ORGANOMETALLICS

Imine-Centered Reactions in Imino-Phosphine Complexes of Iron Carbonyls

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Supporting Information

ABSTRACT: Fundamental reactions of imino-phosphine ligands were elucidated through studies on $Ph_2PC_6H_4CH=NC_6H_4-4-Cl$ (PCHNAr^{Cl}) complexes of iron(0), iron(I), and iron(II). The reaction of PCHNAr^{Cl} with Fe(bda)(CO)₃ gives Fe(PCHNAr^{Cl})(CO)₃ (1), featuring an η^2 -imine. DNMR studies, its optical properties, and DFT calculations suggest that 1 racemizes on the NMR time scale via an achiral N-bonded imine intermediate. The *N*-imine isomer is more stable in Fe(PCHNAr^{OMe})(CO)₃ (1^{OMe}), which crystallized despite being the minor isomer in solution. Protonation of 1 by HBF₄·Et₂O gave the iminium complex [1H]BF₄. The related diphosphine complex Fe(PCHNAr^{Cl})(PMe₃)(CO)₂ (2), which features an η^2 -imine, was



shown to also undergo N protonation. Oxidation of 1 and 2 with FcBF₄ gave the Fe(I) compounds [1]BF₄ and [2]BF₄. The oxidation-induced change in hapticity of the imine from η^2 in [1]⁰ to κ^1 in [1]⁺ was verified crystallographically. Substitution of a CO ligand in 1 with PCHNAr^{Cl} gave Fe[P₂(NAr^{Cl})₂](CO)₂ (3), which contains the tetradentate diamidodiphosphine ligand. This C–C coupling is reversed by chemical oxidation of 3 with FcOTf. The oxidized product of [Fe(PCHNAr^{Cl})₂(CO)₂]²⁺ ([4]²⁺) was prepared independently by the reaction of [1]⁺, PCHNAr^{Cl}, and Fc⁺. The C–C scission is proposed to proceed concomitantly with the reduction of Fe(II) via an intermediate related to [2]⁺.

INTRODUCTION

Although imines are common ligands in classical coordination chemistry, they also serve as platforms for exciting developments in organometallic chemistry. Applications, manifested or promising, include post-metallocene catalysis of alkene polymerization,¹ a theme that exploits the modular synthesis of imines and convenient introduction of chiral centers by reduction to amines.² Imine ligands also support Fe- and Cobased alkene hydrofunctionalization catalysts.³ Excellent electrocatalysts for hydrogen evolution often are imine complexes.⁴ Thus, although imine complexes have been exhaustively studied in classical coordination chemistry, they remain fertile in an organometallic context. In many cases, the intriguing reactivity is attributable to the redox-noninnocent character of α -diimines.⁵

In view of the successes with diimine ligands, hybrids of imines and phosphines represent attractive ligand platforms that combine the modularity of the imine ligands and the high affinity of soft metal centers for phosphine ligands.⁶ Iron(II) complexes of phosphine-imines have been extensively developed.⁷ Chelating phosphine-imine ligands are usually generated by the condensation of *dia*mines with diphenylphosphino-2-benzaldehyde (PCHO)⁸ or the phosphine-substituted acetaldehydes R₂PCH₂CHO.^{9–11} Ligand platforms include, inter alia,

tetradentate 6-5-6 diiminodiphosphines,^{12,13} tetradentate 5-5-5 diiminodiphosphines,¹⁴ tetradentate and macrocyclic 6-5-6-5 diminodiphosphines,¹⁵ and 5-5 diphosphine-imines,¹⁶ where the hyphenated numbers refer to the size of the resulting chelate rings. Other phosphine-imine complexes of iron have been described.^{17,18}

In contrast to the extensive work on tri- and tetradentate phosphine-imines, relatively little effort has focused on the properties of iron complexes of simple bidentate phosphine-imines. To probe this area, the present report examines the iron derivatives of Fe(0), Fe(I), and Fe(II) oxidation states. These studies uncovered an unrecognized and reversible responsiveness of the phosphine-imine platform: redox-induced N complexation vs π complexation and C–C coupling vs scission of the imine center. As is shown below, even the simple Fe(0) complexes exhibit dynamic behavior involving equilibria between N- and π -bonded imine ligands.

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Studies focused on iron carbonyl derivatives of the phosphineimine derived from PCHO and 4-chloroaniline, abbreviated PCHNAr^{Cl}. The new complexes are depicted in Scheme 1.





Fe(PCHNAr^{Cl})(CO)₃. The complex Fe(PCHNAr^{Cl})(CO)₃ (1) has been observed spectroscopically as an intermediate in recent work.²⁰ Treatment of Fe(bda)(CO)₃ (bda = benzylideneacetone) with 1 equiv of PCHNAr^{Cl} gave 1 in high yield. Crude samples of 1 were always contaminated with a small amount of a phosphine-containing complex (³¹P NMR: δ 25.6) later identified as the C–C bond coupled product Fe-[P₂(NAr^{Cl})₂](CO)₂, (3). Recrystallization afforded analytically pure samples of 1 as yellow crystals.

Crystallographic analysis of 1 revealed a chelated complex with a π -bound imine (Figure 1). The complex features Fe(1)–



Figure 1. Structure (50% thermal ellipsoids) of **1**. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Fe(1)– P(1), 2.2510(5); (Fe–C)_{avg}, 1.887(2); (C–O)_{avg}, 1.1367; Fe(1)– N(1), 1.981(2); Fe(1)–C(4), 2.066(2); C(4)–N(1), 1.380(3); P(1)– Fe(1)–C(1), 171.54(8).

C(4) and Fe(1)–N(1) bond distances of 2.066(2) and 1.981(2) Å, respectively. The imine carbon–nitrogen distance of 1.380(3) Å is longer than that of a typical κ^1 -imine (1.25–1.3 Å),^{10–12} suggesting significant π back-donation from the metal center. Related complexes adopting similar structures, but not crystallographically characterized, include the styryl and formyl derivatives Fe(Ph₂PC₆H₄CH=X)(CO)₃ for X = CH₂,²¹ O.

Although π -bonded aldehyde complexes have been characterized,²² η^2 -imines are more typical for early metals:²³ e.g., metallaaziridines.²⁴ Iron phosphine-imine complexes typically are N-bonded,^{11,12,17,25} although a ferraaziridine has been recently reported.¹² Examples of Fe(0) containing π -bound aldimines have been reported:²⁶ e.g., [Fe(DIP)]₂ (DIP = NC₅H₃-2,6-(CH=NAr)₂, Ar = 2,6-C₆H₃(ⁱPr)₂).²⁷

With bands at 2044, 1983, and 1955 cm⁻¹, the IR bands of 1 in the $\nu_{\rm CO}$ region are similar to those in styryl phosphine complex Fe(CO)₃(Ph₂PC₆H₄CH=CH₂), which is yellow: 2039, 1972, 1945 cm⁻¹. In contrast, derivatives with chelating donors exhibit lower frequency modes: 1985, 1913, and 1897 cm⁻¹ (Fe(dppbz)(CO)₃, which is yellow) and 1968, 1897, and 1862 cm⁻¹ (Fe(phen)(CO)₃, which is blue).²⁸ These comparisons are consistent with an η^2 -imine ligand in 1. ¹H NMR spectra for both yellow d_{12} -cyclohexane solutions and green CD₂Cl₂ solutions of 1 are characteristic of η^2 -imine species as indicated by the resonances at $\delta \sim 5$ for the CHN group. In the -100 °C ¹³C NMR spectrum, three ³¹P-coupled signals are observed for Fe-CO groups. At room temperature, these signals coalesce.

Solutions of 1 exhibit a number of properties that indicate dynamics and/or isomerism. Solutions are solvatochromic, being yellow in alkanes and green in chlorocarbons and aromatic solvents. The UV-vis spectrum of 1 exhibited a maximum at 395 nm in pentane that shifts in CH₂Cl₂ to a shoulder ~380 nm (see Figure S6 in the Supporting Information). Pentane solutions of 1 are also thermochromic, changing from yellow to green upon cooling to -78 °C. IR spectra in the ν_{CO} region were very similar for both yellow and green solutions, consisting of the expected three bands (also see below). ¹H NMR and IR spectra for both yellow d_{12} cyclohexane solutions and green CD₂Cl₂ solutions of 1 are similar. The ¹H NMR signals of 1 shift significantly in the aryl region as a function of temperature (see Figures S3 and S5 in the Supporting Information). The signal assigned to the π -CH=NAr ligand is broad near 0 °C, but sharper at higher and lower temperatures. The signal is only slightly shifted from its low-temperature position. The δ 62.8 signal in the ³¹P NMR spectra of 1 remained invariant between -70 and 20 °C. These observations can be explained by first recognizing that 1 is chiral, as are all complexes containing one η^2 -aldimine ligand. On the NMR time scale, the rate of racemization is slow below room temperature. The deep colors arise from traces of the Nbonded isomer, which is an intermediate in the racemization. This hypothesis was verified by experiments on an analogue of 1 and further examined by DFT calculations.

Studies on Fe(PCHNHAr^{OMe})(CO)₃. The analogue of 1 with 4-methoxyphenyl in place of a chlorophenyl group, i.e. 1^{OMe}, was prepared straightforwardly. As substituents on aryl rings, Cl and OMe differ strongly electronically, as reflected by their Hammett constants $(\sigma_{\rm p})$, which are 0.23 and 0.27, respectively.²⁹ The spectroscopy of 1^{OMe} is consistent with the presence of two isomers. The FT-IR spectrum of the product consisted of two sets of bands in the $\bar{\nu}_{CO}$ region, three in the region expected for the η^2 -imine, and a partially overlapping envelope at $\sim 80 \text{ cm}^{-1}$ lower frequency assigned to the Nbonded isomer (Figure 2). The 31 P NMR spectrum of 1^{OMe} in CD_2Cl_2 solutions consists of a broad singlet at δ 64.2 at room temperature. At -100 °C, the spectrum decoalesced into singlets at δ 70.4 and 65.2 in a 1:4.5 ratio. The corresponding ¹H NMR spectrum also showed two sets of signals also in a 1:4 ratio at -100 °C. Signals at δ 8.27 and 4.10 are assigned to



Figure 2. FT-IR spectra of 1 and 1^{OMe} in CH_2Cl_2 solution. Both isomers contribute to the band at 1980 cm⁻¹. Scrutiny of the spectrum of 1 reveals very weak bands in the region expected for the N-bonded isomer.

CH=N for the N-and π -bonded isomers, respectively, in a 1:4.4 ratio. The ¹H NMR signal expected for an N-bonded aldimine is $\delta \sim 9$.¹⁹ The room-temperature ¹H NMR spectrum features a signal at δ 6.25, corresponding to a time average of the signals for the *N*- and π -bonded isomers.

The ¹³C NMR spectrum of 1^{OMe} at -100 °C not only confirms the presence of two isomers but also provides insights into their stereochemistry (Figure 3). A signal near δ 165 was



Figure 3. Low-field portion of the ¹³C NMR spectrum of 1^{OMe} at -100 °C (left) and at room temperature (right). The low-field singlet in the -100 °C spectrum is assigned to the three rapidly interconverting CO ligands of the N-bonded isomer. The multiplets near δ 210 are assigned to the three diastereotopic CO ligands, each exhibiting ³¹P coupling.

assigned to CH==NAr by the ${}^{1}\text{H}{-}{}^{13}\text{C}$ HSQC method. In the CO region, two sets of signals are observed: three doublets and a singlet. The doublets are assigned to ${}^{31}\text{P}{-}\text{coupled}$ signals for the π -bonded isomer, a quasi-octahedral and hence rigidified species relative to the pentacoordinate N-bonded isomer, which gives rise to a singlet owing to Berry pseudorotation. No ${}^{31}\text{P}{-}^{13}\text{CO}$ coupling is observed for this signal, although typically for Fe(CO)_{5-x}(PR₃)_x complexes $J({}^{31}\text{P}{,}^{13}\text{C})$ is ~20–40 Hz.³⁰ Near room temperature, all four CO signals coalesce. Comparable analysis was applied to the ipso aryl carbon centers (Figure S12 in the Supporting Information).

Qualitative experiments were conducted to test other imine substituents. The complexes $Fe(PCHNBu-t)(CO)_3$ and $Fe(PCHNAr^{NMe2})(CO)_3$ were prepared using the phosphineimines derived from *t*-BuNH₂ and 4-dimethylaminoaniline, respectively. These complexes and the ligands were characterized by ¹H and ³¹P NMR spectroscopy. The IR spectra in the ν_{CO} region showed that the $Fe(CO)_3$ derivatives consist of both *N*- and π -bonded isomers in a ratio comparable to that observed for $\mathbf{1}^{OMe}$.

Crystal Structure of Fe(PCHNAr^{OMe})(CO)₃**.** Despite being the minor species in solution, the N-bonded isomer crystallized

from cold CH_2Cl_2 /pentane solutions. Crystallographic analysis revealed a trigonal-bipyramidal complex with a κ^1 -imine ligand bound to a trigonal-bipyramidal Fe(0) center (Figure 4).



Figure 4. Two views of the structure (50% thermal ellipsoids) of 1^{OMe}. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Fe(1)–P(1), 2.2027(5); (Fe–C)_{avg} 1.770; Fe(1)–N(1), 2.033(1); C(10)–N(1), 1.295(2); (C–O)_{avg} 1.1545; P(1)–Fe(1)–N(1), 83.83; C1–Fe1–C2, 86.31(6); C1–Fe1–C3, 117.09(6); C2–Fe1–C3, 95.42(6).

Metrical aspects of the CO ligands are consistent with 1^{OMe} being Fe(0): $(C-O)_{avg} = 1.154$ Å and $(Fe-C)_{avg} = 1.770$ Å. These distances are longer and shorter by 0.02 and 0.02 Å, respectively, with respect to the same parameters in 1 (1.137, 1.80 Å).

Certain structural features of 1^{OMe} are reminiscent of the complex (PNP^{Bu-t})Fe(CO)₂, where PNP is the bulky pincer ligand C₅H₃N-2,5-(PBu^t₂)₂.³¹ In contrast to the related red complex containing PPr¹₂ substituents, the PBu^t₂ derivative is deep blue and adopts an unusual geometry with N–Fe–C angles of 152.52(5) and 101.57(4)° and an C–Fe–C angle of 105°. In 1^{OMe} , these angles are 134, 108, and 117°, respectively.³² In (PNP^{Bu-t})Fe(CO)₂ the Fe–C–O bond angles are 176.68(10) and 171.87(10)°, comparable to the angles for the CO ligands in the trigonal plane: 175.1(1), 173.6(1), 175.1(1)°. However, the complexes Fe(bipy)(CO)₃ and Fe(phen)(CO)₃ also are deep blue and feature comparably distorted Fe-CO linkages, with angles between 175 and 176°.²⁸

DFT Calculations on Fe(PCHNAr^R)(CO)₃. Using the BP86/TZVP setup, the structures of 1 and 1^{OMe} were examined by DFT. The crystallographically observed π - and N-bonded structures were reproduced with good accuracy. The greatest deviation is with regard to the Fe–P bond in 1 (0.05 Å longer in DFT model vs experiment). With respect to the energetics, the calculations suggest that the N- and π -bonded imine complexes have similar energies but that the N-bonding is favored by 1.8–2.9 kcal/mol for 1^{OMe}. The calculations indicate that that barriers for the N- to π -bonded isomerism range from 8.6 to 14 kcal/mol, depending on the functional. These barriers are compatible with the results of the DNMR studies, which indicate fast exchange between π - and N-bonded structures. For the N-bonded isomers, the calculations do not favor N vs P as the apical ligand on the trigonal-bipyramidal Fe(0) center. The $\nu_{\rm CO}$ bands for these two possibilities differ by less than 3 cm⁻¹. When π -bonded, aldimines can exist as cis and trans isomers, but the calculations indicate that the trans isomer is stabilized by 6.8–8.3 kcal/mol, depending on the functional (Scheme 2).

IR spectra are predicted to differ strongly for the *N*- vs π bonded isomers. For both 1 and 1^{OMe}, DFT-calculated $\nu_{\rm CO}$ bands occur on average at 38 cm⁻¹ higher energy for the η^2 imine isomers in comparison to the *N*-bonded isomers. The values are $(\nu_{\rm CO})_{\rm avg}$ 1993 vs 1955 cm⁻¹ for 1 and 1988 vs 1950 Scheme 2. Gas-Phase DFT-Calculated (BP86/TZVP Level) Energies for Isomers of 1, Including Activation Barriers in Two Cases



cm⁻¹ for 1^{OMe}. Calculated IR bands are in satisfying quantitative agreement with experimental observations for the η^2 -imine in both 1 and 1^{OMe}. For the *N*-bonded isomer of 1^{OMe}, the deviation is greater for low-frequency modes. This last issue is probably due to the necessity of calculating an analytical Hessian (and thus bond force constants) of the systems under investigation in the gas phase: i.e., not including solvation effects.

Substitution Reactions of Fe(PCHNAr^{CI})(CO)₃ by PMe₃. Treatment of 1 with excess PMe₃ gave the dicarbonyl $Fe(PCHNAr^{Cl})(PMe_3)(CO)_2$ (2). No evidence of double substitution was observed. Unlike the case for 1, the bright orange complex 2 does not exhibit solvatochromism or thermochromism, consistent with the nearly exclusive existence of the π -bonded isomer. The ³¹P NMR spectrum of 2 was indicative of a bis(phosphine) complex, which exhibited doublets at δ 64.1 and 21.4. The large coupling constant of $J_{P-P} = 166$ Hz suggests that the phosphines are mutually trans, as is typical.³³ The ¹H NMR spectrum is similar to that of 1, with an additional set of doublet of doublets at δ 1.04 for the PMe₃ resonances. At 20 °C, NC₆H₄Cl resonances at δ 6.89– 6.60 were broad, and a dynamic process analyzed for 1 and 1^{OMe} is assumed to apply to 2. The structure of 2 was confirmed crystallographically. It indeed features mutually trans phosphines (Figure 5). The C=N distance of 1.391(2) Å is elongated by only ~0.01 Å in comparison to that in 1, reflecting increased π back-bonding.

Reaction of Fe(PCHNHAr^{CI})(CO)₃ with PCHNHAr^{CI}. When it was heated in solution in the presence of additional PCHNAr^{CI}, 1 converted to the dark blue diamido complex $Fe[P_2(NAr^{CI})_2]CO)_2$ (3), where $[P_2(NAr^{CI})_2]^{2-}$ is the diamide $[Ph_2PC_6H_4CH(NAr^{CI})]_2^{2-}$ arising from coupling of the imine



Figure 5. Structure (50% thermal ellipsoids) of $Fe(PCHNAr^{Cl})-(PMe_3)(CO)_2$ (2). Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Fe(1)-P(1), 2.2465(5); Fe(1)-C(1), 1.847(1); Fe(1)-C(2), 1.844(1); Fe(1)-C(3), 1.801(1); Fe(1)-N(1), 2.021(1); Fe(1)-C(4), 2.975(1); C(6)-N(1), 1.391(2); P(1)-Fe(1)-C(1), 173.29(5).

carbons. An analogous pinacol-type coupling has been observed for iron(0) complexes of $Ph_2PC_6H_4CHO$.²⁰ The diamido complex 3 was also obtained by heating Fe(bda)(CO)₃ with 2 equiv of PCHNAr^{Cl} in a toluene solution. Logically, the formation of 3 follows the steps in Scheme 3.





The ³¹P NMR chemical shifts for this (and related) ferrous dicarbonyl occurs at relatively high fields, near δ 25 (Table 1). The relative donor properties of the ligands $[P_2O_2]^{2-}$, $[P_2O(NAr^{Cl})]^{2-}$, and $[P_2(NAr^{Cl})_2]^{2-}$ are indicated by the energies of $(\nu_{CO})_{avg}$ in the corresponding ferrous dicarbonyl complexes. These values indicate that the amido substituents are stronger donors than alkoxo ligands.

The structure of 3 was confirmed crystallographically (Figure 6). Reduction of the imine functionality is evident from the long N(1)-C(16) and N(2)-C(15) bonds, with an average distance of 1.457 Å. The complex has idealized C_2 symmetry. The average Fe-N_{amide} distance of 2.039 Å for the 18e species 3 is also long in comparison with the Fe-N_{amide} distance of 1.857 Å observed for the 16e phosphine-amido iron complex FeH(PNP)CO (PNP = N(CH₂CH₂PⁱPr₂)₂).³⁴ At 1.779(3) and 1.774(3) Å, the Fe-CO distances are shorter than in 1 and even 2, consistent with strong π back-bonding, enhanced by the presence of the two strongly π donating amido ligands. The length of the unique C(15)-C(16) bond, 1.530(4) Å, is not elongated for a C-C single bond.

Protonation of Fe(PCHNAr^{Cl})(CO)₃. The protonation of 1 was investigated to evaluate the relative basicity of the Fe(0)³⁵ vs the imine centers. Treatment of 1 with H(Et₂O)₂BAr^F₄ (Ar^F = 3,5-(CF₃)₂C₆H₃) gave the corresponding η^2 -iminium complex [Fe(PCHNHAr^{Cl})(CO)₃]BAr^F₄ ([1H]BAr^F₄). Protonation at nitrogen was indicated by ¹H-¹³C HSQC method (Figure S20 in the Supporting Information). Specifically, ¹H NMR signals for the CH=NHAr^{Cl} group manifested at δ 5.56 and 4.70 (1:1 intensity), but only the δ 5.56 signal correlated to the ¹³C signal at δ 63.4, which is thus assigned to CH. Having Table 1. Spectroscopic Properties for New Complexes andSelected Reference Compounds

compound	$ \nu_{\rm CO} \ ({\rm CH}_2{\rm Cl}_2), \ {\rm cm}^{-1} $	$\delta(^{31}P)$ (CD ₂ Cl ₂), ppm	$\delta(^{1}H)$ NCF (CD ₂ Cl ₂), ppm
PCHNAr ^{Cl 20}		-12.4	9.01
$Fe(\kappa^{1}-PCHNAr^{Cl})(CO)_{4}^{20}$	2053, 1981, 1948	68.5	8.51
Fe(PCHNAr ^{Cl})(CO) ₃ (1), π isomer	2044, 1983, 1955 (DFT: 2035, 1981, 1963)	62.9	5.16
Fe(PCHNAr ^{OMe})(CO) ₃ ($\mathbf{1^{OMe}}$), π isomer	2039, 1980, 1949 (DFT: 2030, 1977, 1958)	65.1 ^a	5.0 ^{<i>a</i>}
$\begin{array}{c} Fe(PCHNAr^{OMe})(CO)_{3} \\ (1^{OMe}), N \text{ isomer} \end{array}$	1980, 1902, 1870 (DFT: 1995, 1937, 1919)	70.4 ^{<i>a</i>}	8.27 ^a
$\begin{array}{c} Fe(PCHNAr^{Cl})(PMe_3)\\ (CO)_2 (2) \end{array}$	1965, 1900 ^b	64.1, 21.4	4.27
$\begin{bmatrix} Fe(PCHNHAr^{Cl})(CO)_3 \end{bmatrix} \\ BAr^{F_4}([1H]BAr^{F_4}) \end{bmatrix}$	2089, 2039, 2017	64.8	4.70
$ \begin{array}{c} [Fe(PCHNHAr^{Cl})(PMe_3) \\ (CO)_2]BAr^F_4 \ ([2H] \\ BAr^F_4) \end{array} $	2015, 1956	72.3, 16.9	4.39
$\begin{bmatrix} Fe(PCHNAr^{Cl})(CO)_3 \\ BF_4 ([1]BF_4) \end{bmatrix}$	2080, 2022, 1991		
$ \begin{array}{l} [Fe(PCHNAr^{Cl})(PMe_3) \\ (CO)_2]BF_4 \ ([2]BF_4) \end{array} $	1990, 1920		
$Fe[P_2(NAr^{Cl})_2](CO)_2$ (3)	2010, 1954	25.9	4.37
$Fe(P_2O_2)(CO)_2^{20}$	2025, 1965	21.5	4.49 (OCH)
$Fe[P_2O(NAr^{Cl})](CO)_2^{20}$	2022, 1959	25.9, 21.4	4.14, 4.69 (OCH)
	2059, 2023	40.5	8.26

^aRecorded at -100 °C in CD_2Cl_2 solution. ^bRecorded on THF solution.



Figure 6. Structure (50% thermal ellipsoids) of 3. Selected hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Fe(1)-P(1), 2.2691(8); Fe(1)-P(2), 2.2680(8); Fe(1)-C(1), 1.779(3); Fe(1)-C(2), 1.774(3); Fe(1)-N(1), 2.033(2); Fe(1)-N(2), 2.044(2); N(1)-C(16), 1.456(3); N(2)-C(15), 1.458(3); C(15)-C(16), 1.530 (4); P(1)-Fe(1)-P(2), 168.72(4).

no ¹³C correlation, the δ 4.7 signal is assigned to NH. Although both *cis*- and *trans*-iminium ligands are possible, only one ¹H NMR signal was observed for CH in the BAr^F₄⁻ salt. Nprotonation induced a ~50 cm⁻¹ increase in $\nu_{\rm CO}$ vs that in 1. The iminium cation $[H1]^+$ was unreactive toward excess $H(OEt_2)_2BAr^F_4$.

Although [1H]BAr^F₄ could not be obtained as X-ray-quality crystals, single crystals of [1H]BF₄·THF were obtained by pentane vapor diffusion into a THF/CH₂Cl₂ solution. The crystallographic results were consistent with the structure deduced by NMR spectroscopy for the related BAr^F₄⁻ salt (Figure 7). The η^2 -iminium ligand exhibited trans geometry,



Figure 7. Structure (50% thermal ellipsoids) of $[1H]BF_4$. THF. Selected hydrogen atoms, solvent, and anion have been omitted for clarity. Selected distances (Å) and angles (deg): Fe(1)-P(1), 2.2705(8); Fe(1)-C(1), 1.834(3); Fe(1)-C(2), 1.819(3); Fe(1)-C(3), 1.786(3); Fe(1)-N(1), 2.020(3); Fe(1)-C(4), 2.013(3); C(4)-N(1), 1.427(4); N(1)-H(1), 0.89(5); P(1)-Fe(1)-C(1), 176.8(1).

and the C(4)–N(1) distance (1.427(4) Å) is elongated by 0.04 Å in comparison to that in **1**. A similarly elongated C–N distance, 1.434(5) Å, has been observed for an iron carbonyl complex of a chelating iminium ligand.¹²

In contrast to the case for $[1H]BAr^{F_{4}}$, $[1H]BF_{4}$ exists as isomers in $CD_{2}Cl_{2}$, as indicated by two sets of resonances in the ¹H and ³¹P NMR spectra. The second species is proposed to be the cis isomer of $[1H]^{+}$. The equilibrium ratio *trans*- $[1H]BF_{4}$:*cis*- $[1H]BF_{4}$ is 93:7 (eq 1 and Figures S23–S25 in



the Supporting Information). The isomerization is fast at room temperature but not faster than the NMR time scale: NMR spectra recorded within minutes after dissolution of single crystals of [1H]BF₄ in CD₂Cl₂ always showed a mixture of isomers. The FT-IR spectrum of [1H]BF₄ showed two sets of partially resolved $\nu_{\rm CO}$ signals (see Figure S31 in the Supporting Information).

Qualitative experiments monitored by IR and ³¹P{¹H} NMR spectroscopy showed that **2** also N-protonates to give [2H]⁺. With BAr^F₄⁻ as the anion, only one isomer was observed in the IR spectrum (ν_{CO} 2016, 1956 cm⁻¹). Its ³¹P NMR spectrum was characterized by two doublets (δ 72.1, 16.7). For the BF₄⁻ salt, two isomers (ν_{CO} = 2014, 1952 cm⁻¹ and 2004, 1941 cm⁻¹) were observed.

Redox Properties of Fe(PCHNAr^{CI})(CO)₃. The addition of $FcBF_4$ ($Fc = [Fe(C_5H_5)_2]^+$) to CH_2Cl_2 solutions of 1 gave the green salt [1]BF₄. This solution was unstable at room temperature, as indicated by decomposition to unidentified carbonyl species after a few minutes. Dark green single crystals of [1]BF₄ were obtained when the synthesis was conducted at -35 °C. X-ray crystallographic analysis revealed that oxidation induced a change in the hapticity of the imine, which is *N*-bound in the cation (Figure 8). In comparison to 1^{OMe} , the Fe-



Figure 8. Structure (50% thermal ellipsoids) of $[Fe(PCHNAr^{Cl})-(CO)_3]BF_4$ ([1]BF₄). Hydrogen atoms, solvent, and anion have been omitted for clarity. Selected distances (Å) and angles (deg): Fe(1)-P(1), 2.2465(5); Fe(1)-C(1), 1.847(1); Fe(1)-C(2), 1.844(1); Fe(1)-C(3), 1.801(1); Fe(1)-N(1), 2.021(1); Fe(1)-C(4), 2.975(1); C(4)-N(1), 1.289(2); P(1)-Fe(1)-C(1), 173.29(5).

N distance of 2.021(1) Å is slightly contracted by 0.01 Å, and the Fe–CO distances are elongated by 0.05 Å.^{26,36} Both changes are consistent with a more Lewis acidic Fe center. In contrast to the trigonal-bipyramidal structure exhibited by 1^{OMe} , the $[1]^+$ adopts a distorted-square-pyramidal structure, with the CO ligand occupying the apical position.

Oxidation of 1 induces a shift in $\nu_{\rm CO}$ of ~40 cm⁻¹ to 2044, 1983, 1955 cm⁻¹ vs 2080, 2022, 1991 cm⁻¹. For comparison, a $\Delta\nu_{\rm CO}$ value of ~124 cm⁻¹ is observed for the [Fe-(CO)₃(PR₃)₂]^{+/0} pair (R = Ph, Cy).^{37,38} The observation of a single band for [Fe(CO)₃(PR₃)₂]⁺ has been explained in two distinct ways: retention of the D_{3h} structure of its Fe(0) precursor³⁷ or a distorted-square-pyramidal species that is fluxional on the IR time scale.³⁹ The smaller value of $\Delta\nu_{\rm CO}$ for the [1]^{+/0} couple is attributed to a compensating structural change that accompanies the oxidation: 1 features an η^2 -imine π acceptor, whereas [1]⁺ features a κ^1 -imine σ donor.

For CH₂Cl₂ solutions of 1, $\nu_{C=N}$ was observed at 1584 cm⁻¹; for CH₂Cl₂ solutions of [1]BF₄, $\nu_{C=N}$ was observed at 1599 cm⁻¹. The 15 cm⁻¹ shift to higher energy for $\nu_{C=N}$ upon oxidation of 1 supports the change from the π -accepting η^2 -imine to the σ -donating κ^1 -imine.

The X-band EPR spectrum of $[1]BF_4$ in fluid solution exhibited a doublet pattern centered at g = 2.047, which arises from coupling to the ³¹P center (Figure 9). The hyperfine coupling constant $A(^{31}P)$ is 53.0 MHz. For comparison, the isotropic EPR spectrum of $[Fe(CO)_3(PPh_3)_2]^+$ exhibits a doublet centered at g = 2.053 with $A(^{31}P) = 18.7$ MHz,^{37–39} the smaller hyperfine coupling reflecting the delocalization over two phosphorus centers.

The cyclic voltammogram of a CH₂Cl₂ solution of 1 showed a reversible event at $E_{1/2} = -0.41$ V with $i_{pa}/i_{pc} = 0.915$. This



Figure 9. X-band EPR spectrum of $[1]BF_4$ in CH_2Cl_2 /toluene at 0 °C.

process is assigned to the $[1]^{0/+}$ couple. This redox couple is stable in the electrochemical environment at this scan rate, and repeated cycling of the reversible couple up to three cycles did not give observable changes. When the switching potential was extended to 1 V, a second more complicated event was detected at ~0.6 V (Figure 10). The second oxidation is attributed to the $[1]^{+/2+}$ couple, but the doubly oxidized species is unstable.



Figure 10. Cyclic voltammogram of 1 in CH_2Cl_2 solution at a scan rate of 0.02 V s⁻¹. Conditions: 0.001 M 1 with 0.01 M $[Bu_4N]PF_6$; glassy-carbon working electrode. Potentials are referenced to $Fc^{+/0}$.

The oxidation of **2** by FcBF₄ was also examined briefly. A change in the hapticity of the imine is supported by the relatively small shift of the CO frequencies from **2** to $[\mathbf{2}]^+$ ($\Delta\nu$ (_{CO})_{avg} of 22.5 cm⁻¹). In the FT-IR spectrum, the ν _{C=N} band shifted from 1583 cm⁻¹ for **2** to a broad signal at 1600 cm⁻¹ for $[\mathbf{2}]$ BF₄.

Oxidation of Fe[P₂(NAr^{Cl})₂](CO)₂. The diamido complex 3 is a 2e⁻ reductant. Upon treatment with 2 equiv of FcBAr^F₄, 3 converted to the yellow [4](BAr^F₄)₂. The FT-IR spectrum of this salt exhibited ν_{CO} bands at 2065 and 2030 cm⁻¹, corresponding to a shift of 65 cm⁻¹ vs the neutral precursor 3. ESI-MS revealed strong signals at m/z 455.05 and 427.3, corresponding respectively to [Fe(PCHNAr^{Cl})₂(CO)₂]²⁺ and [Fe(PCHNAr^{Cl})₂]²⁺ (loss of 2 × CO corresponds to m/z 56/2). The ³¹P NMR spectrum showed a singlet at δ 40.5. Oxidation of 3 to [4]²⁺ can also be accomplished using FcBF₄ and FcOTf (OTf⁻ = CF₃SO₃⁻), although [4](BF₄)₂ was unstable in solution, even at -35 °C. The decomposition is proposed to be related to the reaction of the dialkoxo analogue of 3, Fe(P₂O₂)(CO)₂, with FcBF₄ to give the BF₃ adduct Fe[P₂(OBF₃)₂](CO)₂²⁰

Cyclic voltammetry results are consistent with the Fc⁺induced fragmentation of the $[P_2(NAr^{Cl})_2]^{2-}$ ligand in 3. Specifically, the cyclic voltammogram of a CH₂Cl₂ solution of 3 exhibits an irreversible oxidation event at -0.20 V when scan rates were varied between 0.02 and 1 V s⁻¹. This process is assigned to the $3/[4]^{2+}$ couple. Following the irreversible oxidation, the product exhibits reductions at -0.43, -0.84, and -1.37 V. These reductive events only appeared after scanning through the oxidation at -0.20 V.

The ¹H NMR spectrum of $[4]^{2+}$ exhibits an anomalous signal at δ 4.83 integrating for 4H. Through a combination of 2D NMR techniques (¹H-¹³C HMQC and ¹H,¹H-COSY, Figures S32 and S33 in the Supporting Information), the signal at δ 4.83 was determined to arise from the C_6H_4 Cl centers. The imine proton (CH=NAr) was assigned to a signal at δ 8.3. The crystal structure of $[4]^{2+}$ indeed reveals close contacts between 2,6-protons on each C_6H_4 -4-Cl with two arene rings (Figure S35 in the Supporting Information). Ring current effects have been observed in other phosphine complexes.⁴⁰

X-ray crystallographic analysis of $[4](OTf)_2$ confirmed the proposed structure (Figure 11). Complex $[4]^{2+}$ is a rare



Figure 11. Two views of the dication in $[4](OTf)_2$ with hydrogen atoms omitted for clarity (50% thermal ellipsoids). Selected distances (Å) and angles (deg): Fe(1)-P(1), 2.321(2); Fe(1)-P(2), 2.321(2), Fe(1)-N(1), 2.092(3); Fe(1)-N(2), 2.061(4); Fe(1)-C(26), 1.797(5); Fe(1)-C(27), 1.787(4); N(1)-C(7), 1.295(5); N(2)-C(34), 1.298(7); P(1)-Fe(1)-P(2), 176.77(6).

example of a dicationic iron(II) dicarbonyl complex.⁴¹ The C_2 symmetry was retained. The C–N distances of 1.297 Å are significantly shortened in comparison to its diamido precursor 3. The imine carbon centers C(7) and C(34) are well separated at 3.269(5) Å.

To illuminate the mechanism of the oxidation of **3**, we examined its partial oxidation. Upon treatment with 1 equiv of FcBAr^F₄, **3** (ν_{CO} 2010, 1954 cm⁻¹) was completely consumed. IR analysis revealed a mixture characterized by ν_{CO} bands at 2039, 1988, and 1913 cm⁻¹. A similar mixture can be obtained by addition of 1 equiv of PCHNAr^{Cl} to [1]BAr^F₄. For this mixture the band at 1913 cm⁻¹ is more intense than the 2039 and 1988 cm⁻¹ bands. These partially oxidized solutions react with another 1 equiv of FcBAr^F₄ to give [4](BAr^F₄)₂ (see Figures S43 and S44 in the Supporting Information). It is telling that 1e oxidation shifts two ν_{CO} bands to the region exhibited by [Fe(PCHNAr^{Cl})(PMe₃)(CO)₂]⁺ (1990, 1920 cm⁻¹). These results underpin a tentative mechanism involving oxidative-induced reduction of the Fe(II) concomitant with C–C scission (Scheme 4).

Scheme 4. Proposed Pathway for Oxidative C–C Cleavage in the Conversion of 3 to $[4]^{2+}$



CONCLUSIONS

Iron complexes derived from Ph₂PC₆H₄CH=NAr ligands exhibit rich imine-centered reactivity: σ - π isomerism, Nprotonation, and reductive coupling. One of the simplest transformations possible for an imine ligand is demonstrated the isomerization of N-bonded to π -bonded imines. The system Fe(Ph₂PC₆H₄CH=NAr)(CO)₃ exists as an equilibrium mixture of both σ - and π -bonded isomers, and the minor isomer fortuitously crystallizes. This dynamic process illustrates the pathway for racemization of π -bonded imines (Scheme 5).

Scheme 5. Racemization Pathway for the π -Imine Isomer of Fe(PCHNR)(CO)₃ via the Intermediacy of the N-Bonded Isomer



Although the system $Fe(Ph_2PC_6H_4CH=NAr)(CO)_3$ is exquisitely amenable to analysis, related dynamics have been implicated previously. In $W(acac)_2(\eta^2\text{-imine})(CO)$, the imine rapidly diastereomerizes, although the implicated N-bonded intermediate was not detected.⁴² The unsymmetrical bis-(ketimine) Ni(0)-NHC complex Ni($\kappa^1\text{-HNCPh}_2$)(η^2 -HNCPh₂)(IPr) has been examined crystallographically.⁴³ Aldehyde complexes, e.g. [Cp*Re(PPh_3)(NO)(ArCHO)]⁺, participate in very rapid $\kappa^1 \cdot \eta^2$ equilibria.⁴⁴

As verified crystallographically, the $[1]^{0/+}$ couple is an example of a redox-induced hapticity change at an imine ligand. This transformation is proposed to proceed via the sequence π - $[1]^0 \rightarrow N$ - $[1]^0 \rightarrow N$ - $[1]^+$, i.e. the more electron-rich N-bonded Fe(0) complex is oxidized. A related N- vs η^2 -linkage isomerism has been observed for the $[\text{Ru}(\text{NH}_3)_5(\text{Me}_2\text{CO})]^{2+/3+}$ couple.⁴⁵

The new results provide insights into the proposed pathway for the coupling reactions that give rise to $(P_2O_2)^{2-,20,46}$ $(P_2ONAr^{Cl})^{2-,20}$ and $[P_2(NAr^{Cl})_2]^{2-}$ ligands from the respective phosphine-aldehydes and phosphine-imines. The intermediacy of Fe(κ^1, η^2 -PCHNAr^{Cl})(κ^1 -PCHNAr^{Cl})(CO)₂ is strongly implicated. This hypothesis is supported by the characterization of the analogous PMe₃ complex **2**. The C–C coupling is proposed to proceed via attack of uncoordinated imine electrophile with a η^2 -imine nucleophile (Scheme 3). Imine coupling reactions have been observed for earlytransition-metal complexes containing η^2 -imine ligands^{47,48} as well as uranium(IV) complexes.⁴⁹ Reversible bond formation/breakage of the imine carbon bonds is a rare case of mild oxidative cleavage of C–C bonds. The first step in the oxidative scission of the diamide is proposed to be oxidation at iron. The resulting d⁵ center would have a hole delocalized over Fe and the two amide nitrogen centers. In the d⁵ amido complexes [Ru(NH₃)₅(NHCH₂R)]²⁺, α -CH centers are susceptible to deprotonation.⁵⁰ In contrast, Fe[P₂(NAr^{CI})₂](CO)₂ lacks α –C-H groups and thus is susceptible to oxidatively induced C–C heterolysis. The C– C scission leads to formal reduction of Fe(III) to Fe(I).

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise indicated, reactions were conducted using standard Schlenk techniques under an N2 atmosphere at room temperature with stirring. Solvents were highperformance liquid chromatography grade and were dried and deoxygenated on a Glass Contour System or MBraun solvent purification system and stored over 4 Å molecular sieves. The compounds Fe(bda)(CO)₃,⁵¹ FcBF₄,⁵² FcOTf,⁵³ HBAr^F₄·2Et₂O,⁵⁴ PCHNAr^{OMe 19} and PCHNAr^{Cl 55} were synthesized according to literature procedures. HBF4·Et2O was used as received from Sigma-Aldrich. PMe3 was used as received from Strem. ¹H and ³¹P{¹H} NMR spectra were acquired on Varian Unity Inova 500NB and Unity 500 NB instruments at 20 °C unless otherwise noted. ¹H NMR spectra were referenced to residual solvent relative to tetramethylsilane, and ³¹P{¹H} NMR spectra were referenced to an external 85% H₃PO₄ standard. Crystallographic data were collected using either a Siemens SMART diffractometer equipped with a Mo K α source ($\lambda = 0.71073$ Å) and an Apex II detector or a Bruker D8 Venture diffractometer equipped with a Mo K α microfocus source and a Photon 100 detector. EPR spectra were recorded on 1-5 mM solutions in toluene/CH₂Cl₂ (1/1) at 10 °C. The instrument was a Varian E-line E-12 Century Series X-band continuous-wave spectrometer. FT-IR spectra were recorded on a PerkinElmer 100 spectrometer. Cyclic voltammetry experiments were conducted using a 10 mL one-compartment glass cell with a tight-fitting Teflon top inside a N₂-filled glovebox. The working electrode was a glassy-carbon disk (diameter 3.00 mm). The counter electrode was a Pt wire, and a Ag wire was used as a quasireference electrode. Each cyclic voltammogram was referenced to the $Fc^{0/+}$ couple by adding ferrocene to the sample and collecting 1 scan. The School of Chemical Sciences Microanalysis Laboratory utilizing a model CE 440 CHN analyzer performed elemental analyses.

Fe(PCHNAr^{CI})(CO)₃ (1). This compound was synthesized using a procedure modified from a previous report.²⁰ A THF solution (15 mL) of Fe(bda)(CO)₃ (212 mg, 0.74 mmol) was treated with PCHNAr^{Cl} (297 mg, 0.74 mmol). This orange mixture was stirred in a 55 °C oil bath for 16 h to give a dark green solution. After the solution was cooled, solvents were removed under reduced pressure to yield a dark green powder. The crude material was dissolved in a minimal amount of CH_2Cl_2 (ca. 3 mL). The solution was layered with pentane (15 mL) and then maintained at -35 °C. After 48 h, yellow crystals appeared of the target compound. Yield: 272 mg (68%). Single crystals suitable for X-ray diffraction were obtained by storing a pentane solution of 1 at -35 °C for 24 h. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.94 (br, 2H), 7.73–7.67 (m, 1H), 7.55–7.34 (m, 10H), 7.31–7.21 (m, 1H), 7.13–7.04 (m, 2H), 7.02–6.87 (m, 2H), 5.12 (br, 1H). ¹H NMR (500 MHz, C₆D₁₂): δ 7.94 (br, 2H), 7.57 (m, 1H), 7.44-7.15 (m, 11H), 7.08-7.01 (m, 1H), 6.98-6.88 (m, 2H), 6.85-6.80 (m, 2H), 5.16 (br, 1H). ³¹P NMR (202 MHz, CD₂Cl₂): δ 62.9 (s). IR spectrum (CH₂Cl₂): ν_{CO} 2044, 1983, 1955 cm⁻¹. Anal. Calcd for C28H19NClFeO3P (found): C, 62.31 (61.91); H, 3.55 (3.43); N, 2.60 (2.90)

Fe(PCHNAr^{OMe})(CO)₃ (1^{OMe}). This compound was synthesized analogously to 1. A THF solution of $Fe(bda)(CO)_3$ (100 mg, 0.35 mmol) was treated with a THF solution of PCHNAr^{OMe} (138 mg, 0.35 mmol). The resulting dark green solution was stirred at room temperature for 16 h, followed by cooling and removal of the THF solvent under vacuum. The solid residue was washed with dry pentane

(3 × 20 mL) and dried under vacuum. Yield: 171 mg, 0.32 mmol (91%). Crystals of 1^{OMe} were grown by slow diffusion of pentane into CH₂Cl₂ solutions. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.95–7.19 (br, overlapping signals, 14H), 6.98 (br, 2H), 6.75 (br, 2H), 6.14 (br, 1H), 3.75 (s, 3H). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, -100 °C, π -bonded isomer): δ 212 (d, *J* = 62 Hz, CO), 211 (d, *J* = 59 Hz, CO), 208.40 (d, *J* = 49 Hz, CO), 157 (s), 153.40 (s), 153 (s), 133 (s), 131.14 (s), 131 (s), 131 (s), 130 (s), 130 (s), 129.76 (s), 128.31 (s), 126.64 (s), 125.88 (s), 125.49 (s), 119 (s), 114 (s), 111 (s), 73.8 (s, CH=NAr), 54.9(s, OMe). ³¹P NMR (202 MHz, CD₂Cl₂): δ 64.2 (s). IR spectrum (CH₂Cl₂): ν_{CO} 2039, 1980, 1949, 1902, 1870 cm⁻¹. Anal. Calcd for C₂₈H₁₉NCIFeO₃P (found): C, 65.07 (64.81); H, 4.14 (4.09); N, 2.62 (2.76).

Fe(PCHNBu-t)(CO)₃. The ligand, PCHNBu-*t*, was prepared by the reaction of *t*-BuNH₂ with 2-(diphenylphosphino)benzaldehyde. A 50 mL glass bomb was charged with toluene (20 mL), PCHO (600 mg, 2.07 mmol, 1 equiv), *t*-BuNH₂ (2.2 mL, 1.51 g, 20.7 mmol, 10 equiv), and approximately 500 mg of 4 Å molecular sieves. The bomb was sealed and heated at 110 °C. After 18 h the reaction mixture was cooled to room temperature, and the bomb opened. The molecular sieves were removed, and the solvent was removed by rotary evaporation. A pinkish solid was obtained and used without further purification. Yield: 523 mg (73%). ¹H NMR (500 MHz, CD₂Cl₂): δ 8.77 (d, *J* = 5 Hz, 1H), 7.93 (m, 1H), 7.59–7.17 (m, 12H), 6.82 (m, 1H), 1.05 (s, 9H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ –11.6 (s).

Inside a nitrogen-filled glovebox, a THF solution of Fe(bda)(CO)₃ (428 mg, 1.50 mmol, 1 equiv) was treated with a THF solution of PCHNBu-*t* (517 mg, 1.50 mmol, 1 equiv). The reaction mixture was stirred at room temperature for 18 h, during which time the solution changed color from orange to dark blue. The solvent was removed under vacuum, and the residual solid was washed with pentane (3×20 mL) and then dried under vacuum. Yield: 395 mg, 0.81 mmol (54%). IR spectrum (CH₂Cl₂): ν_{CO} 2023, 1971, 1936, 1887, 1858 cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.74–7.25 (overlapping signals, 11H), 7.29 (m, 2H), 7.08 (m, 1H), 1.04 (s, 9H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ 64.4 (s). Fe(PCHNAr^{NMe2})(CO)₃. The ligand, PCHNAr^{NMe2}, was prepared

Fe(PCHNAr^{NMe2})(CO)₃. The ligand, PCHNAr^{NMe2}, was prepared by the reaction of 4-Me₂NC₆H₄NH₂ with 2-(diphenylphosphino)benzaldehyde. A 50 mL glass bomb was charged with toluene (20 mL), 2-(diphenylphosphino)benzaldehyde (600 mg, 2.07 mmol, 1 equiv), Me₂NC₆H₄NH₂ (281 mg, 20.7 mmol, 1 equiv), and approximately 500 mg of 4 Å molecular sieves. The bomb was sealed from the surrounding atmosphere and heated to 110 °C for 18 h. The reaction mixture was then cooled to room temperature and the bomb opened to ambient atmosphere. The molecular sieves were removed by filtration, and the solvent was removed by rotary evaporation. A brown solid was obtained and used without further purification. Yield: 774 mg, 1.90 mmol (92%). ¹H NMR (500 MHz, CDCl₃): δ 9.09 (d, *J* = 6 Hz, 1H), 8.17 (m, 1H), 7.63–7.15 (m, 11H), 6.98 (d, *J* = 9 Hz, 1H), 6.87 (m, 1H), 6.62 (d, *J* = 9 Hz, 2H), 2.90 (s, 6H). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ –12.9 (s).

Inside a nitrogen-filled glovebox, a THF solution of Fe(bda)(CO)₃ (428 mg, 1.50 mmol, 1 equiv) was treated with a THF solution of PCHNBu-*t* (517 mg, 1.50 mmol, 1 equiv). The reaction mixture was stirred at room temperature for 18 h, during which time the solution changed colors from orange to dark blue. The solvent was removed under vacuum, and the residual solid was washed with pentane (3 × 20 mL) and then dried under vacuum. Yield: 916 mg, 1.67 mmol, (90%). IR spectrum (CH₂Cl₂): ν_{CO} 2037, 1980, 1945, 1990, 1887, 1868 cm⁻¹. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.74–7.25 (overlapping signals, 14H), 6.99 (d, *J* = 8 Hz, 2H), 6.60 (d, *J* = 8 Hz, 2H), 2.92 (s, 6H). ³¹P{¹H</sup> NMR (202 MHz, CD₂Cl₂): δ 64.0 (s).

Fe(PCHNAr^{CI})(PMe₃)(CO)₂ (2). A THF solution (5 mL) of 1 (21.2 mg, 0.039 mmol) was treated with PMe₃ (0.2 mL, 1.9 mmol). This mixture was stirred at room temperature for 16 h to give an orange solution. Solvents were then removed under reduced pressure, and the solids were washed with pentane to give the target compound as orange microcrystals. Longer reaction times were required when less PMe₃ was used. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH₂Cl₂ solution. ¹H

NMR (500 MHz, CD_2Cl_2): δ 7.95–7.86 (m, 2H), 7.64–7.58 (m, 1H), 7.44–7.27 (m, 11H), 7.13–7.07 (m, 1H), 6.88 (d, J = 8.4 Hz, 1H), 6.83–6.54 (br, 2H), 4.27 (dd, J = 5.6, 1.9 Hz, 1H), 1.07 (dd, J = 9.3, 1.6 Hz, 9H). ³¹P{¹H} NMR (202 MHz, CD_2Cl_2): δ 64.10 (d, J = 165 Hz), 21.4 (d, J = 165 Hz). IR spectrum (THF): ν_{CO} 1965, 1900 cm⁻¹. Anal. Calcd for $C_{30}H_{28}$ NCIFeO₂P₂ (found): C, 61.3 (61.31); H, 4.8 (4.64); N, 2.38 (2.65).

 $[Fe(PCHNHAr^{Cl})(CO)_3]X ([1H]X; X^- = BF_4^-, BAr^F_4^-).$ To an Et₂O solution (30 mL) of 1 (75 mg, 0.139 mmol) was added 5 drops of HBF₄·Et₂O. A bright yellow solid precipitated immediately. After it was stirred for 1 h, the slurry was concentrated to ca. 5 mL. Pentane (10 mL) was added, and the mixture was filtered to give the target compound as a pale yellow powder. Yield: 75 mg (86%). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a THF/CH2Cl2 solution of this salt. ¹H NMR (500 MHz, CD₂Cl₂), trans-[1H]BF₄: δ 8.20 (dd, J = 7.5, 3.1 Hz, 1H), 7.89-7.76 (m, 3H), 7.75-7.59 (m, 6H), 7.52 (td, J = 7.9, 3.1 Hz, 2H), 7.45 (q, J = 8.8 Hz, 4H), 7.33 (dd, J = 12.8, 7.9 Hz, 2H), 5.86 (br, 1H), 5.76 (br, 1H). ¹H NMR (500 MHz, CD_2Cl_2), cis-[1H]BF₄: δ 8.30 (dd, J = 8.0, 3.4 Hz, 1H), 7.87–7.09 (m), 6.58–6.46 (m, 4H). Resonances at δ 7.87-7.09 were not integrated due to overlapping trans-[1H]BF4 resonances. The iminium resonances were not observed due to overlapping resonances from trans-[1H]BF4. 31P{1H} NMR (202 MHz, CD_2Cl_2): δ 65.7 (trans), 56.5 (cis). IR (CH_2Cl_2), trans-[1H]BF₄ and cis-[1H]BF₄: 2087, 2084, 2036, 2032, 2010 cm⁻¹. Anal. Calcd for C28H20BClF4FeNO3P.0.5CH2Cl2 (found): C, 51.09 (51.08); H, 3.16 (3.16); N, 2.09 (2.36). The salt [H2]BAr^F₄ was prepared similarly: combining a CH₂Cl₂ (3 mL) solution of 2 (4.4 mg, 0.0094 mmol) with a CH₂Cl₂ (2 mL) solution of HBAr^F₄·2Et₂O (9 mg, 0.088 mmol) converted the green solution immediately to bright orange-yellow. Solvent was then removed under reduced pressure to yield a bright yellow solid. ¹H NMR (500 MHz, CD_2Cl_2): δ 8.06 (dd, J = 7.8, 3.5 Hz, 1H), 7.85-7.51 (m, 23H), 7.49 (d, J = 8.8 Hz, 2H), 7.40-7.32 (m, 2H), 7.28 (d, J = 8.7 Hz, 2H), 5.56 (dd, J = 7.1, 4.4 Hz, 1H), 4.74–4.64 (m, 1H). ³¹P{¹H} NMR (202 MHz, CD_2Cl_2): δ 64.8 (s). IR (CH₂Cl₂): ν_{CO} 2089, 2039, 2017 cm⁻¹. [Fe(PCHNAr^{Cl})(CO)₃]BF₄ ([1]BF₄). A solution of FcBF₄ (24.9 mg,

[Fe(PCHNAr^{Cl})(CO)₃]BF₄ ([1]BF₄). A solution of FcBF₄ (24.9 mg, mmol) in CH₂Cl₂ (7 mL), cooled to -35 °C, was added to a CH₂Cl₂ solution (2 mL) of 1 (50 mg, mmol), also cooled to -35 °C. The resulting dark green solution was immediately layered with pentane (ca. 15 mL), and the mixture was maintained at -35 °C. After 1 week, dark green crystals were produced that were suitable for X-ray crystallography. IR (CH₂Cl₂): ν_{CO} 2084, 2022, 1991 cm⁻¹. Anal. Calcd for C₂₈H₁₉NBClF₄FeO₃P·CH₂Cl₂ (found): C, 48.96 (48.92); H, 2.97 (2.91); N, 1.97 (2.14).

 $Fe[P_2(NAr^{Cl})_2)](CO)_2$ (3). In a 250 mL thick-walled round-bottom flask, a solution of $Fe(bda)(CO)_3$ (344 mg, 1.2 mmol) in toluene (30 mL) was treated with PCHNAr^{Cl} (847 mg, 2.1 mmol). The flask was sealed, and the orange solution was stirred in a 80 °C oil bath for 16 h, resulting in a dark blue solution. After the solution was cooled, solvents were removed under reduced pressure. The blue residue was extracted into THF (20 mL) and filtered through a short plug of Celite. The filtrate was concentrated to ca. 5 mL and layered with pentane (15 mL). Upon standing at -35 °C for 48 h, the solution yielded the target compound as dark blue crystals. Yield: 476 mg (49%). Single crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a concentrated CH₂Cl₂ solution. ¹H NMR (500 MHz, CD_2Cl_2): δ 7.76–7.68 (m, 2H), 7.57 (t, J = 7.5 Hz, 2H), 7.53-7.41 (m, 6H), 7.32-7.23 (m, 6H), 7.16 (t, J = 7.5 Hz, 2H), 7.07 (q, J = 3.2 Hz, 8H), 6.97–6.93 (m, 2H), 6.37 (d, J = 8.9 Hz, 2H), 6.07 (d, J = 8.8 Hz, 2H), 4.38 (t, J = 2.4 Hz, 2H). ³¹P NMR (202 MHz, CD₂Cl₂): δ 25.9 (s). IR (CH₂Cl₂): ν_{CO} 2011, 1954 cm⁻¹. Anal. Calcd for C₅₂H₃₈N₂Cl₂FeN₂O₂P₂·0.5C₅H₁₀ (found): C, 69.15 (69.22); H, 4.58 (4.7); N, 2.96 (3.09).

 $[Fe(PCHNAr^{Cl})_2(CO)_2](OTf)_2$ ([4](OTf)_2). To a CH₂Cl₂ (10 mL) solution of 3 (45 mg, 0.049 mmol) was added FcOTf (30 mg, 0.090 mmol), and a color change from dark blue to green was immediately observed. This solution was stirred for 30 min, followed by filtration through a short plug of Celite. The filtrate was diluted with 15 mL of pentane to precipitate a yellow solid, which was collected by filtration

and washed with Et₂O. Yield: 38 mg (64%). IR (CH₂Cl₂): ν_{CO} 2059, 2023 cm⁻¹. Anal. Calcd for C₅₄H₃₈Cl₂F₆FeN₂O₈P₂S₂·2.5CH₂Cl₂ (found): C, 47.72 (47.33); H, 3.05 (2.85); N, 1.97 (2.13). The analogous [Fe(PCHN^{ArCl})₂(CO)₂](BAr^F₄)₂ was prepared in a similar manner using FcBAr^F₄, and NMR spectra were collected on [Fe(PCHN^{ArCl})₂(CO)₂](BAr^F₄)₂ due to its favorable solubility in CD₂Cl₂ in comparison to the poorly soluble [Fe(PCHN^{ArCl})₂(CO)₂](OT₁)₂. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.30 (t, *J* = 2.9 Hz, 2H), 8.07 (t, *J* = 7.6 Hz, 2H), 7.93–7.84 (m, 4H), 7.81–7.65 (m, 26H), 7.62 (t, *J* = 7.8 Hz, 4H), 7.53 (s, 8H), 7.37 (d, *J* = 7.3 Hz, 4H), 7.30–7.24 (m, 4H), 7.14 (d, *J* = 8.5 Hz, 4H), 6.83–6.74 (m, 2H), 4.80 (br, 2H). ³¹P NMR (202 MHz, CD₂Cl₂): δ 37.2 (s). ¹³C{¹H</sup> NMR (151 MHz, CD₂Cl₂, 25 °C): δ 207 (t, *J* = 22 Hz, CO), 182 (s, CH=NAr), 162 (dd, *J* = 100, 50 Hz, BAr^F₄), 135 (s), 133 (s), 132 (s), 131 (s). 131 (s), 131 (s), 130 (q, *J* = 32 Hz, BAr^F₄), 126 (t, *J* = 26 Hz), 118 (s, BAr^F₄), 123 (s), 121 (t, *J* = 18 Hz), 120 (t, *J* = 26 Hz), 118 (s, BAr^F₄).

DFT Methods. Computations have been carried out with the TURBOMOLE suite of programs.⁵⁶ A valence triple- ζ basis set with polarization functions on all atoms (TZVP)⁵⁷ has been adopted. Both pure (BP86)⁵⁸ and hybrid (B3LYP)⁵⁹ density functionals have been used, in order to test the effect of the level of theory on computed structures and energies. The resolution-of-identity technique (RI)⁶⁰ has been used to speed up BP86 computations, by reducing all fourcenter two-electron Coulomb integrals to precomputed three- and two-center integrals.

Harmonic vibrational frequencies were calculated (at the same level of theory) in order to define the nature of each stationary point of the energy hypersurface and to verify whether computed structures correspond to genuine minima (absence of imaginary frequencies). The search and optimization of transition states have been carried out with a pseudo-Newton–Raphson method. First, a guess transitionstate structure is optimized, by constraining the degrees of freedom related to the reaction coordinate (RC). Then, a vibrational analysis on the constrained structure is performed, in order to pinpoint the single negative eigenmode associated with the RC of interest. The negative eigenmode is thus followed, in order to locate the first-order saddle point representing the pure transition-state structure.

Free energy (*G*) values can be obtained by including enthalpy, zeropoint energy (ZPE), and entropy contributions to the self-consistentfield SCF electronic energy. To do so, three different contributions ($q_{translational}$, $q_{vibrational}$, and $q_{rotational}$) have been considered to evaluate the overall partition function.⁶¹ The *T* and *P* values have been set to 298.15 K and 1 bar, respectively. The scaling factor for SCF wavenumbers has been set to 0.9914 for BP86 (default value implemented in TURBOMOLE⁵⁶) and to 0.9679 for the B3LYP functional.⁶²

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00318.

NMR and IR spectra (PDF) Cartesian coordinates (PDF) X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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