 (s, 6H, $CH(CH_3)_2$), -5.1 (s, 6H, $CH(CH_3)_2$). ¹³C NMR (150.92 MHz, toluene-d₈, 295 K): δ 1132.2 (s, 2C, CH(CH₃)₂, C^{16}), 985.2 (s, 2C, $C_{Carb8a/9a}$), 808.5 (s, 2C, $C_{Carb4a/4b}$), 386.5 (s, 2C, $C_{Carb1/8}$), 329.5 (s, 2C, CH(CH₃)₂, C¹⁴), 293.8 (s, 2C), 266.2 (s, 2C), 224.5 (s, 2C), 223.2 (s, 2C), 107.0 (q, ${}^{1}J_{CH} = 125.4$ Hz, 6C, $CH(CH_3)_2$, C^{11}), 10.8 (d, ${}^{1}J_{CH} = 151.1$ Hz, $C_{Carb4/5}$), 2.7 (s, 2C), 0.6 (s, 2C), -26.1 (d, ${}^{1}J_{CH} = 151.1$ Hz, 2C, $C_{Carb2/7}$), -50.4 (s, 2C, CH_{2} , C^{12}). μ_{eff} = 4.8 μ_B (Evans, toluene- d_8 , 295 K). Anal. Calcd for C₃₄H₅₄ClFeNP₂: C, 64.82; H, 8.64; N, 2.22. Found: C, 64.67; H, 8.75; N, 2.45.

Synthesis of (PNP)Fe(CO)₂Cl (2). To a solution of 1 (20 mg, 31.7 μ mol) in C₆D₆ (0.5 mL) was added an atmosphere of CO (5 bar). The color of the solution changed immediately from red to dark red. The reaction product was identified as 2-trans. After 18 h under a CO atmosphere, full conversion to 2-cis was observed. Both compounds resisted further purification. Characterization of 2-trans. ¹H NMR (600.13 MHz, C₆D₆, 295 K): δ 8.25 (s, 2H, H_{Carb}), 7.25 (s, 2H, H_{Carb}), 3.51 (bs, 4H, CH₂), 2.50 (bs, 4H, CH(CH₃)₂), 1.51 (s, 18H, $C(CH_3)_3$, 1.23 (bs, 12H, $CH(CH_3)_2$), 1.13 (bs, 12H, $CH(CH_3)_2$). ¹³C NMR (150.92 MHz, toluene- d_8 , 295 K): δ 217.0 (t, ² J_{CP} = 22.7 Hz, CO), 148.5 (s), 139.1 (s), 129.5 (s), 124.8 (vt, J = 3.8 Hz), 117.3 (s), 115.2 (s), 34.5 (s), 32.4 (s), 26.4 (t, J = 11.3 Hz), 24.3 (t, J = 9.9Hz), 19.2 (s), 18.2 (s). ${}^{31}P{}^{1}H{}$ NMR (242.92 MHz, C₆D₆, 295 K): δ 46.0 (s). IR: (cm⁻¹) 1977 (CO). Characterization of 2-cis. ¹H NMR (600.13 MHz, C_6D_6 , 295 K): δ 8.40 (s, 2H, H_{Carb}), 7.28 (s, 2H, H_{Carb}), 3.99 (bs, 2H, CH₂), 3.27 (bs, 2H, CH₂), 2.86 (bs, 2H, CH(CH₃)₂), 1.89 (bs, 2H, CH(CH₃)₂), 1.55 (s, 18H, C(CH₃)₃), 1.24-1.17 (m, $6H, CH(CH_3)_2$, 1.10–1.06 (m, $6H, CH(CH_3)_2$), 0.95–0.87 (m, 12H, CH(CH₃)₂). ¹³C NMR (150.92 MHz, toluene- d_8 , 295 K): δ 215.2 (t, ${}^{2}J_{CP}$ = 24.8 Hz, CO), 213.7 (bs, CO), 148.6 (s), 139.3 (s), 128.8 (s), 124.1 (vt, J = 4.0 Hz), 118.4 (s), 115.3 (s), 34.6 (s), 32.5 (s), 26.9 (t, J = 10.9 Hz), 26.2 (t, J = 11.2 Hz), 23.9 (vt, J = 8.9 Hz), 19.9 (s), 19.4 (s), 18.3 (s), 17.7 (s). ${}^{31}P{}^{1}H{}$ NMR (242.92 MHz, C₆D₆, 295 K): δ 50.4 (bs). IR (cm⁻¹): 2015 (CO), 1960 (CO).

Synthesis of (PNP)Fe(CH₂SiMe₃) (3a). Method A. To a solution of (PNP)H (30 mg, 55.6 μ mol, 1.0 equiv) in C₆H₆ (0.5 mL) was added a solution of (tmeda)Fe(CH₂SiMe₃)₂ (19.3 mg, 55.6 μ mol, 1.0 equiv) in C₆H₆ (0.5 mL). The color of the reaction mixture changed to yellow immediately, and the reaction was allowed to stir for 30 min at room temperature. All volatiles were removed in vacuo, and the residue was taken up in *n*-hexane, filtered through a pad of Celite, and kept at -40 °C overnight. The yellow crystals were washed with cold *n*-pentane to yield **3a** as a yellow solid (19.6 mg, 26.4 μ mol, 51%).

Method B. To a stirred solution of 1 (400 mg, 0.63 mmol, 1.0 equiv) in toluene (10 mL) was added dropwise a solution of (trimethylsilyl)methyllithium (59.8 mg, 0.63 mmol, 1.0 equiv) in toluene (3 mL). The yellow, cloudy suspension was allowed to stir at room temperature overnight and then filtered through a pad of Celite. All volatiles were removed in vacuo, and the crude product was recrystallized from *n*-hexane at -40 °C to yield 3a as a yellow solid (261.5 mg, 383.5 μ mol, 60%). Single crystals of 3a suitable for X-ray crystallography were obtained as dark-yellow crystals by recrystallization from *n*-hexane at -40 °C. ¹H NMR (600.13 MHz, C₆D₆, 295 K): δ 232.8 (s, 2H, CH(CH₃)₂), 121.0 (s, 2H, CHHP), 116.1 (s, 2H, CHHP), 72.7 (s, 2H, CH(CH₃)₂), 46.7 (s, 2H, H_{Carb4/5}), 30.0 (s, 6H, $CH(CH_3)_2$), 20.2 (s, 6H, $CH(CH_3)_2$), 19.1 (s, 9H, $Si(CH_3)_3$), 4.1 (s, 2H, $H_{Carb2/7}$), 1.7 (s, 18H, C(CH₃)₃), -11.1 (bs, 12H, CH(CH₃)₂). ^{13}C NMR (150.92 MHz, C₆D₆, 295 K): δ 1167.0 (s, 2C, CH(CH_3)_2, C¹⁶), 1101.5 (s, 2C, C_{Carb8a/9a}), 741.5 (s, 2C), 727.0 (s, 2C), 440.5 (s, 3C, Si(CH₃)₃, C²⁰), 374.7 (s, 2C, C_{Carb1/8}), 328.1 (s, 2C, C_{Carb3/6}), 299.2 (s, 2C), 292.4 (s, 2C), 245.4 (s, 2C, CH(CH₃)₂, C¹⁸), 102.9 (q, ${}^{1}J_{CH} = 125.4 \text{ Hz}, 6C, C(CH_{3})_{3}, C^{11}), 45.0 (s, 2C, CH(CH_{3})_{2}, C^{17}),$ 12.5 (d, ${}^{1}J_{CH}$ = 150.3 Hz, $C_{Carb4/5}$), -27.0 (d, ${}^{1}J_{CH}$ = 150.3 Hz, 2C, $C_{Carb2/7}$), -46.1 (s, 2C, $C(CH_3)_3$, C¹⁰), -173.7 (s, 2C, CH_2P , C¹²). μ_{eff} = 4.9 μ_B (Evans, C₆D₆, 295 K). Anal. Calcd for C₃₈H₆₅FeNP₂Si: C, 66.94; H, 9.61; N, 2.05. Found: C, 66.65; H, 9.65; N, 2.04.

Synthesis of (PNP)FeMe (3b). To a stirred solution of 1 (200.0 mg, 0.32 mmol, 1.0 equiv) in THF (10 mL) was added methyllithium (12.6 mg, 0.57 mmol, 1.8 equiv). The yellow suspension stirred at room temperature for 24 h. The solvent was removed in vacuo, and the residue was taken up in *n*-pentane and filtered through a pad of Celite. The reaction mixture was concentrated in vacuo and kept at -40 °C overnight to yield **3b** as yellow crystals (146 mg, 0.24 mmol, 75%). ¹H NMR (600.13 MHz, C₆D₆, 295 K): δ 89.6 (bs, 2H), 66.2 (bs, 2H), 43.0 (s, 2H, H_{Carb}), 33.9 (bs, 4H), 4.9 (bs, 24H), 2.9 (s, 2H, H_{Carb}), 1.3 (s, 18H, C(CH₃)₂). ¹³C NMR (150.92 MHz, C₆D₆, 295 K): δ 949.9 (s, 2C), 706.7 (bs, 2C), 357.2 (s, 2C), 309.8 (s, 2C), 306.0 (bs, 4C), 97.3 (q, ¹J_{CH} = 126.0 Hz, C(CH₃)₃, C¹¹), 17.4 (d, ¹J_{CH} = 152.0 Hz, C_{Carb}), -84.4 (d, ¹J_{CH} = 152.0 Hz, C_{Carb}), -41.2 (s, 2C), -70.3 (bs, 2C). $\mu_{eff} = 4.9 \mu_{B}$ (Evans, C₆D₆, 295 K). Anal. Calcd for C₃₃H₅₇FeNP₂: C, 68.96; H, 9.42; N, 2.30. Found: C, 68.93; H, 9.70; N, 2.26.

Synthesis of (PNP)FeBn (3c). To a stirred solution of 1 (200.0 mg, 0.32 mmol, 1.0 equiv) in THF (10 mL) was added dropwise a solution of Bn₂Mg(THF)₂ (132.6, 0.38 mmol, 1.2 equiv) in THF (2 mL). The yellow solution was stirred at room temperature for 3 h. The solvent was removed in vacuo, and the residue was taken up in nhexane and filtered through a pad of Celite. The reaction mixture was concentrated in vacuo and kept at -40 °C overnight to yield 3c as dark-yellow crystals (0.1571 mg, 0.23 mmol, 72%). Single crystals of 3c suitable for X-ray crystallography were obtained as dark-yellow crystals by recrystallization from n-pentane at -40 °C. ¹H NMR (600.13 MHz, C₆D₆, 295 K): δ 240.3 (s, 2H), 119.8 (s, 2H), 72.8 (s, 2H), 64.2 (s, 2H), 43.8 (s, 2H), 40.1 (s, 2H), 28.8 (s, 6H, CH(CH₃)₂), 24.4 (s, 6H, CH(CH₃)₂), 3.6 (s, 2H), 1.0 (s, 18H), -6.0 (s, 6H, $CH(CH_3)_2$, -15.0 (s, 6H, $CH(CH_3)_2$), -38.3 (s, 2H) -73.1 (s, 1H, H_{p-Ph}). ¹³C NMR (150.92 MHz, C₆D₆, 295 K): δ 1062.5 (s, 2C), 1026.7 (s, 2C), 854.5 (s, 2C), 756.6 (s, 2C), 721.8 (s, 2C), 638.2 (s, 2C), 394.7 (s, 2C), 369.1 (s, 2C), 334.4 (s, 2C), 302.1 (s, 2C), 252.7 (s, 2C), 99.8 (q, ${}^{1}J_{CH}$ = 125.2 Hz, 2C), 69.2 (t, ${}^{1}J_{CH}$ = 149.4 Hz, 2C), 25.3 (t, ${}^{1}J_{CH}$ = 135.2 Hz, 2C), 13.5 (d, ${}^{1}J_{CH}$ = 153.4 Hz, 2C), 13.5 (s, 2C), 10.2 (s, 2C), -17.3 (d, ${}^{1}J_{CH}$ = 153.4 Hz, 2C), -44.8 (s, 2C), -215.2 (d, ${}^{1}J_{CH} = 153.4$ Hz, 2C). $\mu_{eff} = 4.8 \ \mu_{B}$ (Evans, C₆D₆, 295 K). Anal. Calcd for C41H61FeNP2: C, 71.81; H, 8.97; N, 2.04. Found: C, 71.60; H, 9.28; N, 2.06.

Synthesis of [(PNP)Fe(\mu-H)]₂ (4). *Method A*. To a stirred solution of 1 (20 mg, 31.7 μ mol, 1.0 equiv) in toluene (1.0 mL) was added a solution of potassium triethylborohydride (4.4 mg, 31.7 μ mol, 1.0 equiv) in toluene (0.5 mL). The dark-brown reaction mixture was allowed to stir at room temperature for 30 min. All volatiles were removed in vacuo, and the dark-brown residue was taken up in little *n*-pentane, filtered through Celite, and kept at -40 °C for 2 days to yield 4 as dark-red crystals (14.6 mg, 24.4 μ mol, 77%).

Method B. A solution of 3a (40.0 mg, 58.7 μ mol) in C₆D₆ (0.8 mL) was filled in a NMR tube with a J. Young Teflon valve and set under an atmosphere of hydrogen (8 bar) for 24 h. The NMR tube was shaken at irregular intervals, and the reaction progress was monitored via ¹H NMR spectroscopy. After the reaction was complete, all volatiles were removed in vacuo, and the dark-brown residue was taken up in a little *n*-pentane, filtered through Celite, concentrated, and kept at -40 °C for 2 days to yield 4 as dark-red crystals (29.0 mg, 48.7 μ mol, 83%). Single crystals of 4 suitable for X-ray crystallography were obtained as dark-red crystals by recrystallization from *n*-pentane at -40 °C. ¹H NMR (600.13 MHz, C₆D₆, 295 K): δ 52.3 (s), 38.7 (s), 37.1 (s), 22.0 (s), 15.2 (s), 7.4 (s), 4.1 (s), 3.7 (s), 1.4 (s), -1.3 (s), -4.5 (s), -16.3 (s), -44.9 (s), -65.3 (s). $\mu_{eff} = 6.8 \ \mu_{B}$ (Evans, C₆D₆, 295 K). Anal. Calcd for C₆₈H₁₁₀Fe₂N₂P₄: C, 68.56; H, 9.31; N, 2.35. Found: C, 69.05; H, 9.02; N, 2.13.

Synthesis of (PNP)Fe(CO)₂H (5). To a solution of 4 (40 mg, 67.3 μ mol) in C₆D₆ was added an atmosphere of CO (5 bar). The color of the solution changed from brown to deep purple. After 30 min, all volatiles were removed in vacuo, and the crude product was taken up in a little *n*-pentane, filtered, and kept at -40 °C overnight. The darkbrown solution was separated from the purple crystals. The solution was evaporated to dryness to yield 5 as a dark-brown solid (23.1 mg, 35.5 μ mol, 53%). ¹H NMR (600.13 MHz, C₆D₆, 295 K): δ 8.35 (d, ${}^{4}J_{\text{HP}}$ = 1.5 Hz, 2H, $H_{\text{Carb}2/7}$), 7.33 (s, 2H, $H_{\text{Carb}4/5}$), 3.40–3.36 (m, 2H, CHHP), 3.28–3.23 (m, 2H, CHHP), 2.10–1.97 (m, 4H, CH(CH₃)₂), 1.57 (s, 18H, C(CH₃)₃), 1.06 (dd, ${}^{3}J_{HH} = 16.2$ Hz, ${}^{3}J_{HP} = 7.0$ Hz, 6H, $CH(CH_3)_2$), 1.02 (dd, ${}^{3}J_{HH} = 16.2$ Hz, ${}^{3}J_{HP} = 7.0$ Hz, 6H, $CH(CH_3)_2$), 0.83 (dd, ${}^{3}J_{HH} = 14.7$ Hz, ${}^{3}J_{HP} = 7.0$ Hz, 6H, CH(CH₃)₂), 0.81 (dd, ${}^{3}J_{\text{HH}} = 14.7 \text{ Hz}, {}^{3}J_{\text{HP}} = 7.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{H}, CH(CH_{3})_{2}), -6.32 \text{ (t, } {}^{2}J_{\text{HP}} = 53.0 \text{ Hz}, 6\text{Hz}, 6\text{Hz$ Hz, 1H, FeH). ¹³C{¹H} NMR (150.92 MHz, C₆D₆, 295 K): δ 217.3 (t, ${}^{2}J_{CP}$ = 26.3 Hz, CO), 211.7 (t, ${}^{2}J_{CO}$ = 9.6 Hz, CO), 147.9 (vt, J_{CP} = 4.2 Hz, $C_{\text{Carb8a/9a}}$), 137.9 (s, $C_{\text{Carb3/6}}$), 128.3 (s, $C_{\text{Carb1/8}}$), 124.0 (vt, J_{CP} = 4.4 Hz, $C_{Carb2/7}$), 118.1 (s, $C_{Carb4a/4b}$), 115.1 (s, CH, $C_{Carb4/5}$), 34.5 (s, $C(CH_3)_3$, 32.5 (s, $C(CH_3)_3$), 26.7 (t, ${}^{1}J_{CP} = 10.5$ Hz, $CH(CH_3)_2$), 26.5 (t, ${}^{1}J_{CP}$ = 15.3 Hz, CH(CH₃)₂), 25.9 (t, ${}^{1}J_{CP}$ = 10.5 Hz, CH₂P), 18.3 (s, CH(CH₃)₂), 18.2 (s, CH(CH₃)₂), 17.6 (s, CH(CH₃)₂), 17.3 (s, CH(CH₃)₂). ³¹P{¹H} NMR (242.92 MHz, C₆D₆, 295 K): δ 62.6 (s). IR (cm⁻¹): 1936 (CO), 1859 (CO). Anal. Calcd for C36H55FeNO2P2: C, 66.36; H, 8.51; N, 2.15. Found: C, 66.25; H, 8.38; N, 2.20. Occasionally isolated samples contained 6 as an impurity.

Synthesis of (PNP)Fe(CO)₂ (6). To a solution of 4 (40 mg, 67.3 μ mol) in C₆D₆ was added an atmosphere of 4 bar of CO. The color of the solution changed from brown to deep purple. After 30 min, all volatiles were removed in vacuo, and the crude product was taken up in little n-pentane, filtered, and kept at -40 °C overnight. The darkbrown solution was separated from the purple crystals by decantation. The resulting deep-purple crystals were washed with cold *n*-pentane, and all volatiles were removed in vacuo to yield 6 as a dark-purple solid (2.1 mg, 3.2 µmol, 10%). Single crystals of 6 suitable for X-ray crystallography were obtained as dark-purple crystals by recrystallization from *n*-pentane at -40 °C. ¹H NMR (600.13 MHz, C₆D₆, 295 K): δ 13.5 (bs), 11.3 (bs), 1.7 (bs). μ_{eff} = 2.0 μ_{B} (Evans, C₆D₆, 295 K). IR (cm⁻¹): 2001 (CO), 1925 (CO). Anal. Calcd for C₃₆H₅₄FeNO₂P₂: C, 66.46; H, 8.37; N, 2.15. Found: C, 66.47; H, 8.22; N, 2.31. ESR (Xband, C_6D_{61} 9.447856 GHz, 295 K): g = 2.036. Occasionally isolated samples contained 5 as an impurity.

General Synthetic Procedure for the Hydrogenation of Alkenes. Complex 3b (2.0 mg, 3.28 μ mol, 1.0 equiv) and the alkene (0.328 mmol, 100 equiv) were dissolved in C₆D₆ (0.4 mL) and filled in a high-pressure J. Young tube. The reaction mixture was set under a pressure of 8 bar of H₂ and shaken at irregular intervals. The reaction was kept under hydrogen from 2 to 72 h, while the reaction progress was monitored periodically by ¹H NMR spectroscopy. The percentage conversion values were obtained from the relative ¹H NMR integrations of the substrate and product.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b03227.

Text, figures, and tables giving full experimental procedures, representative NMR spectra, DFT data, and crystallographic data (PDF)

Accession Codes

CCDC 1812479–1812483 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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