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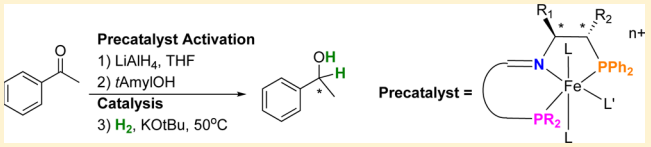
Synthesis of Iron P-N-P′ and P-NH-P′ Asymmetric Hydrogenation Catalysts

Jessica F. Sonnenberg, Alan J. Lough, and Robert H. Morris*

Davenport Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

Supporting Information

ABSTRACT: Complexes of the type *mer,trans*-[Fe(P-N-P′)$(CO)_2$Br]BF_4 are known to be precatalysts for the asymmetric direct hydrogenation of ketones and imines. Employing related ligand scaffolds, we successfully generated and tested the series of three new precatalysts [Fe$(PCy_2CH_2CH{=}NCH(R)CH_2PPh_2)(CO)_2Br]BF_4$ with chirality derived from (*S*)-amino alcohols with phenyl, benzyl, and isopropyl substituents (R), yielding fairly active and selective systems. For the reduction of acetophenone to (*S*)-1-phenylethanol turnover frequencies up to 920 h^{-1} and up to 74% enantiomeric excess at 50 °C and 5−25 atm of H_2 were obtained. We found, however, that placing these large groups R next to nitrogen was found to be deleterious to catalytic activity. Extending the scope of the ligand structure, we then developed a series of six P-N-P and five P-NH-P′ systems starting with *o*-diphenylphosphinobenzaldehyde and the phosphine-amines $PPh_2CHR^1CHR^2NH_2$ (R^1 = H, Ph, CH_2Ph, iPr with R^2 = H or R^1 = Me, Ph with R^2 = Ph) as well as their corresponding [Fe(P-N-P′)$(NCMe)_3][BF_4]_2$ and [Fe(P-NH-P′)$(NCMe)_3][BF_4]_2$ complexes, which were not catalytically active. Finally, we made the new achiral iron complex *mer,cis*-Fe$(PPh_2(o\text{-}C_6H_4)CHNCH_2CH_2PPh_2)(CO)Br_2$, which was active for the direct hydrogenation of acetophenone, achieving turnover frequencies of 800 h^{-1} at 50 °C and 25 atm of H_2.



INTRODUCTION

The synthesis of enantiopure alcohols and amines is of significant importance to the pharmaceutical, fragrance, and fine chemical industries and is typically achieved via the hydrogenation of ketones and imines, respectively, using precious metal catalysts.[1,2] There has been tremendous interest recently in developing greener catalysts based on period 4 transition metals to replace iridium, ruthenium, and rhodium catalysts, as they are much cheaper, more earth abundant, and less toxic.[3−5] Our group has been primarily focused on the development and mechanistic investigation of iron carbonyl P-N-N-P catalysts for asymmetric transfer hydrogenation (ATH);[6−17] however, we often encountered problems with product racemization due to equilibration. We therefore sought to develop asymmetric direct hydrogenation systems that could use hydrogen gas to prevent reversibility.

Recently, Milstein et al. reported iron systems with tridentate P-N-P ligands capable of directly hydrogenating polar double bonds using H_2(g).[18,19] These complexes, shown in Figure 1, achieved turnover frequencies (TOF) up to 430 h^{-1} at 40 °C and 4.1 atm of H_2. Beller and co-workers also used a similar ligand system on iron for the release of H_2 gas from methanol and water with TOFs up to 720 h^{-1}.[20] He also recently detailed the use of the same system for the hydrogenation of esters,[21] as did Chakraborty et al., who characterized a reactive dihydride intermediate.[22] In their hydrogen evolution paper, Beller and co-workers hypothesized that the system goes through reactive amide-hydride species, which can be generated from a Fe(P-NH-P)(CO)(H)(OR) complex using base. This type of Fe(P-N-P)H(CO) amide structure has been recently crystallographically characterized by Chakraborty et al. in their study of the dehydrogenation and hydrogenation of N-heterocycles.[23]

Prior to the aforementioned work with the P-N-P systems, Casey and Guan developed a Shvo-type system using iron capable of hydrogenating aldehydes and ketones, via an outer-sphere (bifunctional) mechanism, at modest temperatures and pressures.[24,25] This ligand scaffold was then used by Berkessel in conjunction with a chiral phosphorus ligand[26] and by Beller in conjunction with a chiral phosphonic acid[27] to yield alcohols and amines in modest to high enantiomeric excess (ee), respectively. Our group has also developed a series of iron-(P-N-N-P) systems, also shown in Figure 1, capable of hydrogenating ketones with TOFs up to 1000 h^{-1} and ee values up to 76% at 50 °C and 25 atm of H_2.[11] The most efficient direct hydrogenation catalyst known to date was developed by Noyori et al. and is a ruthenium-based catalyst containing a chiral, bidentate phosphorus ligand (BINAP) and a chiral diamine ligand.[28,29] The catalyst, upon activation with base to generate a reactive hydride complex, is capable of achieving a total turnover number (TON) of up to 100,000 and an ee of 99% at ambient temperature and 8 atm of H_2. The catalyst operates via a bifunctional, outer-sphere mechanism that takes advantage of the "N-H effect", whereby the Ru-hydride and ligand N-H add directly to the substrate polar double bond, resulting in a metal amido intermediate that then heterolytically splits H_2.[30−33] Under basic conditions using KO*t*Bu an alternative pathway may involve an anionic

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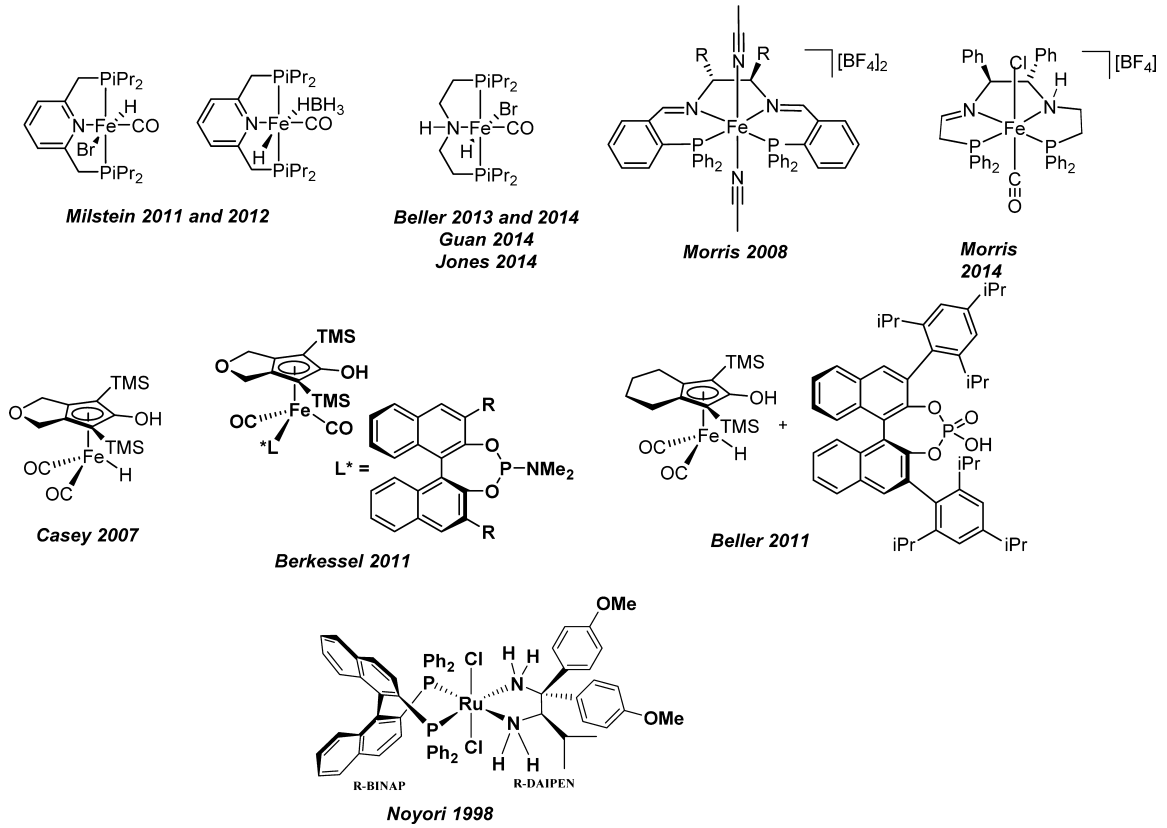
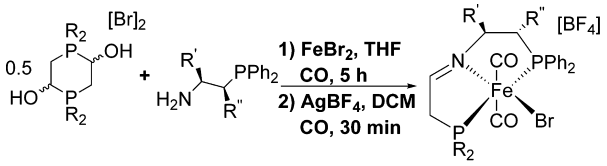


Figure 1. Catalysts used for the direct hydrogenation of polar double bonds.

Scheme 1. Synthesis of $[Fe(P\text{-}N\text{-}P')(CO)_2Br]BF_4$ Precatalysts 1a–f



1a R = iPr, R' = R" = H, 83% yield (ref 36)
1b R = Cy, R' = R" = H, 89% yield (ref 36)
(***S,S***)**-1c** R = Cy, R' = Me, R" = Ph, 82% yield (ref 36)
(***S***)**-1d** R = Cy, R' = Ph, R" = H, 86% yield (this work)
(***S***)**-1e** R = Cy, R' = CH_2Ph, R" = H, 84% yield (this work)
(***S***)**-1f** R = Cy, R' = iPr, R" = H, 78% yield (this work)

hydridoamido complex stabilized by potassium that transfers the hydride without participation of an NH group.[34] We were interested in developing a new series of direct hydrogenation catalysts based on iron that would be chiral, would be able to potentially take advantage of the N–H effect, and would employ pincer ligands.[35]

Combining these key structural features, we developed a P-N-P′ ligand scaffold that incorporated chiral centers, yielding highly active and enantioselective direct hydrogenation catalysts based on iron that could operate under mild conditions.[36] The precatalysts could be generated using a template method employing air-stable phosphonium dimers,[10] chiral PN ligands, and $FeBr_2$ under a CO(g) atmosphere, followed by silver-assisted ligand exchange[37] to cleanly generate *mer,trans*-$[Fe(Br)(CO)_2(P\text{-}CH{=}N\text{-}P')][BF_4]$ (where P-CH═N-P′ = $R_2PCH_2CH{=}NCH_2CH_2PPh_2$ and R = iPr (**1a**), Cy (**1b**) or P-CH═N-P′ = (*S,S*)-$Cy_2PCH_2CH{=}NCH(Me)CH(Ph)PPh_2$ (**1c**)). For the direct hydrogenation of acetophenone at 50 °C and 5 atm of H_2, achiral catalysts **1a,b** achieved turnover frequencies (TOF) of 1980 h^{-1}, and the chiral catalyst (*S,S*)-**1c** achieved a TOF of 1980 h^{-1} with an ee value of 80% (*S*). The precatalysts must be activated prior to use in catalysis; precatalysts are first treated with $LiAlH_4$ in THF under an inert atmosphere followed by addition of alcohol, typically *tert*-amyl alcohol (*t*AmOH), to generate Fe(P-NH-P′)(H)(OR)-(CO).[36] These species are further treated with base and hydrogen in a Parr reactor to generate the catalytically active $Fe(P\text{-}NH\text{-}P')(H)_2(CO)$ species currently under investigation in our group.

Keeping this activation process in mind, we were interested in developing a new series of catalysts that employed a cheaper and more variable chiral center(s). It was previously established that when both P and P′ are PPh_2 groups there is no activity. Therefore, ligands with a PCy_2 substituent were targeted in the current work. We explored the effect on direct hydrogenation activity and selectivity of changing the ligand sterics and chirality (number and type of chiral centers) using alternative PN ligands, the effect of changing the ligand structure and

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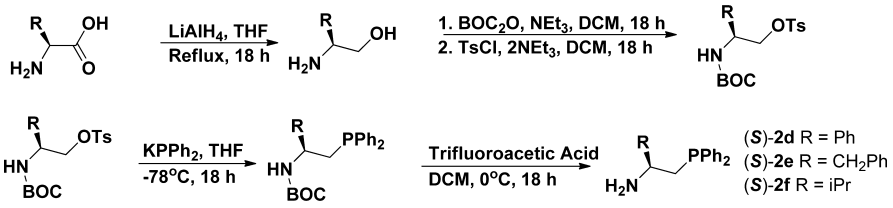
Scheme 2. Synthetic Pathway for the Formation of Chiral PN Complexes 2d−f



flexibility using *o*-phenylene linkers on the achiral side of the ligand, and the effect of incorporating an N-H functionality into the ligand backbone.

RESULTS AND DISCUSSION

Modifying the Catalyst Chirality. As outlined in Scheme 1, the precatalysts are formed using an iron-templated Schiff base condensation reaction of a phosphonium dimer[10,38] and a chiral PN ligand under a CO(g) headspace,[13] followed by halide abstraction and carbonyl ligand substitution using $AgBF_4$ also under CO(g)[37] to yield the *trans*-[Fe(P-N-P′)$(CO)_2$Br]-[BF_4] catalysts. Unlike the Milstein system discussed previously (Figure 1),[18] where a *trans*-Fe(P-N-P)$(CO)Br_2$ complex could be isolated and used to form the reactive iron hydride species, a mixture of *cis*- and *trans*-bromide species were isolated using our P-N-P′ template approach. To avoid the two-isomer problem, we applied the approach developed by Kirchner and co-workers.[37] His group also isolated a mixture of isomers using his P-N-P ligands on iron[39,40] but found that the use of $AgBF_4$ allowed for the clean formation of a *trans*-CO dicarbonyl complex as the sole isomer. This selectivity was shown to arise from the addition of CO to the coordinatively unsaturated [Fe(P-N-P)$(CO)Br]^+$ complex (formed from the loss of one Br^- to Ag^+) to selectively form the dicarbonyl complex *trans*-[Fe(P-N-P)$(CO)_2$Br]$^+$.

The chirality in the previously developed complex **1c** was derived from (*S*,*S*)-phenylpropanolamine, or norephedrine, which is a controlled substance and expensive. We therefore turned our attention to amino acids as a potential source of chirality, as they are more cost efficient. The synthesis of chiral PN ligands from amino acids is well-known,[41−46] and we chose to study valine, phenylglycine, and phenylalanine as sources of *i*Pr, Ph, and CH_2Ph chiral groups, respectively. The steps for the formation of chiral PN ligands from amino acids are shown in Scheme 2 and given in detail in the Supporting Information. The amino acid is first reduced with $LiAlH_4$ to yield the amino alcohol, followed by protection of the nitrogen with a BOC group to prevent unwanted side reactions. The alcohol is then tosylated to allow for a facile substitution with potassium diphenylphosphide. The last step involves the removal of the BOC protecting group with strong acid to give the chiral PN compound with overall yields of 20−30% from the amino alcohol.

With the three new chiral PN-ligands (*S*)-**2d−f**, we followed the procedure outlined in Scheme 1 to generate precatalysts (*S*)-**1d−f**. All three new complexes were fully characterized by NMR, MS, elemental analysis, and IR and, in the case of **1d**, by single-crystal X-ray diffraction (Figure 2). The new complexes are structurally similar to the previously reported precatalysts **1b**,**c**, with $^{31}P\{^1H\}$ NMR shifts, $^2J_{PP}$ coupling constants, and IR ν(CO) stretching frequencies, in wavenumbers, shown in Table 1. All major carbonyl IR stretching frequencies are within the range 2000−2010 cm^{-1} for the *trans*-CO ligands, and all $^2J_{PP}$ couplings are within the range 81−85 Hz for the *trans*-^{31}P nuclei of the P-N-P′ ligand, indicative of the *mer* conformation of the pincer ligand about the catalyst, as observed in the crystal structures of **1a−c**[36] and **1d**. Relevant bond lengths and angles for **1d** are given in Figure 2 and are quite similar to the values obtained in previous systems. In the pincer ligand, N(1)−C(2) and N(1)−C(3) bond lengths of 1.286(11) and 1.511(7) Å, respectively, demonstrate that the ligand does contain an imine group. The P−Fe−P bond angle is 170.25(7)°, and the CO−Fe−CO bond angle is 172.5(4)°, indicative of a slightly distorted octahedral complex.

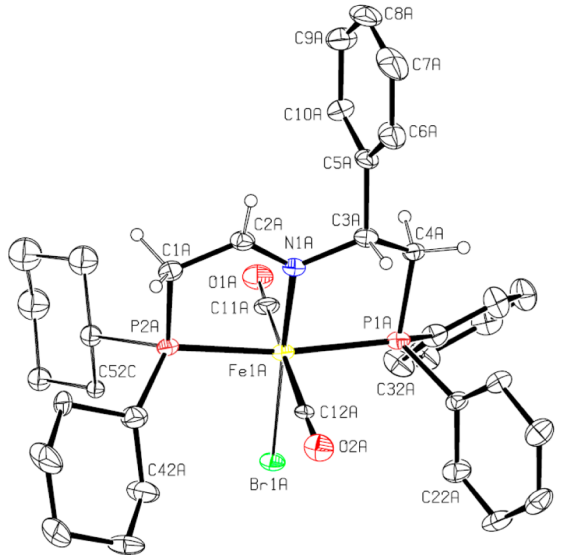


Figure 2. Molecular structure (thermal ellipsoids at 30% probability) of precatalyst **1d**. Hydrogen atoms of Ph and Cy groups are removed for clarity, as is the BF_4 counterion. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1), 2.245(2); Fe(1)−P(2), 2.277(2); Fe(1)−N(1), 1.998(5); Fe(1)−Br(1), 2.4732(14); N(1)−C(2), 1.286(8); N(1)−C(3), 1.511(7), O(1)−C(11), 1.126(11); O(2)−C(12), 1.044(8); P(2)−Fe(1)−P(1), 170.25(7); C(11)−Fe(1)−C(12), 172.5(4).

Table 1. Comparative $^{31}P\{^1H\}$ NMR Shifts, $^2J_{PP}$ Coupling Constants, and IR Major ν(CO) Stretches for Precatalysts 1b−f

precatalyst	$^{31}P\{^1H\}$ NMR shift (ppm)[a]	$^2J_{PP}$ coupling constant (Hz)	IR ν(CO) (cm^{-1})[b]
1b	70.8 (d), 45.7 (d)	85.0	2005
1c	69.2 (d), 67.8 (d)	81.0	2000
1d	66.8 (d), 39.4 (d)	81.6	2009
1e	64.2 (d), 42.6 (d)	82.1	2004
1f	63.3 (d), 46.3 (d)	81.6	2006

[a]Solvent THF-d_8. [b]KBr disk.

Catalytic Asymmetric Hydrogenation of Acetophenone. Table 2 gives the catalytic activity of these new iron(II)

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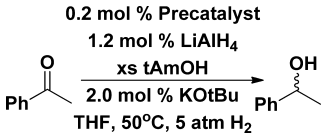
Table 2. Catalytic Activity and Selectivity for the Asymmetric Hydrogenation of Acetophenone to 1-Phenylethanol at 50 °C



precatalyst	pressure of H_2 (atm)	TOF (h^{-1})	ee (%)	ref
1a	5	1980	n/a	ref 36
1b	5	1980	n/a	ref 36
(*S*,*S*)-**1c**	5	1980	80 (*S*)	ref 36
(*S*)-**1d**	5	920	55 (*S*)	this work
(*S*)-**1e**	5	460	13 (*S*)	this work
(*S*)-**1f**	25	250[a]	74 (*S*)[a]	this work
8a	25	800	n/a	this work

[a] H_2 pressure 20 atm.

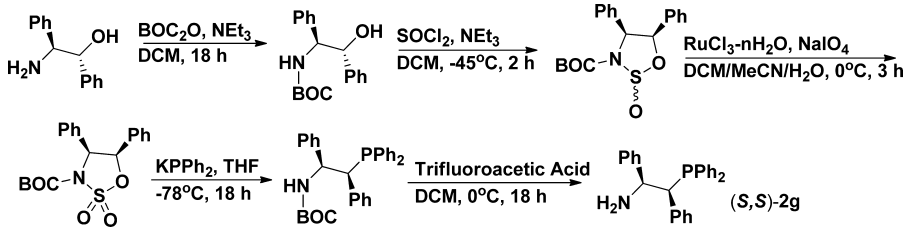
complexes for the direct hydrogenation of acetophenone to chiral 1-phenylethanol using the previously established activation methodology ($LiAlH_4$, *t*AmOH, base). As reported earlier, achiral complexes **1a,b** with no substituents on the ligand backbone were as active as the complex (*S*,*S*)-**1c** with the methyl group next to nitrogen and the phenyl group next to phosphorus, which provided (*S*)-1-phenylethanol in 80% ee. Under the same conditions complexes **1d−f** with larger substituents next to nitrogen (phenyl, benzyl, isopropyl, respectively) were less active. There is strong evidence that this imine nitrogen is converted to an amine in the catalytically active hydride complex $Fe(CO)(H)_2(PPh_2\text{-}NH\text{-}PCy_2)$; restricting access to this amino group by adding steric bulk nearby may hinder the participation of the nitrogen in the bifunctional reduction of the ketone. Complex **1f** with a large isopropyl group next to nitrogen was significantly less active, achieving a TOF of 250 and an ee of 74% at much higher pressures of 20 atm of H_2. The ee values ranging from 13 to 74% for (*S*)-1-phenylethanol produced by using **1d−f** with one substituent on the carbon of the Fe−P−C−C−N ring were lower than that using (*S*,*S*)-**1c** with two. This might be explained by a greater flexibility of the five-membered ring and/or freer movement of the PPh_2 group. The preliminary calculated structure of $Fe(CO)(H)_2(PPh_2CHPhCHMeNHCH_2CH_2PCy_2)$, which is thought to be the active catalyst and is under active investigation in our group, shows that the phenyl group on the carbon next to phosphorus locks the movement of the PPh_2 group, thus enhancing the enantioselectivity.

Synthesis of Fe Complexes Bearing Multiple Stereogenic Centers. This significant influence on both activity and selectivity observed on going from two chiral centers to one prompted us to investigate other possible PN ligands bearing two chiral centers. Given our tremendous success with the diphenylethylenediamine (dpen) backbone in our ATH Fe-(P-N-N-P) catalysts,[6,15,47] we were interested in developing PN ligands bearing this type of functionality. Using commercially available (1*R*,2*S*)-2-amino-1,2-diphenylethanol, the aminophosphine compound (1*S*,2*S*)-2-(diphenylphosphino)-1,2-diphenylethanamine (**2g**) can be synthesized in an overall 37% yield by employing the process previously developed by Guo et al.[48] and depicted in Scheme 3. To summarize, the amine is first protected with a BOC group to prevent unwanted side reactions with the primary amine functionality, followed by cyclization using thionyl chloride to form a sulfamidite. This could then be oxidized to the sulfamidate using a catalytic amount of $RuCl_3{\cdot}nH_2O$ and sodium periodate. Then, using potassium diphenylphosphide, the sulfamidate can be ring opened in an S_N2 fashion, reversing the chirality of the nearest chiral center, to yield the BOC-protected PN ligand, which can be readily deprotected under strongly acidic conditions.

With (*S*,*S*)-**2g** in hand, we attempted to synthesize the corresponding *trans*-$[Fe(P\text{-}N\text{-}P')(CO)_2Br]^+$ complex using the method detailed in Scheme 1. Unfortunately, the synthesis was not as straightforward as was previously described, likely due to significant steric and electronic changes when the diphenyl backbone is used. Using a wide range of reaction solvents (THF, MeOH, acetone), temperatures (0 °C, room temperature, and 70 °C reflux), and orders of reagent addition, we were not able to synthesize the desired complex but rather isolated brown powders. Upon crystallization and analysis using single-crystal X-ray diffraction, we were able to identify the major product of our reaction attempts as *cis*-$[Fe(PN)_2(CO)Br][BF_4]$ (**3**), as shown in Figure 3.

Interested in the potential reactivity of this complex, we devised an alternative route to the clean and efficient synthesis of **3**, depicted in Scheme 4. Using 2 equiv of **2g** with $FeBr_2$ under a CO(g) atmosphere, followed by salt metathesis with $NaBPh_4$, we were able to isolate the BPh_4 salt of **3** as a clean brown powder that could be characterized by NMR, MS, IR and, upon recrystallization, by single-crystal X-ray diffraction. Complex **3** exhibited a much lower ν(CO) at 1944 cm^{-1} in comparison to those of **1b−f** at 2000−2010 cm^{-1} (Table 1), indicative of a more electron rich iron(II) containing only one π-acidic CO ligand. The $^{31}P\{^1H\}$ NMR spectrum exhibited two doublets at 84.6 and 76.6 ppm with $^2J_{PP}$ = 145.8 Hz, larger than the 81−85 Hz observed for **1a−f** but still indicative of *trans*-phosphorus donors as observed in the X-ray structure. The P−Fe−P bond angle is 172.20(5)°, slightly greater than the corresponding angles 168.38(4) and 167.40(5)° in **1b** and **1a**, respectively, while the Fe−P and Fe−N bond lengths are similar. As would be expected from the IR ν(CO) difference, the C−O bond of the carbonyl in **3** is longer than that of **1b** and **1a**: 1.17(1) Å in **3** versus 1.144(6) Å in **1a** or 1.104(4) and 1.132(4) Å in **1b**, indicative of more electronic back-donation into the carbonyl antibonding orbital in the new system.

Scheme 3. Synthetic Pathway for the Formation of the Chiral PN Compound (*S*,*S*)-2g



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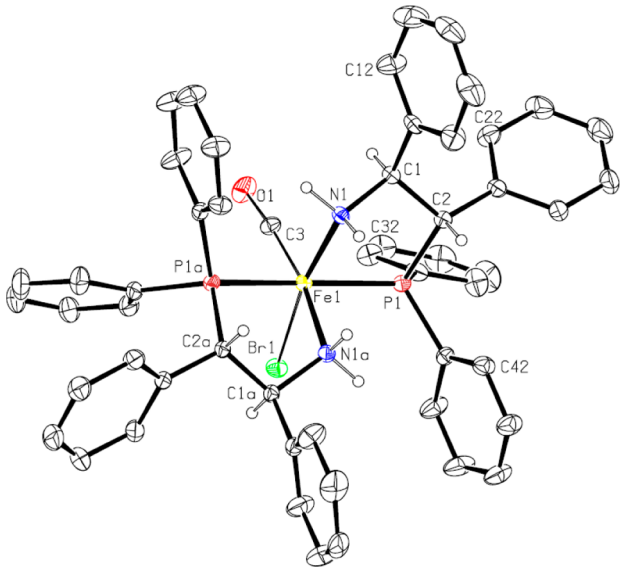
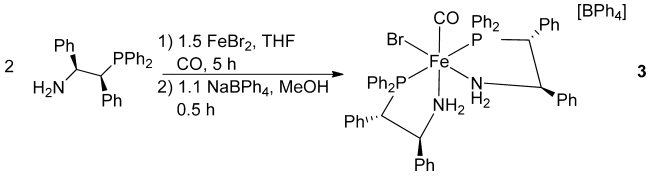


Figure 3. Molecular structure (thermal ellipsoids at 30% probability) of *cis*-$[Fe(PN)_2(CO)Br]BF_4$ (**3**). Hydrogen atoms of Ph groups and the BF_4 anion are removed for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1), 2.2701(9); Fe(1)−P(1a), 2.2702(9); Fe(1)−N(1), 2.045(3); Fe(1)−N(1a), 2.045(3); Fe(1)−Br(1), 2.4514(16); Fe(1)−C(3), 1.764(12); O(1)−C(3), 1.169(12); P(1)−Fe(1)−P(1a), 172.20(5); N(1)−Fe(1)−N(1a), 92.10(18); P(1)−Fe(1)−N(1), 83.27(10).

Scheme 4. Synthesis of *cis*-$[Fe(PN)_2(CO)Br][BPh_4]$ (3)



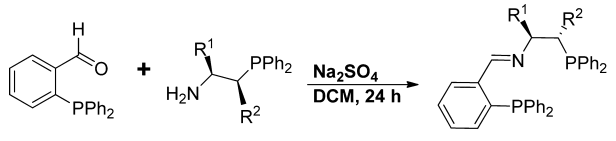
Still intent on generating the corresponding $[Fe(P\text{-}N\text{-}P')(CO)_2Br]^+$ complex with the 1,2-diphenylethylene backbone, we attempted to react **3** with phosphine-aldehyde and CO(g) under varying conditions to generate the desired complex. We were still unable, however, to generate the target precatalyst. Given the presence of two chiral centers to provide structural rigidity, we hypothesize that, if such a precatalyst could be formed, it is likely that it would be quite selective for direct hydrogenation of polar double bonds, and therefore further attempts to synthesize this elusive complex are still underway.

Although **3** does not possess the initially desired structure, we were interested in whether it could be catalytically active under reaction conditions similar to those employed with **1a**−**f**. Unfortunately, under pressures of up to 25 atm of H_2 and temperatures of up to 50 °C we saw no conversion of ketones or imines to their corresponding alcohols or amines. Given the structural similarities of our new iron system to our $[Fe(P\text{-}N\text{-}N\text{-}P)(CO)Br]^+$ TH catalysts,[6,10,12] we were also interested in testing the hydrogenation of ketones or imines using isopropyl alcohol as the proton and hydride source. Unfortunately, the system using base and isopropyl alcohol was inactive for TH catalysis. It is worth pointing out that, with the tetradentate system, a variant of the catalyst was made where there were amine linkages, $[Fe(P\text{-}NH\text{-}NH\text{-}P)(CO)Br]^+$; however, this system was found to be significantly less active than its diimine counterpart.[8] It is interesting that, unlike Noyori's system which contained NH_2 groups, iron systems appear to be negatively affected by the presence of the NH_2 group. We are currently unsure as to why this is occurring; however, it likely has to do with the varied electronics of the system, specifically the basicity of the nitrogen group.

Changing the Catalyst Structure Using 6,5-(P-N-P′) Ligands. Given that catalysis and enantioselectivity appeared to be strongly influenced by the structure and flexibility of the P-N-P′ pincer ligand, we chose to explore a new class of ligands on iron with a more flexible ligand architecture. Our group has previously developed three generations of iron-(P-N-N-P) catalysts for use in hydrogenation.[6,10,11] All catalyst ligands are formed via the condensation of a diamine with phosphine-aldehydes, much like the formation of the P-N-P′ ligands previously discussed. In the first-generation TH systems, *o*-phenylene linkers were utilized, making a 6,5,6-ring system around iron, which gave the ligand the flexibility to bend up and form ferraaziridine and ferraaziridinido species.[7,16] In the second- and third-generation P-N-N-P catalysts, much like the P-N-P′ systems discussed here, phosphonium dimers were used to generate smaller phosphine-aldehydes in situ, which gave rise to 5,5,5-ring systems on iron.[6,10] These 5,5,5-systems were rigid and prevented the folding of the ligand during TH catalysis.[8,49] Another interesting feature of the ligands in the different generations was the fact that the 6,5,6-(P-N-N-P) ligands could be made without the presence of iron, unlike the 5,5,5-systems that required iron as a template. This made the reduction of the imine functionalities to amines feasible with the 6,5,6-system, allowing for the introduction of an N-H functionality.[50−52]

Combining these concepts, we sought to develop a new generation of P-N-P′ ligands using larger and more flexible *o*-phenylene linkers, as well as a related series of P-NH-P′ ligands, all of which were to be tested for hydrogenation as iron catalysts. To synthesize the 6,5-(P-N-P′) ligands, we applied a methodology similar to that previously developed for the synthesis of P-N-N-P ligands:[11,50−53] the condensation of *o*-(diphenylphosphino)benzaldehyde with PN ligands **2** in the presence of a drying agent, as shown in Scheme 5. Upon workup, this preparation yielded a wide variety of chiral P-N-P′ ligands **4**, in yields varying from 46 to 75%. All of the compounds were characterized by NMR, MS, and elemental analysis. In the NMR, ^1H chemical shifts for the imine ranged from 8.4 to 9.0 ppm, and all species showed two sharp singlets in the ^{31}P NMR. **4a** has peaks at −13.2 and −19.5 ppm, **4c** at −8.1 and −14.5 ppm, **4d** at −12.8 and −22.9 ppm, **4e** at −14.1 and −23.1 ppm, **4f** at −13.3 and −22.0 ppm, and **4g** at −7.2

Scheme 5. Condensation Reaction of Phosphine-Aldehyde with 2 To Generate Enantiopure P-N-P′ Ligands 4



4a $R^1 = R^2 = H$
(***S,S***)-**4c** $R^1 = Me$, $R^2 = Ph$
(***S***)-**4d** $R^1 = Ph$, $R^2 = H$
(***S***)-**4e** $R^1 = CH_2Ph$, $R^2 = H$
(***S***)-**4f** $R^1 = iPr$, $R^2 = H$
(***S,S***)-**4g** $R^1 = R^2 = Ph$

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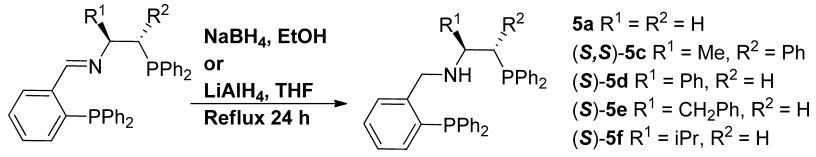
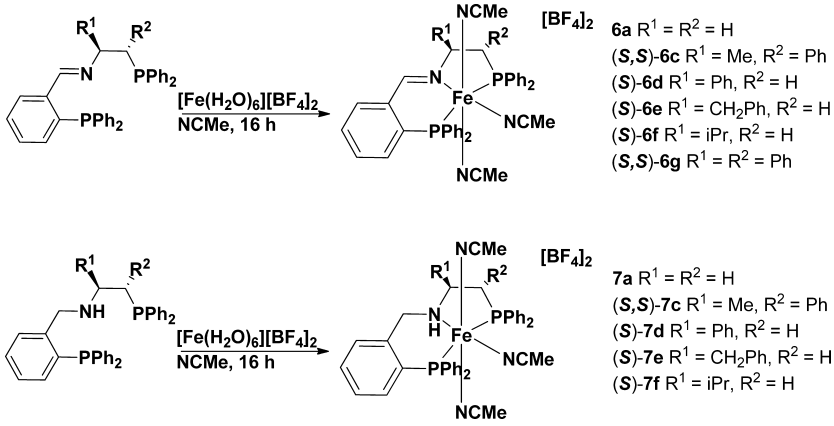
Scheme 6. Reduction of P-N-P′ Ligands 4 To Form Chiral P-NH-P′ Ligands 5



Scheme 7. Synthesis of $[Fe(P\text{-}N\text{-}P')(NCMe)_3][BF_4]_2$ (6) and $[Fe(P\text{-}NH\text{-}P')(NCMe)_3][BF_4]_2$ (7) from P-N-P′ (4) and P-NH-P′ (5), Respectively



and −15.4 ppm. The achiral ligand **4a** was synthesized and characterized previously by Bluhm et al.,[54] who also made a large series of structurally similar achiral ligands containing P, N, S, and O donor groups. All of these pincer ligands were used in the synthesis of Cr("Y′N′Z")Cl_3 systems, such as Cr(P-N-P)Cl_3; these complexes in turn were used for the oligomerization and polymerization of ethylene, as well as for the selective formation of 1-hexene. Similar achiral P-N-N ligands have also been developed, where in place of the diphenylphosphine moiety of the PN ligand Wehman et al. used a pyridine group, which allowed for the synthesis of stable Pd(II) and Pd(0) P-N-N complexes.[55] Kawamura et al. reported the synthesis of a chiral P-N-P ligand derived from valine that is similar to **4f** which contained a 3,5-di-*tert*-butylphenylene linker in place of our unfunctionalized phenylene linker.[56] They used this ligand with copper in the asymmetric 1,4-addition of diethylzinc to 2-cyclohexen-1-one; however, the ee of the resulting ketone was only moderate and the activity was quite low.

The next stage of our investigation was the synthesis of the corresponding series of P-NH-P′ ligands **5**, as depicted in Scheme 6. It was previously reported that the P-N-N-P ligands could be reduced in the presence of $NaBH_4$ to yield the corresponding P-NH-NH-P ligands, and we therefore tested $NaBH_4$ first.[8,50−52] This was effective for the achiral system **5a**, as was also reported by Bluhm,[54] who tested the chromium complex as discussed previously. The use of $NaBH_4$ was also effective for the generation of **5c**, with the Me/Ph PN backbone; however, **5d−f** could not be effectively reduced. Under similar reaction conditions and times, **4d−f** was less than half reduced to **5d−f**, and prolonged exposure gradually led to decomposition and some ligand oxidation (some phosphine oxides were detected). To form **5d−f**, $LiAlH_4$ was used, which allowed for the clean reduction of the imine bond in those cases. Therefore, the imine bonds of the ligands with a single chiral center with a large substituent next to nitrogen are more difficult to reduce, once again supporting the observation that these systems have significantly different behavior than the achiral and norphedrine derivatives. The P-NH-P′ ligands were fully characterized by NMR, MS, and elemental analysis. ^{1}H NMR showed the disappearance of the imine proton, and $^{31}P\{^1H\}$ spectra once again exhibited two sharp singlets for the inequivalent phosphorus atoms. **5a** has peaks at −16.1 and −20.6 ppm, **5c** at −11.2 and −16.2 ppm, **5d** at −16.4 and −23.5 ppm, **5e** at −16.0 and −23.4 ppm, and **5f** at −16.1 and −22.2 ppm. With the exception of the achiral P-NH-P′ ligand developed by Bluhm,[54] this is a new and novel series of ligands. Structurally similar P-N-N ligands bearing an N-H group have been developed and studied extensively by Clarke et al. for the direct and transfer hydrogenation of ketones using ruthenium.[57−59] They have also investigated the effect of varying the substituents on phosphorus,[60] much like our group has done with our P-N-N-P ligands,[13,14] to improve the ee of the hydrogenation reactions. Furthermore, they explored the role of the N-H group in catalysis by designing a series of P-NR-NR′$_2$ ligands[61] and found these to be less active in ketone hydrogenation than their P-NH-NH_2 counterparts, indicating the importance of the N-H group in the ligand structure.

Following the successful synthesis and characterization of a new library of P-N-P′ and P-NH-P′ ligands, we then investigated their coordination to iron. This was initially probed using $[Fe(H_2O)_6][BF_4]_2$ in MeCN under ambient conditions and an inert atmosphere to generate the corresponding $[Fe(P\text{-}N\text{-}P')(NCMe)_3][BF_4]_2$ (**6**) and $[Fe(P\text{-}NH\text{-}P')(NCMe)_3][BF_4]_2$ (**7**) complexes, as depicted in Scheme 7. The reactions were very clean, and most were nearly quantitative, with yields ranging from 83 to 99%. The complexes with imine functionalities **6** were isolated as deep red powders, and the complexes with the N−H ligand **7** were isolated as bright pink-purple powders.

All of the new complexes were characterized using NMR, MS, and elemental analysis techniques, and **6a**,**e** were characterized crystallographically as depicted in Figures 4 and 5, respectively. The ^{1}H NMR spectra of **6** have singlets for the imine proton in the range of 7.9−8.8 ppm, which are no longer

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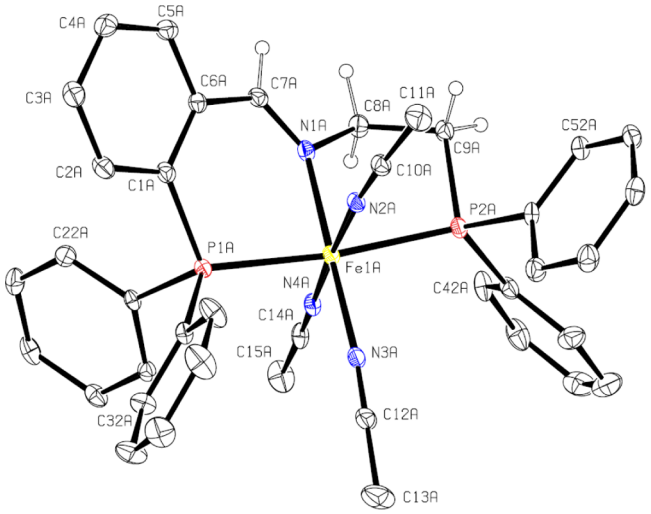

Figure 4. Molecular structure (thermal ellipsoids at 30% probability) of precatalyst **6a**. Hydrogen atoms of Ph groups and BF_4 anion are removed for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1), 2.2732(8); Fe(1)−P(2), 2.3044(8); Fe(1)−N(1), 1.9724(19); Fe(1)−N(2), 1.922(2); Fe(1)−N(3), 1.932(2); Fe(1)−N(4), 1.907(2); N(1)−C(7), 1.279(3); N(1)−C(8), 1.485(3), P(2)−Fe(1)−P(1), 173.82(3); N(1)−Fe(1)−P(1), 89.82(6); N(1)−Fe(1)−P(2), 84.76(6).

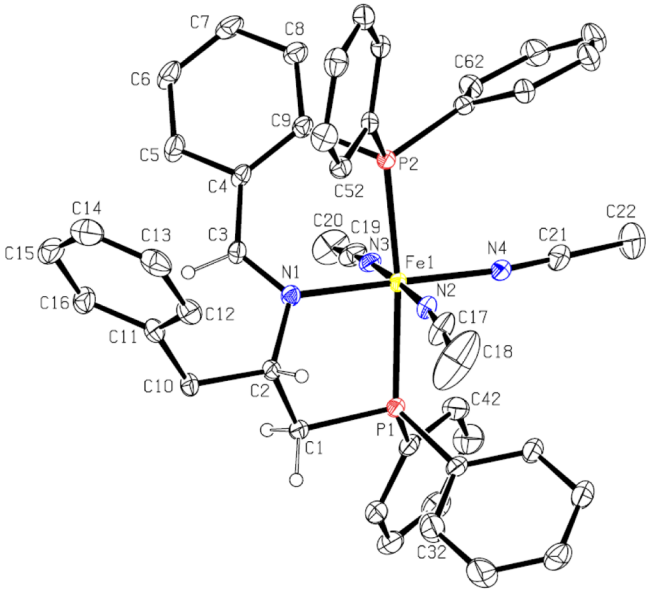

Figure 5. Molecular structure (thermal ellipsoids at 30% probability) of precatalyst **6e**. Hydrogen atoms of Ph groups and BF_4 anion are removed for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1), 2.2867(11); Fe(1)−P(2), 2.2558(11); Fe(1)−N(1), 1.976(3); Fe(1)−N(2), 1.896(4); Fe(1)−N(3), 1.928(4); Fe(1)−N(4), 1.925(3); N(1)−C(3), 1.291(5); N(1)−C(2), 1.495(5), P(2)−Fe(1)−P(1), 173.44(4); N(1)−Fe(1)−P(1), 84.32(9); N(1)−Fe(1)−P(2), 89.12(9).

present in **7**. $^{31}P\{^1H\}$ NMR spectra of these species proved to be quite useful for their characterization, as they exhibited two doublets in the 40−70 ppm range with $^2J_{PP}$ values in the range 138−152 Hz. Complex **6** had slightly larger $^2J_{PP}$ values in the range 149−152 Hz, versus **7**, which were in the range 138−142 Hz. In the $^{31}P\{^1H\}$ NMR spectra, complexes with two chiral centers exhibited distinctly different doublets, whereas the doublets for the complexes with a single chiral center exhibited a slight roofing effect (second-order patterning). The achiral complexes, on the other hand, demonstrated extreme second-order patterns. The crystal structures of **6a**,**e** were quite similar in terms of common bond lengths and angles. The imine C═N bond length for both was 1.279−1.291 Å, indicative of a C−N double bond, in comparison to the other side of the ligand, which had C−N bonds with lengths of 1.485−1.495 Å, indicative of a C−N single bond.

Following the development of a new library of chiral and achiral iron-(P-N-P′) and iron-(P-NH-P′) complexes, we tested **6** and **7** for various types of catalysis. Unfortunately, neither series of complexes was active for the direct or transfer hydrogenation of ketones or activated imines. Direct hydrogenation trials were conducted at 50 °C and 25 atm of H_2, employing the previously developed $LiAlH_4$/*t*AmOH/KO*t*Bu activation process. A simplified process employing only KO*t*Bu was tested as well. Transfer hydrogenation was tested in an argon glovebox at 28 °C in *i*PrOH using KO*t*Bu. Unfortunately, the hydrogenation of ketones to alcohols and imines to amines was not successful under any of the conditions explored. Given the success of our previously developed [Fe(P-N-N-P)-$(NCMe)_2$][BF_4]$_2$ systems to dehydrogenate ammonia−borane,[62] we also tested the achiral complexes **6a** and **7a** for the catalytic release of H_2. Unfortunately, these systems were once again inactive in the presence of base. Although straightforward to synthesize and handle, these systems appear to be too stable to be catalytically active for the transformations we have explored, and a more complete investigation into potential applications of these systems is still required.

The next phase of our investigation was to explore the newly developed ligand scaffolds using $FeBr_2$ and CO(g), as has been previously discussed. Beginning with the achiral imine ligand **4a**, we investigated potential routes for synthesizing Fe(P-N-P′)(CO)Br_2 complexes. Stirring **4a** and 1 equiv of $FeBr_2$ under N_2 for 45 min, followed by rapid freezing of the reaction solution with liquid nitrogen and atmosphere evacuation, along with subsequent introduction of CO(g) and thawing, led to the clean formation of Fe(P-N-P′)(CO)Br_2 (**8a**) in 85% yield as a red-orange powder. The complex **8a** could also be synthesized using a template reaction with $FeBr_2$, **2a**, and *o*-(diphenylphosphino)benzaldehyde; however, the product was more difficult to extract and purify because unidentified side products were also forming. The structure of **8a** was confirmed by X-ray crystallography, as shown in Figure 6, and the complex was fully characterized using NMR, IR, MS, and elemental analysis. The imine proton was seen in the ^1H NMR spectrum at 8.36 ppm, and this was also confirmed by the crystal structure, which had C(2)−N(1) and C(3)−N(1) bond lengths of 1.489(3) and 1.283(3) Å corresponding to the C−N and C═N bonds of the ligand backbone, respectively. In the IR spectrum of **8a**, the carbonyl stretching frequency was 1961 cm^{-1}, much lower than that of **1a**−**f** (2000−2010 cm^{-1}), indicating a more electron rich iron center in comparison to that in the *trans*-dicarbonyl species. The inequivalent phosphorus atoms of the ligand appear as doublets in the $^{31}P\{^1H\}$ NMR spectrum at 44.0 and 39.6 ppm with $^2J_{PP}$ = 216.9 Hz, indicative of *trans*-phosphorus donors. This implies a *mer* geometry for the ligand, as observed in the crystal structure, yielding the overall geometry of *mer,cis*-Fe(P-N-P′)(CO)Br_2 (bromides *cis*). Also observed in the $^{31}P\{^1H\}$ NMR spectrum was a second set of doublets at 64.8 and 57.8 ppm with $^2J_{PP}$ = 184 Hz. This was identified as the *trans*-Br species from the

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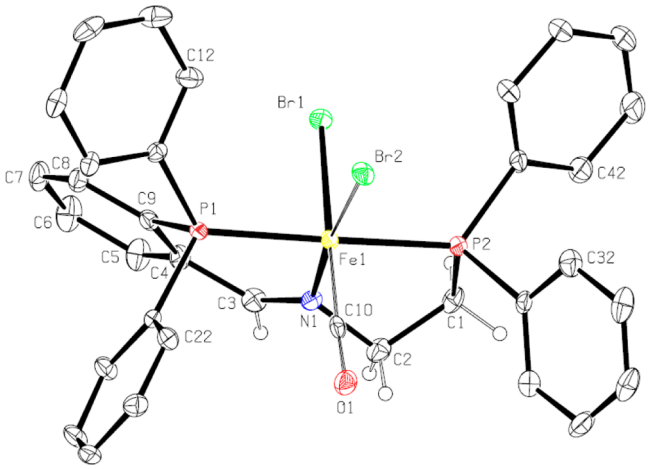

Figure 6. Molecular structure (thermal ellipsoids at 30% probability) of precatalyst **8a**. Hydrogen atoms of Ph groups are removed for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1), 2.2668(8); Fe(1)−P(2), 2.2653(8); Fe(1)−N(1), 1.987(2); Fe(1)−Br(1), 2.4821(5); Fe(1)−Br(2), 2.4787(5); Fe(1)−C(10), 1.776(4); N(1)−C(2), 1.489(3); N(1)−C(3), 1.283(3), O(1)−C(10), 1.097(5); P(2)−Fe(1)−P(1), 174.36(3); C(10)−Fe(1)−Br(1), 178.20(10); Br(2)−Fe(1)−Br(1), 96.518(18).

crystal structure, present in 8% on the basis of the *cis* Br/CO disorder.

With **8a** in hand, we tested the direct hydrogenation of ketones using the $LiAlH_4$/*t*AmOH/KO*t*Bu process previously developed. At 50 °C and 5 atm of H_2 catalysis was slow and irreproducible. At 50 °C and 25 atm of H_2, catalysis with the ratio **8a**:KO*t*Bu:acetophenone = 1:13:500 was 80% complete in 30 min and 98% complete in 1 h, yielding a TOF of 800 h^{-1}. This is lower than the those for the corresponding achiral precatalysts **1a**,**b**, which exhibited TOFs of 1980 h^{-1} under the milder H_2 pressure of 5 atm. However, **8a** has diphenylphosphine groups on both sides of the P-N-P′ ligand, unlike **1a**,**b**, which have a diphenylphosphine group on one side and required an alkyl-substituted phosphorus donor on the other side. For the achiral 5,5-P-N-P′ iron complex, when both phosphorus donors were diphenylphosphine groups, the precatalyst was completely inactive,[36] indicating that the incorporation of the *o*-phenylene linker to generate a 6,5-(P-N-P′) system may have positively influenced reactivity as targeted.

Although previous investigations demonstrated that the various complexes **1d**−**f** with one stereogenic center yielded lower ee values than the complex with two centers, **1c**, we were interested in synthesizing and testing the complete series with the *o*-phenylene linker, as was done with **8a**, to determine whether the same trends were maintained on changing the ligand structure and flexibility. Unfortunately, we ran into difficulties attempting to coordinate our presynthesized chiral P-N-P′ and P-NH-P′ ligands to $FeBr_2$. Following various methodologies, we were unable to cleanly isolate Fe(P-N-P′)(CO)Br_2 or [Fe(P-N-P′)$(CO)_2$Br]$^+$ complexes bearing the new chiral ligands developed. Using in situ $^{31}P\{^1H\}$ NMR of reaction solutions under a CO(g) headspace, we were able to detect a pair of doublets, indicating that a single iron species was forming; however, upon workup, decomposition occurred. Investigating this decomposition, we learned that the iron species were unstable when no longer under a CO(g) atmosphere, leading to the formation of several species, some of which were paramagnetic, as evidenced by the highly broadened NMR spectra. Confirming the presence of paramagnetic species, Fe($PPh_2C_6H_4CHNCHiPrCH_2PPh_2$)$Br_2$ crystallized out of the reaction mixture while attempting to synthesize **8f** and was characterized crystallographically, as shown in Figure 7. The complex is trigonal bipyramidal with a

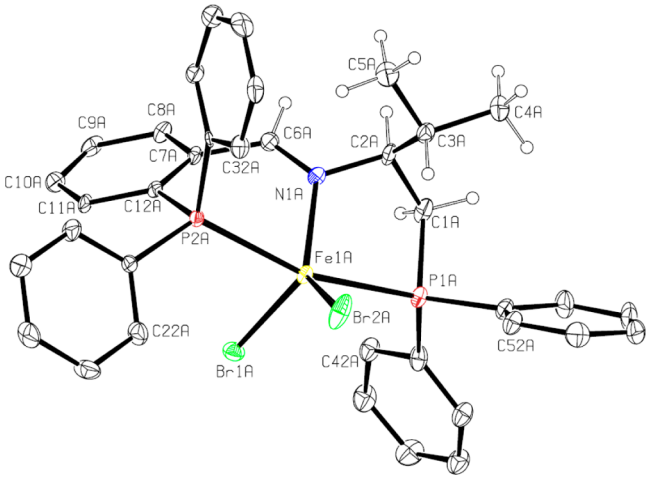

Figure 7. Molecular structure (thermal ellipsoids at 30% probability) of Fe(P-N-P′)Br_2(*i*Pr). Hydrogen atoms of Ph groups are removed for clarity. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1), 2.620(4); Fe(1)−P(2), 2.500(3); Fe(1)−N(1), 2.249(10); Fe(1)−Br(1), 2.453(2); Fe(1)−Br(2), 2.377(2); N(1)−C(2), 1.482(16); N(1)−C(6), 1.298(17), P(2)−Fe(1)−P(1), 158.78(13); Br(2)−Fe(1)−Br(1), 122.25(10); N(1)−Fe(1)−P(1), 78.1(3); N(1)−Fe(1)−P(2), 80.8(3).

much narrower P−Fe−P angle of 158.78(13)° versus the 170−175° range seen with the previously characterized octahedral Fe(P-N-P) complexes. The Fe−Br bonds have lengths comparable to those of the previous complexes. However, the Fe−N and two Fe−P bonds are much longer: Fe(1)−N(1) at 2.249(10) Å versus 1.97−2.04 Å and Fe(1)−P(1) and Fe(1)−P(2) at 2.620(4) and 2.500(3) Å versus 2.25−2.30 Å. This indicates a more weakly and loosely bound ligand in this case, explaining why they decompose so readily. This is also consistent with a paramagnetic species. The imine moiety is maintained in the complex with C(6)−N(1) and C(2)−N(1) bonds of 1.298(17) and 1.482(16) Å for the C═N and C−N bonds, respectively.

CONCLUSIONS

Following the successful development of a highly active asymmetric direct hydrogenation catalyst based on iron, we further expanded the range of available precatalysts by synthesizing a series of enantiopure PN ligands derived from amino acids. These were condensed with phosphonium dimers and used to synthesize *mer,trans*-[Fe(P-N-P′)$(CO)_2$Br][BF_4] complexes **1d**−**f** derived from (*S*)-phenylglycine, (*S*)-phenylalanine, and (*S*)-valine, respectively, which were shown to be catalytically active for the direct hydrogenation of ketones under mild conditions. The new systems were slower and less enantioselective than the original catalyst, which contained a PN ligand derived from (*S*,*S*)-norephedrine (**1c**). Under comparable conditions the TOF values for acetophenone hydrogenation decreased in the order **1a**−**c** (1980 h^{-1}) > **1d** (920 h^{-1}) > **1e** (460 h^{-1}) > **1f** (250 h^{-1}) while the ee values of

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the (*S*)-1-phenylethanol produced decreased in the order **1c** (80%) > **1f** (74%) > **1d** (55%) > **1e** (13%). Thus, it seems that for activity a CHMe or CH_2 group next to nitrogen is optimum while for enantioselectivity a CHPh group next to PPh_2 is best.

Given the subtle interplay of ligand rigidity, and the involvement of an N−H in the ligand backbone in the reaction mechanism, we developed a new series of P-N-P′ and P-NH-P′ ligands with an *o*-phenylene linker on one side of the ligand to significantly increase ligand flexibility. This new library of ligands was coordinated to iron to make the series of complexes $[Fe(P\text{-}N\text{-}P')(NCMe)_3][BF_4]_2$ (**6**) and $[Fe(P\text{-}NH\text{-}P')(NCMe)_3][BF_4]_2$ (**7**), which were shown to be quite stable but inactive toward hydrogenation (direct or transfer) and ammonia−borane dehydrogenation. Finally, we coordinated our achiral P-N-P′ ligand **4a** to $FeBr_2$ under CO(g) to generate the new precatalyst *mer,cis*-$Fe(P\text{-}N\text{-}P')(CO)Br_2$, which was active for the direct hydrogenation of acetophenone with a TOF value of 800 h^{-1} at 50 °C and 25 atm of H_2. Unfortunately, the chiral variants of this system decomposed on removal from a CO(g) atmosphere. Judging from the success of the use of the complexes $FeH(X)(CO)(PiPr_2CH_2CH_2NHCH_2CH_2PiPr_2)$ in ester and imine hydrogenation,[22,23] a future direction will be to incorporate alkyl groups on both phosphorus donors of our more active 5,5-systems.

EXPERIMENTAL SECTION

General Considerations. All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk line and glovebox techniques unless stated otherwise. The reagents and amino acids were purchased from Sigma-Aldrich, and the chiral diphenyl amino alcohol was purchased from ACE Synthesis. The phosphonium dimer $[PCy_2CHOHCH_2-]_2Br_2$ and the PN compounds **2d−g** were published as described elsewhere,[41−46,48] and the series of steps required for the generation of the PN ligands illustrated in Schemes 2 and 3 are briefly summarized in the Supporting Information. All solvents were degassed and dried using standard procedures prior to all manipulations and reactions unless stated otherwise. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma-Aldrich, degassed, and dried over activated molecular sieves prior to use. All other reagents were purchased from commercial sources and utilized without further purification. NMR spectra were recorded at ambient temperature and pressure using a Varian Gemini 400 MHz spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, 376 MHz for ^{19}F, and 161 MHz for ^{31}P) or an Agilent DD2 600 MHz spectrometer (600 MHz for ^1H, 151 MHz for ^{13}C, 564 MHz for ^{19}F, and 243 MHz for ^{31}P) unless stated otherwise. The ^1H and ^{13}C NMR were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). All ^{31}P chemical shifts were measured relative to 85% phosphoric acid as an external reference. Gas chromatography was done on a PerkinElmer Clarus 400 chromatograph equipped with a chiral column (CP Chirasil-Dex CB 25 m × 2.5 mm) to determine substrate conversion and enantiopurity. Hydrogen gas was used as the mobile phase, and the oven temperature was set at 130 °C. Retention times for phenylethanol are 7.58 and 8.03 min, and that for acetophenone is 4.56 min. All of the hydrogenation reactions were performed in a 50 mL stainless steel Parr hydrogenation reactor at constant temperatures and pressures. The temperature was maintained at 50 °C using a constant-temperature water bath and was purged of oxygen by flushing the reactor several times with 5 atm of H_2(g). The elemental analyses were performed on a PerkinElmer 2400 CHN elemental analyzer. Some complexes gave unsatisfactory carbon analyses but acceptable hydrogen and nitrogen content because of a combustion problem due to the tetrafluoroborate, hexafluorophosphate, and tetraphenylborate anions, as previously reported in the literature.[63] These complexes are denoted with ** following the elemental analysis results.

Catalysis. *Hydrogenation Studies.* In an argon-filled glovebox, a vial was charged with precatalyst (0.006 mmol) and 3 mL of THF. To this solution was added 0.05 mL of $LiAlH_4$ (1.0 M in THF), and the solution immediately changed from pink to dark brown. After the solution was stirred for 5 min, 2-methyl-2-butanol (0.5 mL) was added and the solution was stirred for an additional 10 min. The solution was transferred to a syringe equipped with a 12 in. needle. The same vial was then charged with acetophenone (0.35 mL, 3.0 mmol) and 3 mL of THF. The solution was taken up into the same syringe that already contained the precatalyst solution and stoppered. In a second syringe equipped with a 12 in. needle, a solution of base (0.08 mmol) in 3 mL of THF was taken up and stoppered. Both syringes were removed from the glovebox and injected into Parr reactors heated to 50 °C and pressurized to 5 atm H_2(g) against a flow of hydrogen. At set times, small amounts of sample were removed from the reactor using a needle and syringe under a flow of hydrogen and injected into the gas chromatograph for analysis.

Transfer Hydrogenation Catalysis. In a vial containing precatalyst (0.007 mmol) and KO*t*Bu (6 mg, 0.054 mmol), isopropyl alcohol (6 mL, 78 mmol) and acetophenone (0.5 mL, 4.3 mmol) were added at 28 °C, in an argon -filled glovebox. Solutions were stirred vigorously, and samples were taken from the mixture, quenched by exposure to air, and analyzed by gas chromatography. All of the catalytic results were reproduced to ensure consistency.

Ammonia−Borane Dehydrogenation Catalysis. In an argon-filled glovebox, precatalyst (0.007 mmol) and ammonia−borane (AB; 10 mg, 0.32 mmol) were placed in a 25 mL two-neck round-bottom flask which was sealed with a rubber septum and a 10 mL dry-addition flask containing KO*t*Bu (8 mg, 0.071 mmol). The sealed system was removed from the glovebox and submerged in a 24 °C water bath before 5 mL of THF was added to the flask and the mixture was stirred for 10 min. A cannula needle was used to pierce the septum, and an upturned 50 mL buret filled with water was used to measure the evolution of gas. To start the reaction, the dry-addition flask was tilted, and base was added to the reaction mixture, which was stirred vigorously. Hydrogen production was measured in terms of volume displacement of water in the buret as a measure of time. All catalytic results were reproduced to ensure consistency (C:B:S = 1:10:45).

Synthesis. *Synthesis of mer,trans-[Fe(Br)(CO)$_2$(P-N-P′)][BF$_4$] Precatalysts **1d−f**. General Synthesis.* In a nitrogen-filled glovebox, dicyclohexylphosphonium dimer (0.05 g, 0.078 mmol) and potassium *tert*-butoxide (0.018 g, 0.16 mmol) were stirred in 8 mL of THF for 10 min to yield a cloudy white solution. To this solution were added the PN ligand **2d−f** (0.16 mmol) and $FeBr_2$ (0.05 g, 0.23 mmol), yielding a pale yellow solution, and the flask was transferred to a Schlenk line and put under a CO(g) atmosphere. Immediately upon exposure the solution turned purple. The solution was stirred under CO(g) (∼2 atm) for 5 h to yield a deep red-purple solution. The solution was dried under reduced pressure, transferred to a nitrogen-filled glovebox, and redissolved in 8 mL of DCM. The solution was filtered through Celite, transferred back to the Schlenk line, and exposed to a CO(g) atmosphere. $AgBF_4$ (0.033 g, 17 mmol) in 2 mL of THF was injected into the solution, and the mixture was stirred for 30 min. The solvent was removed under reduced pressure, and the flask was transferred back into a nitrogen-filled glovebox. The residue was redissolved in 5 mL of DCM, filtered through Celite, and concentrated to ∼1 mL under reduced pressure. A 5 mL portion of pentane was added to crash out the product as a deep purple powder, which was subsequently washed with diethyl ether and dried under reduced pressure.

***1d**: R^1 = Ph, R^2 = H.* Yield: 110 mg, 86%. ^1H NMR (400 MHz, THF-d_8): δ 8.15 (m, 2H, Ar-CH and P-Ar-CH), 8.01 (m, 2H, Ar-CH and P-Ar-CH), 7.1−7.6 (m, Ar-CH and P-Ar-CH), 7.21 (N═CH, determined indirectly from $^1H-^1H$ COSY), 4.51 (t, 1H, N−CH, J = 11.6 Hz), 3.63 (CH_2-PPh_2, determined indirectly from $^1H-^1H$ COSY), 3.58 (CH_2-PCy_2, determined indirectly from $^1H-^1H$ COSY), 3.39 (CH_2-PCy_2, determined indirectly from $^1H-^1H$ COSY), 3.13 (dd, 1H, CH_2-PPh_2, J = 5.1 and 13.1 Hz), and 0.9−2.6 (m, PCy-H)

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ppm. $^{31}P\{^1H\}$ NMR (161 MHz, THF-d_8): δ 66.76 (d, $^2J_{PP}$ = 81.9 Hz), and 39.35 (d, $^2J_{PP}$ = 81.6 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 181.6 (N=CH), 128−133 (Ar-CH and P-Ar-CH), 74.1 (N-CH), 38.5 (PCy-C), 36.1 (PCy_2-CH_2), 34.5 (PPh_2-CH_2), 25−29 (PCy-C), and 13.3 (PCy_2-C) ppm. $^{19}F\{^1H\}$ NMR (356 MHz, THF-d_8): δ −153 ppm. Anal. Calcd for $[FeC_{36}H_{43}P_2NO_2Br][BF_4]$: C, 53.6; H, 5.40; N, 1.70. Found: C, 41.93; H, 4.98; N, 1.40.** MS (ESI, m/z^+): 720.1 $[FeC_{36}H_{43}P_2NO_2Br]^+$. IR: ν(CO) 2009.2 cm^{-1}.

1e: *R^1 = CH_2Ph, R^2 = H.* Yield: 110 mg, 84%. ^1H NMR (400 MHz, THF-d_8): δ 8.13 (m, 1H, N=CH), 7.74 (m, 1H, Ar-CH and P-Ar-CH), 6.9−7.5 (m, 14H, Ar-CH and P-Ar-CH), 3.61 (N−CH, determined indirectly from $^1H-^1H$ COSY), 3.30 (CH_2-PCy_2, determined indirectly from $^1H-^1H$ COSY), 3.03 (CH_2-PPh_2, determined indirectly from $^1H-^1H$ COSY), 2.86 ((CH_2-PPh_2, determined indirectly from $^1H-^1H$ COSY), 1.33 (CH_2-Ph, determined indirectly from $^1H-^1H$ COSY), and 0.8−2.5 (m, PCy-H) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, THF-d_8): δ 64.20 (d, $^2J_{PP}$ = 82.1 Hz), and 42.55 (d, $^2J_{PP}$ = 82.1 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 146.7 (N=CH), 127−133 (Ar-CH and P-Ar-CH), 66.5 (N-CH), 41.1 (CH_2-PPh_2), 38.6 (CH_2-PCy_2), 26.9 (CH_2-Ph), and 22−28 (PCy-C), and 13.6 (PCy_2-C) ppm. $^{19}F\{^1H\}$ NMR (356 MHz, THF-d_8): δ −153.3 ppm. Anal. Calcd for $[FeC_{37}H_{45}P_2NO_2Br][BF_4]$: C, 54.2; H, 5.5; N, 1.7. Found: C, 47.35; H, 5.39; N, 1.83.** MS (ESI, m/z^+): 734.1 $[FeC_{37}H_{45}P_2NO_2Br]^+$and 676.1 $[FeC_{35}H_{45}P_2NBr]^+$ (loss of two −CO). IR: ν(CO) 2004.4 cm^{-1}.

1f: *R^1 = iPr, R^2 = H.* Used $AgPF_6$ instead of $AgBF_4$. Yield: 120 mg, 78%. ^1H NMR (400 MHz, THF-d_8): δ 8.16 (m, 1H, Ph−CH), 7.92 (m, 1H, Ph−CH), 7.05−7.68 (m, 9H, Ph−CH and N=CH at 7.58− determined indirectly for $^1H-^{13}C$ HSQC), 3.26 (m, 1H, N-C(*i*Pr)*H*), 2.98 (m, 2H, CH_2-PPh), 2.35 (m, 2H, CH_2-PCy), 1.21 (*i*Pr-CH, determined indirectly for $^1H-^1H$ COSY), 0.75 (m, 6H, iPr-CH_3), and 0.6−2.1 (m, PCy-H) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, THF-d_8): δ 63.28 (d, $^2J_{PP}$ = 81.6 Hz), 46.26 (d, $^2J_{PP}$ = 81.6 Hz), and −137.56 (m, PF_6^-) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 163.19 (N=CH), 129−135 (Ph−CH), 67.02 (N-C(*i*Pr)H), 42.70 (CH_2-PPh), 35.80 (PCy_2-C), 32.52 (CH_2-PCy), 20−30 (PCy_2-*C*), 24.07 (*i*Pr-CH), and 15.23 (*i*Pr-CH_3) ppm. $^{19}F\{^1H\}$ NMR (356 MHz, THF-d_8): δ −64.13 (d, PF_6^-, J = 790 Hz) ppm. Anal. Calcd for $[FeC_{37}H_{45}P_2NO_2Br][PF_6]$: C, 47.73; H, 5.46; N, 1.69. Found: C, 40.09; H, 6.17; N, 1.80.** MS (ESI, m/z^+): 686.1 $[FeC_{33}H_{45}P_2NO_2Br]^+$and 628.2 $[FeC_{31}H_{45}P_2NBr]^+$ (loss of two −CO). IR: ν(CO) 2005.8 cm^{-1}.

*Synthesis of $[Fe(PN)_2(CO)(Br)]BPh_4$ (**3**).* In a nitrogen-filled glovebox, **2g** (0.074 g, 0.19 mmol) and $FeBr_2$ (0.028 g, 0.13 mmol) were stirred in 4 mL of THF for 30 min and then transferred to a Schlenk line and stirred under CO(g) (∼2 atm) for 2.5 h to yield a deep brown solution. The solution was dried under reduced pressure and transferred to a nitrogen-filled glovebox. The residue was dissolved in ∼5 mL of DCM and filtered through Celite to remove salts. The DCM solution was concentrated under reduced pressure to ∼1 mL, $NaBPh_4$ (0.033 g, 0.096 mmol) in 5 mL of methanol was added, and the mixture was stirred for 15 min to precipitate a pale purple solid. The solid was collected, washed with cold methanol, and dried under reduced pressure. Yield: 100 mg, 87%.

^1H NMR (400 MHz, THF-d_8): δ 6.6−8.1 (m, 40H, Ph-CH), 5.23 (m, 1H, C(Ph)H), 5.00 (m, 1H, C(Ph)H, correlates to 5.23 proton), 4.85 (m, 1H, C(Ph)H), 3.43 (m, 1H, C(Ph)H, correlates to 4.85 proton), 3.48 (broad s, 1H (should be 2H, likely solvent exchange), NH_2), and 2.66 (broad s, 2H, NH_2) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, THF-d_8): δ 84.62 (d, $^2J_{PP}$ = 145.8 Hz), and 76.58 (d, $^2J_{PP}$ = 145.8 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 126−137 (Ph-C), 68.5 (C(Ph)H, correlates to 3.43 proton), 64.4 (C(Ph)H, correlates to 5.00 proton), 50.0 (C(Ph)H, correlates to 5.23 proton), 49.3 (C(Ph)H, correlates to 4.85 proton) ppm. Anal. Calcd for $[FeC_{53}H_{48}P_2NOBr][BPh_4]$: C, 74.23; H, 5.50; N, 2.25. Found: C, 64.66; H, 5.43; N, 2.36.** MS (ESI, m/z^+): 927.2 $[FeC_{53}H_{48}P_2N_2OBr]^+$, IR: ν(CO) 1943.6 cm^{-1}.

*Synthesis of P-N-P′ Ligands **4a,c−g**.* *As illustrated for **4a**, complete details for each system areavailable in the Supporting Information.

4a: *R^1 = R^2 = H.* In a nitrogen-filled glovebox, **2a** (0.6 g, 2.6 mmol) was added to a solution of *o*-(diphenylphosphino)benzaldehyde (0.76 g, 2.6 mmol) and Na_2SO_4 (5 g, 35 mmol) in 30 mL of DCM. The mixture was stirred for 24 h and then filtered through a frit and concentrated to 2 mL. With rigorous stirring, 8 mL of cold ethanol was added and the flask was sealed and stored at −30 °C for 48 h to yield a white powder. The powder was filtered and washed with cold ethanol and then dried under reduced pressure to yield pure P-N-P′ ligand. Yield: 980 mg, 75%.

^1H NMR (400 MHz, CD_2Cl_2): δ 8.77 (d, 1H, HC=N, $^4J_{HH}$ = 4.7 Hz), 7.8 (dd, 1H, Ar-CH, J = 3.9, 7.5 Hz), 7.1−7.4 (m, 22H, Ar-CH, P-Ar-CH), 6.8 (dd, 1H, Ar-CH, J = 7.4, 4.6 Hz), 3.5 (t, 2H, N−CH_2, $^3J_{HH}$ = 7.8 Hz), and 2.1 (t, 2H, P-CH_2, $^3J_{HH}$ = 7.8 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −13.2 (s), −19.5 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 159.5 (d, HC=N, J = 20 Hz), 137−139 (Ar-C, P-Ar-C), 127−134 (Ar-C, P-Ar-C), 57.8 (d, N−CH_2, J = 21.1 Hz), and 29.5 (d, P-CH_2, J = 12.8 Hz) ppm. Anal. Calcd for $[C_{33}H_{29}P_2N]$: C, 79.0; H, 5.82; N, 2.79. Found: C, 77.83; H, 5.59; N, 2.81. MS (TOF-DART, m/z^+): 502.185 $[C_{33}H_{30}P_2N]^+$. The complex was made multiple times in an attempt to synthesize pure compound (acceptable elemental analysis); however, silica grease impurities (observed in ^1H NMR) caused the carbon analyses to be low. The compound could therefore not be isolated as 100% pure.

4c: *R^1 = Me, R^2 = Ph.* From **2c** (0.1 g, 0.31 mmol), Yield: 120 mg, 65%. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.80 (d, 1H, HC=N, $^4J_{HH}$ = 4.90 Hz), 7.6 (m, 2H, Ar-CH), 7.0−7.4 (m, 26H, Ar-CH, P-Ar-CH), 6.8 (m, 1H, Ar-CH), 3.72 (d, 1H, *CH*(Ph), $^3J_{HH}$ = 5.6 Hz), 3.63 (dq, 1H, *CH*(CH_3), $^3J_{HH}$ = 5.6 and 6.1 Hz), and 0.95 (d, 3H, CH_3, $^3J_{HH}$ = 6.1 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −8.1 (s), −14.5 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 157.7 (C=N), 132−134 (Ar-C, P-Ar-C), 126−130 (Ar-C, P-Ar-C), 68.6 (CH-Me), 51.3 (*C*H-Ph), and 19.8 (CH_3) ppm. Anal. Calcd for $[C_{40}H_{35}P_2N]$: C, 81.19; H, 5.96; N, 2.37. Found: C, 80.75; H, 5.10; N, 1.93. MS (TOF-DART, m/z^+): 592.232 $[C_{40}H_{36}P_2N]^+$.

4d: *R^1 = Ph, R^2 = H.* From **2d** (0.15 g, 0.49 mmol), Yield: 150 mg, 55%. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.68 (d, 1H, N=CH, $^4J_{HH}$ = 4.6 Hz), 7.76 (ddd, 1H, Ar-CH, J = 1.5, 3.9, and 7.8 Hz), 7.05−7.32 (m, 27H, Ar-CH), 6.78 (ddd, 1H, Ar-CH, J = 1.3, 4.6, and 7.7 Hz), 4.16 (quart., 1H, C(Ph)H, $^3J_{HH}$ = 7.8 Hz), and 2.41 (qd, 2H, CH_2, $^2J_{HH}$ and $^3J_{HH}$ = 13.6 and 7.1 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −12.8 (s), −22.9 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 158.8 (d, C=N, J = 19.8 Hz), 126−135 (Ar-C and P-Ar-C), 72.5 (d, CH, J = 16.4 Hz), and 53.4 (quint, CH_2, J = 27.2 Hz) ppm. Anal. Calcd for $[C_{39}H_{33}P_2N]$: C, 81.1; H, 5.76; N, 2.43. Found: C, 79.07 H 5.79; N, 2.36. MS (ESI, m/z^+): 578.2 $[C_{39}H_{34}P_2N]^+$. Complex was made multiple times in an attempt to synthesize pure compound (acceptable EA) however silica grease impurities (observed in ^1H NMR) caused the carbon analyses to be low. The compound could therefore not be isolated as 100% pure.

4e: *R^1 = CH_2Ph, R^2 = H.* From **2e** (0.27 g, 0.85 mmol), Yield: 230 mg, 46%. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.37 (d, 1H, N=CH, $^4J_{HH}$ = 4.7 Hz), 7.71 (ddd, 1H, Ar-CH, J = 1.6, 3.9, and 7.6 Hz), 7.15−7.45 (m, 25H, Ar-CH), 7.01 (dd, 2H, Ar-CH, J = 1.7 and 7.9 Hz), 6.86 (ddd, 1H, Ar-CH, J = 1.5, 4.5, and 7.6 Hz) 3.28 (m, 1H, CH) 2.99 (dd, 1H, CH-P, $^3J_{HH}$ and $^2J_{HH}$ = 4.9 and 13.3 Hz), 2.74 (dd, 1H, CH-P, $^3J_{HH}$ and $^2J_{HH}$ = 8.1 and 13.3 Hz), 2.33 (dd, 1H, CH-Ph, $^3J_{HH}$ = 5.1 and 13.6 Hz), and 2.13 (dd, 1H, CH-Ph, $^3J_{HH}$ = 8.1 and 13.6 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −14.1 (s), −23.1 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 158.1 (d, C=N, J = 19.3 Hz), 125−140 (Ar-C and P-Ar-C), 70.3 (d, CH, J = 14.1 Hz) 43.5 (d, CH_2-P, J = 9.0 Hz), and 34.5 (d, CH_2-Ph, J = 12.8 Hz) ppm. Anal. Calcd for $[C_{40}H_{35}P_2N]$: C, 80.2; H, 5.96; N, 2.37. Found: C, 79.29; H, 6.18; N, 2.27. MS (ESI, m/z^+): 592.2 $[C_{40}H_{36}P_2N]^+$.

4f: *R^1 = iPr, R^2 = H.* From **2f** (0.1 g, 0.37 mmol), Yield: 100 mg, 50%. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.65 (d, 1H, HC=N, $^4J_{HH}$ = 4.77 Hz), 7.75 (ddd, 1H, Ar-CH, J = 1.4, 3.9, and 7.7 Hz), 7.70 (dd, 1H, Ar-CH, J = 3.3 and 5.7 Hz), 7.55 (dd, 1H, Ar-CH, J = 3.3 and 5.7 Hz), 7.2−7.4 (m, 20H, P-Ar-CH), 6.85 (ddd, 1H, Ar-CH, J = 1.4, 4.6, and 7.7 Hz), 2.88 (m, 1H, N−C−H), 2.31 (dd, 1H, CH_2, $^3J_{HH}$ and

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$^2J_{HH}$ = 4.3 and 13.8 Hz), 2.15 (dd, 1H, CH_2, $^3J_{HH}$ and $^2J_{HH}$ = 8.9 and 13.8 Hz), 1.82 (m, 1H, *i*Pr-CH), and 0.73 (dd, 6H, *i*Pr-CH_3, $^3J_{HH}$ = 5.0, 6.7 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −13.3 (s), −22.0 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 158.5 (d, C=N, J = 19.8 Hz), 128−140 (Ar-C and P-Ar-C), 74.3 (d, N−C, J = 13 Hz), 33.6 (d, *i*Pr-CH, J = 8.6 Hz), 32.7 (d, CH_2, J = 13 Hz), 19.3 (s, *i*Pr-CH_3), and 17.6 (s, *i*Pr-CH_3) ppm. Anal. Calcd for $[C_{36}H_{35}P_2N]$: C, 79.5; H, 6.49; N, 2.58. Found: C, 78.6; H, 7.04; N, 2.19. MS (ESI, m/z^+): 544.23 $[C_{36}H_{36}P_2N]^+$.

4g: *R^1 = R^2 = Ph.* From **2g** (0.15 g, 0.41 mmol), Yield: 151 mg, 58%. ^1H NMR (400 MHz, CD_2Cl_2): δ 8.99 (d, 1H, N=CH, $^4J_{HH}$ = 5.6 Hz), 7.68 (td, 2H, Ar-CH, J = 1.7 and 7.7 Hz), 6.85−7.45 (m, 31H, Ar-CH), 6.81 (ddd, 1H, Ar-CH, J = 1.4, 4.8, and 7.6 Hz), 4.83 (dd, 1H, N-C*H*Ph, $^3J_{HH}$ = 5.8 and 8.2 Hz), and 4.22 (dd, 1H, P−C*H*Ph, $^3J_{HH}$ and $^3J_{HP}$ = 5.5 and 8.2 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −7.17 (s), −15.36 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 158.4 (C=N), 133−135 (Ar-C and P-Ar-C), 126−131 (Ar-C and P-Ar-C), 78.9 (d, N-CHPh, J = 21.0 Hz), and 52.0 (d, P-CHPh, J = 16.1 Hz) ppm. Anal. Calcd for $[C_{45}H_{37}P_2N]$: C, 82.68; H, 5.70; N, 2.14. Found: C, 82.50; H, 6.16; N, 2.14. MS (ESI, m/z^+): 654.2 $[C_{45}H_{38}P_2N]^+$.

*Synthesis of P-NH-P′ Ligands **5a,c−f.*** The synthesis is illustrated for **5a**; complete details for each system are available in the Supporting Information.

5a: *R^1 = R^2 = H.* In a nitrogen-filled glovebox, **4a** (0.055 g, 0.11 mmol) and $NaBH_4$ (0.012 g, 0.31 mmol) were dissolved in 5 mL of ethanol, sealed, and transferred to a Schlenk line. The solution was refluxed under argon for 24 h, and then 8 mL of distilled water was added to neutralize the excess $NaBH_4$. The flask was then opened to air, and the product was extracted with 20 mL of DCM. The aqueous phase was further extracted with DCM (2 × 15 mL), and the combined organics were washed with saturated NH_4Cl solution (3 × 15 mL) and water (3 × 15 mL), dried with Na_2SO_4, and dried under reduced pressure to yield a clean, white powder. Yield: 54 mg, 97%.

^1H NMR (400 MHz, CD_2Cl_2): δ 7.2−7.4 (m, 22H, Ar-CH), 7.15 (td, 1H, Ar-CH, J = 1.4 and 7.4 Hz), 6.78 (ddd, 1H, Ar-CH, J = 1.4, 4.5, and 7.7 Hz), 3.8 (d, 2H, N-CH_2-Ph, $^3J_{HH}$ = 1.8 Hz), 2.51 (quart, 2H, N-CH_2, $^3J_{HH}$ = 8.1 Hz), 1.94 (t, 2H, P-CH_2, $^3J_{HH}$ = 8.1 Hz), 1.28 (br-s, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −16.1 (s), −20.6 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 128−135 (Ar-C and P-Ar-C), 52.0 (N-CH_2-Ph), 45.8 (N-CH_2-CH_2), and 28.7 (P-CH_2) ppm. Anal. Calcd for $[C_{33}H_{31}P_2N]$: C, 78.71; H, 6.21; N, 2.78. Found: C, 78.82; H, 6.66; N, 2.40. MS (ESI, m/z^+): 504.2 $[C_{33}H_{32}P_2N]^+$.

5c: *R^1 = Me, R^2 = Ph.* From **4c** (0.052 g, 0.088 mmol), Yield: 37 mg, 71%. ^1H NMR (600 MHz, CD_2Cl_2): δ 7.57 (m, 2H, Ph−CH), 7.10−7.42 (m, 26H, Ph-CH), 6.85 (ddd, 1H, Ph-CH, J = 1.4, 4.5, and 7.7 Hz), 3.96 (dd, 1H, N-CH_2, $^3J_{HH}$ and $^2J_{HH}$ = 2.2 and 13.7 Hz), 3.87 (dd, 1H, N-CH_2, $^3J_{HH}$ and $^2J_{HH}$ = 2.4 and 13.7 Hz), 3.83 (m, 1H, P-C(Ph)H), 2.77 (m, 1H, N-C(Me)H), 1.29 (br-s, 1H, NH), and 1.00 (d, 3H, CH_3, $^3J_{HH}$ = 6.7 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −11.15 (s), −16.15 (s) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, CD_2Cl_2): δ 126−135 (Ph−C), 53.39 (N−C(Me)H), 49.22 (N−CH_2), 48.36 (P-C(Ph)H), and 17.16 (−CH_3) ppm. Anal. Calcd for $[C_{33}H_{31}P_2N]$: C, 80.92; H, 6.28; N, 2.36 Found: C, 80.62; H, 6.31; N, 2.34. MS (ESI, m/z^+): 594.2 $[C_{40}H_{38}P_2N]^+$.

5d: *R^1 = Ph, R^2 = H.* From **4d** (0.13 g, 0.23 mmol), Yield: 120 mg, 92%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.15−7.45 (m, 28H, Ar-CH), 6.89 (m, 1H, Ar-CH), 3.71 (s, 2H, N−CH_2-Ph), 3.62 (m, 1H, N-CH), 2.33 (d, 2H, CH_2-PPh_2, $^3J_{HH}$ = 7.1 Hz), and 1.29 (br s, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −16.4 (s), −23.5 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 132−134 (Ar-C and P-Ar-C), 127−129 (Ar-C and P-Ar-C), 60.0 (d, N-CH, J = 15.9 Hz), 50.1 (d, N-CH_2-Ph, J = 20.7 Hz), and 38.2 (d, CH_2-PPh_2, J = 14.3 Hz) ppm. Anal. Calcd for $[C_{39}H_{35}P_2N]$: C, 80.81; H, 6.09; N, 2.42. Found: C, 79.19; H, 6.80; N, 2.26. MS (ESI, m/z^+): 580.2 $[C_{39}H_{36}P_2N]^+$. The complex was made multiple times in an attempt to synthesize pure compound (acceptable elemental analysis); however, silica grease impurities (observed in ^1H NMR) caused the carbon analyses to be low. The compound could therefore not be isolated as 100% pure.

5e: *R^1 = CH_2Ph, R^2 = H.* From **4e** (0.075 g, 0.13 mmol), Yield: 66 mg, 89%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.0−7.3 (m, 26H, Ar-CH), 6.97 (m, 2H, Ar-CH), 6.74 (m, 1H, Ar-CH), 3.80 (d, 2H, N−CH_2-Ph, $^3J_{HH}$ = 2.0 Hz), 2.76 (m, 1H, N−CH), 2.70 (m, 2H, CH_2-P), 2.03 (d, 2H, CH_2-Ph, $^3J_{HH}$ = 6.1 Hz), and 1.20 (br s, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −16.0 (s), −23.4 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 132−134 (Ar-C and P-Ar-C), 126−129 (Ar-C and P-Ar-C), 56.2 (N-CH), 49.0 (N-CH_2-Ph) 41.2 (CH_2-P), and 33.3 (CH_2-Ph) ppm. Anal. Calcd for $[C_{40}H_{37}P_2N]$: C, 80.92; H, 6.28; N, 2.36. Found: due to the glassy nature of compound, sample could not be extracted for elemental analysis. MS (ESI, m/z^+): 594.2 $[C_{40}H_{38}P_2N]^+$.

5f: *R^1 = iPr, R^2 = H.* From **4f** (0.133 g, 0.24 mmol), Yield: 120 mg, 90%. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.21−7.45 (m, 22H, Ph-CH), 7.15 (td, 1H, Ph-CH, J = 1.4 and 7.5 Hz), 6.86 (ddd, 1H, Ph−CH, J = 1.3, 4.5, and 7.7 Hz), 4.28 (m, 1H, N-CH_2), 4.17 (m, 1H, N-CH_2), 3.88 (m, 2H, CH_2-P), 2.40 (m, 1H, N-CH), 1.95 (m, 1H, *i*Pr-CH), 1.62 (br-m, 1H, NH), and 0.79 (dd, 6H, *i*Pr-CH_3, $^3J_{HH}$ = 6.8 and 3.7 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ −16.09 (s), −22.15 (s) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 127−134 (Ph-C), 62.07 (N-CH_2), 59.80 (N-CH), 49.89 (CH_2-P) 20.31 (*i*Pr-CH), and 17.10 (*i*Pr-CH_3) ppm. Anal. Calcd for $[C_{36}H_{37}P_2N]$: C, 79.24; H, 6.84; N, 2.57, Anal. Calcd for $[C_{36}H_{37}P_2N]$-$2H_2O$ (observed in ^1H NMR, from aqueous workup steps): C, 74.30; H, 7.10; N, 2.40. Found: C, 74.69; H, 7.81; N, 1.58. MS (ESI, m/z^+): 546.2 $[C_{36}H_{38}P_2N]^+$.

*Synthesis of [Fe(P-N-P′)(NCMe)$_3$][BF$_4$]$_2$ (**6a,c−g**) and [Fe(P-NH-P′)(NCMe)$_3$][BF$_4$]$_2$ (**7a,c−f**).* The synthesis is illustrated for **6a**; complete details for each system are available in the Supporting Information.

6a: *R^1 = R^2 = H.* In a nitrogen-filled glovebox, **4a** (0.097 g, 0.19 mmol) and $[Fe(H_2O)_6][BF_4]_2$ (0.065 g, 0.19 mmol) were stirred in 12 mL of acetonitrile for 16 h. The solution was then concentrated to 1.5 mL and washed with pentane (2 × 6 mL). The acetonitrile layer was then dried to yield the pure product as a deep red solid. Yield: 160 mg, 98%.

^1H NMR (400 MHz, CD_3CN): δ 8.75 (s, 1H, N=CH), 7.45−7.93 (m, 23H, Ph-CH), 7.40 (m, 1H, Ph-CH), 3.84 (dt, 2H, N-CH_2, $^3J_{HH}$ = 14.0 and 6.8 Hz), 3.02 (dt, 2H, CH_2-PPh_2, $^3J_{HH}$ = 6.4 and 2.9 Hz), and 1.99 (s, NC−CH_3/NC-CD_3) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_3CN): δ extreme second order doublets centered at 54.94 ppm (apparent coupling $^2J_{PP}$ = 151.7 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 176.9 (N=CH), 129−137 (Ar-C and P-Ar-C), 117.3 (NCMe), 67.8 (N-CH_2), 22.7 (CH_2-PPh_2), and 0.77 (NC-CH_3) ppm. Anal. Calcd for $[FeC_{39}H_{38}P_2N_4][BF_4]_2$: C, 54.8; H, 4.5; N, 6.6. Found: C, 54.22; H, 4.48; N, 6.59. MS (ESI, m/z^+): 278.6 [Fe $C_{33}H_{29}P_2N]^{+2}$ (loss of three MeCN).

6c: *R^1 = Me, R^2 = Ph.* From **4c** (0.038 g, 0.063 mmol), Yield: 58 mg, 97%. ^1H NMR (400 MHz, CD_3CN): δ 8.67 (s, 1H, N=CH), 7.16−7.92 (m, 27H, Ar-CH and P-Ar-CH), 7.00 (d, 2H, Ar-CH and P-Ar-CH, J = 7.45 Hz), 4.14 (1H, C(Me)H, overlapping, determined indirectly using $^1H-^{13}C$ HSQC), 4.10 (1H, C(Ph)H, overlapping, determined indirectly using $^1H-^{13}C$ HSQC), 1.29 (d, 3H, −CH_3, $^3J_{HH}$ = 4.71 Hz), 1.99 (s, 9H, CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_3CN): δ 72.31 (d, $^2J_{PP}$ = 149.4 Hz), and 54.31 (d, $^2J_{PP}$ = 149.4 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 175.5 (N=CH), 127−137 (Ar-C and P-Ar-C), 119.8 (NCMe), 73.38 (C(Me)H), 49.07 (C(Ph)H), 19.22 (−CH_3), and 0.49 ($NCCH_3$) ppm. Anal. Calcd for $[FeC_{46}H_{44}P_2N_4][BF_4]_2$: C, 58.51; H, 4.70; N, 5.93. Found: C, 55.19; H, 4.53; N, 4.93.** MS (DART, m/z^+): 388.3 $[FeC_{46}H_{44}P_2N_4]^{2+}$.

6d: *R^1 = Ph, R^2 = H.* From **4d** (0.238 g, 0.41 mmol), Yield: 365 mg, 97%. ^1H NMR (400 MHz, CD_3CN): δ 7.92 (N=CH, determined indirectly via $^1H-^{13}C$ HSQC), 7.96 (m, 3H, Ar-CH and P-Ar-CH), 7.84 (m, 2H, Ar-CH and P-Ar-CH), 7.23−7.77 (m, 22H, Ar-CH and P-Ar-CH), 7.16 (m, 2H, Ar-CH and P-Ar-CH), 4.72 (td, 1H, C(Ph)H, $^3J_{HH}$ = 3.4 and 11.5 Hz), 3.66 (ddd, 1H, CH_2, $^3J_{HH}$ and $^2J_{HH}$ = 4.0, 13.0, and 14.7 Hz), 3.26 (ddd, 1H, CH_2, $^3J_{HH}$ and $^2J_{HH}$ = 7.0, 12.5, and 14.6 Hz), 1.99 (s, 9H, CH_3CN) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_3CN): δ 54.8 (d, $^2J_{PP}$ = 151 Hz), and 50.5 (d, $^2J_{PP}$ = 151 Hz) ppm

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(roofing doublets). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 176.8 (N=CH), 129−137 (Ar-C and P-Ar-C), 120.8 (NCMe), 77.4 (N−C(Ph)H), 27.4 (CH_2), and 1.0 ($NCCH_3$) ppm. Anal. Calcd for $[FeC_{45}H_{42}P_2N_4][BF_4]_2$: C, 58.1; H, 4.6; N, 6.0. Found: C, 55.01; H, 4.26; N, 5.35.** MS (ESI, m/z^+): 337 $[C_{41}H_{36}P_2N_2]^{2+}$ (loss of two MeCN), and 316.6 $[C_{39}H_{33}P_2N]^{2+}$ (loss of three MeCN).

6e: *R^1 = CH_2Ph, R^2 = H.* From **4e** (0.086 g, 0.15 mmol), Yield: 136 mg, 96%. ^1H NMR (400 MHz, CD_3CN): δ 8.33 (d, 1H, N=CH, $^4J_{HH}$ = 5.4 Hz), 7.92 (t, 2H, Ph−CH, J = 8.0 Hz), 7.2−7.8 (m, 25H, Ph−CH), 6.95 (d, 2H, Ph−CH, J = 4.8 Hz), 4.00 (m, 1H, N−CH), 3.27 (CH_2-Ph, 1H, overlapping with 3.20 - determined indirectly from $^1H-^1H$ COSY), 3.20 (CH_2-PPh_2, 1H, overlapping with 3.27, determined indirectly from $^1H-^1H$ COSY), 3.08 (dd, 1H, CH_2-PPh_2, $^3J_{HH}$ and $^2J_{HH}$ = 7.7 and 14.0 Hz), 2.80 (m, 1H, CH_2-Ph), and 2.00 (s, NC−CH_3/NC-CD_3) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_3CN): δ 54.7 (d, $^2J_{PP}$ = 151 Hz), and 51.7 (d, $^2J_{PP}$ = 151 Hz) ppm (roofing doublets). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 176.1 (d, N=CH, J = 5.4 Hz), 127−137 (Ar-C and P-Ar-C), 118.6 (NCMe), 76.1 (N-CH), 39.3 (CH_2-PPh_2), 27.8 (CH_2-Ph), and 0.5 (NC−CH_3) ppm. Anal. Calcd for $[FeC_{46}H_{44}P_2N_4][BF_4]_2$: C, 58.5; H, 4.7; N, 5.9. Found: C, 56.39; H, 5.0; N, 5.49.** MS (ESI, m/z^+): 606.2 $[FeC_{36}H_{35}P_2N]Li^+$ (loss of three MeCN).

6f: *R^1 = iPr, R^2 = H.* From **4f** (0.099 g, 0.18 mmol), Yield: 152 mg, 94%. ^1H NMR (400 MHz, CD_3CN): δ 8.58 (s, 1H, N=CH), 7.96 (m, 2H, Ph−CH), 7.4−7.8 (m, 18H, Ph−CH), 7.30 (m, 4H, Ph-CH), 3.74 (dm, 1H, N-CH), 3.32 (m, 1H, CH_2-PPh_2), 2.84 (dd, 1H, CH_2-PPh_2, $^3J_{HH}$ and $^2J_{HH}$ = 7.8 and 14.7 Hz), 1.94 (s, NC-CH_3/NC-CD_3), 1.25 (m, 1H, *i*Pr-CH), 0.87 (d, 3H, *i*Pr-CH_3, $^3J_{HH}$ = 6.2 Hz), and 0.00 (d, 3H, *i*Pr-CH_3, $^3J_{HH}$ = 6.5 Hz) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_3CN): δ 53.8 (d, $^2J_{PP}$ = 151.6 Hz), and 57.3 (d, $^2J_{PP}$ = 151.6 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 177.9 (N=CH), 129−138 (Ar-C and P-Ar-C), 121.0 (NCMe), 87.5 (N-CH), 30.0 (*i*Pr-CH), 24.4 (CH_2-PPh_2), 19.2 (*i*Pr-CH_3), 18.1 (*i*Pr-CH_3), and 1.2 (NC-CH_3) ppm. Anal. Calcd for $[FeC_{42}H_{44}P_2N_4][BF_4]_2$: C, 58.9; H, 4.7; N, 5.9. Found: C, 47.08; H, 4.44; N, 4.87.** MS (ESI, m/z^+): 606.2 $[FeC_{36}H_{35}P_2N]Li^+$ (loss of three MeCN).

6g: *R^1 = R^2 = Ph.* From **4g** (0.038 g, 0.058 mmol), Yield: 55 mg, 96%. ^1H NMR (400 MHz, CD_3CN): δ 8.15 (s, 1H, N=CH), 6.95−7.80 (m, 34H, Ph−CH), 5.17 (dd, 1H, N-CH(Ph), $^3J_{HH}$ = 13.0 and 7.3 Hz), 4.88 (dd, 1H, CH(Ph)-PPh_2, $^3J_{HH}$ = 7.7 and 13.0 Hz), and 2.00 (s, 9H, NC−CH_3) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_3CN): δ 69.79 (d, $^2J_{PP}$ = 148.5 Hz), and 53.34 (d, $^2J_{PP}$ = 148.5 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 177.9 (N=CH), 127−137 (Ar-C and P-Ar-C), 117.6 (NCMe), 81.7 (N−CH(Ph)), 46.6 (CH(Ph)-PPh_2), and 0.34 (NC-CH_3) ppm. Anal. Calcd for $[FeC_{51}H_{46}P_2N_4][BF_4]_2$: C, 60.87; H, 4.61; N, 5.57. Found: C, 59.57; H, 4.67; N, 5.07. MS (ESI, m/z^+): 415.2 $[FeC_{51}H_{46}P_2N_4]^{+2}$.

7a: *R^1 = R^2 = H.* From **5a** (0.103 g, 0.20 mmol), Yield: 167 mg, 98%. 1H NMR (400 MHz, CD_3CN): δ 7.90 (m, 2H, Ph-CH), 7.80 (m, 2H, Ph-CH), 7.45−7.75 (m, 17H, Ph-CH), 7.37 (t, 1H, Ph-CH, J = 8.3 Hz), 7.28 (m, 2H, Ph-CH), 3.54 (dd, 1H, Ph-CH_2-NH, $^3J_{HH}$ and $^4J_{HH}$ = 13.0 and 3.8 Hz), 3.44 (t, 1H, CH_2-PPh_2, $^3J_{HH}$ = 14.6 Hz), 3.19 (m, 1H, Ph-CH_2-NH), 3.10 (m, 1H, NH-CH_2-CH_2), 2.49 (m, 1H, CH_2-PPh_2), 2.38 (m, 1H, N*H*), 2.32 (m, 1H, NH-CH_2-CH_2), and 1.99 (s, NC-CH_3/NC-CD_3) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_3CN): δ 58.69 (d, $^2J_{PP}$ = 141.9 Hz), and 43.74 (d, $^2J_{PP}$ = 141.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 127−141 (Ar-C and P-Ar-C), 119.1 (NCMe), 57.3 (Ph-CH_2-NH), 53.8 (HN-CH_2-CH_2), 24.2 (CH_2-PPh_2), and 0.49 (NC-CH_3) ppm. Anal. Calcd for $[FeC_{39}H_{40}P_2N_4]$-$[BF_4]_2$: C, 54.7; H, 4.7; N, 6.5. Found: C, 53.22; H, 4.96; N, 6.27.** MS (ESI, m/z^+): 339.3 $[FeC_{39}H_{40}P_2N_4]^{2+}$, 318.1 (loss of MeCN), 300.1 (loss of two MeCN), and 279.6 (loss of three MeCN).

7c: *R^1 = Me, R^2 = Ph.* From **5c** (0.030 g, 0.050 mmol), Yield: 47 mg, 99%. ^1H NMR (500 MHz, CD_3CN): δ 7.00−7.68 (m, 29H, Ph-CH), 3.99 (dd, 1H, P-C(Ph)*H*, J = 7.7 and 12.2 Hz), 3.82 (dd, 1H, N-CH_2, $^4J_{HH}$ and $^3J_{HH}$ = 5.1 and 13.1 Hz), 3.04 (m, 1H, N-CH_2), 2.88 (m, 1H, N-C(Me)*H*), 1.99 (s, NC−CH_3/NC-CD_3), 1.92 (NH, determined indirectly using $^1H-^1H$-COSY), and 1.17 (d, 3H, CH_3, $^3J_{HH}$ = 5.8 Hz) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN): δ 74.30 (d, $^2J_{PP}$ = 138.4 Hz), and 43.31 (d, $^2J_{PP}$ = 138.4 Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN): δ 126−137 (Ph-C), 122.0 (NCMe), 62.50 (N-C(Me)H), 52.78 (N-CH_2), 50.50 (P-C(Ph)H), 17.11 (−CH_3), and 1.31 (NC-CH_3) ppm. Anal. Calcd for $[FeC_{46}H_{46}P_2N_4][BF_4]_2$ (extra MeCN in solution, verified by NMR): C, 58.39; H, 5.00; N, 7.09. Found: C, 48.80; H, 4.58; N, 7.85.** MS (ESI, m/z^+): 656.2 $[FeC_{40}H_{37}P_2N][Li]^+$ (loss of three MeCN).

7d: *R^1 = Ph, R^2 = H.* From **5d** (0.075 g, 0.13 mmol), Yield: 114 mg, 99%. ^1H NMR (600 MHz, CD_3CN): δ 7.25−7.88 (m, 28H, Ph-CH), 6.76 (s, 1H, Ph-CH), 3.63 (t, 1H, P-CH_2, $^3J_{HH}$ = 13.8 Hz), 3.46 (m, 1H, N-C(Ph)H), 3.15 (m, 1H, N-CH_2), 2.94 (t, 1H, N-CH_2), 2.77 (m, 1H, P-CH_2), 2.00 (NH, determined indirectly using $^1H-^1H$-COSY), and 1.98 (s, NC-CH_3/NC-CD_3) ppm. $^{31}P\{^1H\}$ NMR (242 MHz, CD_3CN): δ 49.07 (d, $^2J_{PP}$ = 139.1 Hz), and 41.22 (d, $^2J_{PP}$ = 139.1 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, CD_3CN): δ 126−133 (Ph-C), 120.4 (NCMe), 67.24 (N-C(Ph)H), 53.84 (N-CH_2), 32.92 (P-CH_2), and 0.68 (NC-CH_3) ppm. Anal. Calcd for $[FeC_{45}H_{44}P_2N_4][BF_4]_2$: C, 57.98; H, 4.76; N, 6.01. Found: C, 54.66; H, 4.92; N, 6.04.** MS (DART, m/z^+): 380.2 $[FeC_{45}H_{44}P_2N_4]^{2+}$.

7e: *R^1 = CH_2Ph, R^2 = H.* From **5e** (0.025 g, 0.042 mmol), Yield: 38 mg, 95%. ^1H NMR (600 MHz, CD_3CN): δ 7.06−7.83 (m, 29H, Ph-CH), 3.90 (m, 1H, N-CH_2), 3.73 (m, 1H, P-CH_2), 3.13 (m, 1H, CH_2-Ph), 3.02 (m, 1H, N-CH_2), 2.71 (m, 1H, N-C(Bn)H), 2.60 (m, 1H, P-CH_2), 2.23 (m, 1H, Ph-CH_2), 1.98 (s, NC-CH_3/NC-CD_3), 1.97 (NH, determined indirectly using $^1H-^1H$-COSY) ppm. $^{31}P\{^1H\}$ NMR (242 MHz, CD_3CN): δ 48.82 (d, $^2J_{PP}$ = 139.9 Hz), and 41.38 (d, $^2J_{PP}$ = 139.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, CD_3CN): δ 126−133 (Ph-C), 123.0 (NCMe), 63.78 (N-C(Bn)H), 52.72 (N-CH_2), 37.87 (P-CH_2), 30.1 (Ph-CH_2), and 1.06 (NC-CH_3) ppm. Anal. Calcd for $[FeC_{46}H_{46}P_2N_4][BF_4]_2$: C, 58.39; H, 4.90; N, 5.92. Found: C, 49.34; H, 4.78; N, 5.56.** MS (ESI, m/z^+): 656.2 $[FeC_{40}H_{37}P_2N][Li]^+$ (loss of three MeCN).

7f: *R^1 = iPr, R^2 = H.* From **5f** (0.063 g, 0.12 mmol), Yield: 88 mg, 83%. ^1H NMR (400 MHz, CD_3CN): δ 7.22−7.86 (m, 24H, Ph-CH), 4.12 (m, 1H, N-CH(*i*Pr)), 3.66 (m, 1H, N-CH_2), 3.44 (m, 1H, P-CH_2), 2.84 (m, 1H, N-CH_2), 2.13 (P-CH_2, determined indirectly from $^{13}C-^1H$ HSQC), 1.99 (s, NC-CH_3/NC-CD_3), 1.43 (br s, 1H, NH), 1.19 (m, 1H, *i*Pr-CH), and 0.77 (br m, 6H, *i*Pr-CH_3) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, CD_3CN): δ 49.55 (d, $^2J_{PP}$ = 139.8 Hz), and 41.25 (d, $^2J_{PP}$ = 139.8 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 128−135 (Ar-C and P-Ar-C), 121.90 (NCMe), 62.01 (N-CH(*i*Pr)) 51.69 (N-CH_2), 23.95 (P-CH_2), 20.64 (*i*Pr-CH), 12.55 (*i*Pr-CH_3), and 0.83 (NC-CH_3) ppm. Anal. Calcd for $[FeC_{42}H_{46}P_2N_4][BF_4]_2$: C, 56.16; H, 5.16; N, 6.23. Found: C, 47.42; H, 4.38; N, 6.23.** MS (ESI, m/z^+): 362.2 $[FeC_{42}H_{46}P_2N_4]^{2+}$and 608.2 $[FeC_{36}H_{37}P_2N]Li^+$.

*Synthesis of Fe(P-N-P′)(CO)Br_2 (**8**).* In a nitrogen-filled glovebox, **4a** (0.05 g, 0.1 mmol) was added to a solution of $FeBr_2$ (0.22 g, 0.1 mmol) in 5 mL of THF and the mixture was stirred at room temperature for 45 min. The solution was then frozen using liquid nitrogen, and the gases were removed under reduced pressure. A carbon monoxide headspace was introduced, and the solution was warmed to room temperature and stirred for an additional 2 h. The solvent was removed under reduced pressure, and the crude product was washed with ether and hexanes. The residue was dissolved in a minimal amount of DCM, and the product was precipitated out with cold pentane. The powder was filtered and washed with cold pentane and then dried under reduced pressure to yield pure Fe-P-N-P′ product. Yield: 63 mg, 85%.

^1H NMR (600 MHz, CD_2Cl_2): δ 8.36 (s, 1H, N=CH), 8.25 (dd, 2H, Ph-CH, J = 7.7 and 10.0 Hz), 8.08 (m, 2H, Ph-CH), 8.03 (m, 2H, Ph-CH), 7.31−7.65 (m, 17H, Ph-CH), 7.26 (t, 1H, Ph-CH, J = 8.1 Hz), 4.00 (m, 1H, N-CH_2), 3.43 (m, 1H, N-CH_2), 3.02 (m, 1H, P-CH_2), and 2.55 (m, 1H, P-CH_2) ppm. $^{31}P\{^1H\}$ NMR (242 MHz, CD_2Cl_2): δ 44.01 (d, $^2J_{PP}$ = 216.9 Hz), 39.55 (d, $^2J_{PP}$ = 216.9 Hz) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, CD_2Cl_2): δ 173.7 (N=CH),126−137 (Ph-C), 71.5 (N-CH_2), and 24.1 (P-CH_2) ppm. Anal. Calcd for $[C_{34}H_{29}NP_2OFeBr_2]$: C, 54.8; H, 3.92; N, 1.88. Found: C, 54.93; H, 4.19; N, 2.74. MS (TOF-ESI, m/z^+): 636.0 $[C_{33}H_{29}NP_2FeBr]^+$ (loss of CO, Br). IR: ν(CO) 1960.6 cm^{-1}.

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Note: synthesis yields a *cis*/*trans* mixture with a ratio of 8% *trans* on the basis of the *cis* Br/CO disorder in the crystal structure. Minor *trans* species also observable by ^{31}P NMR at 64.8 and 57.8 ppm (doublets, J = 184 Hz).

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving detailed synthetic routes and spectroscopic characterization data for all new complexes, as well as crystal structure data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for R.H.M.: Robert.Morris@utoronto.ca.

Notes

The authors declare no competing financial interest.

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