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C−H Activation of Imines by Trimethylphosphine-Supported Iron Complexes and Their Reactivities

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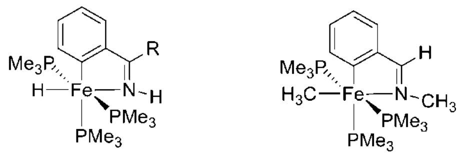
Introduction

The direct and catalytic transformation of hydrocarbons to various useful chemicals via C−H bond activation is of considerable interest to chemical industries and remains a challenge to chemists due to the inherent difficulty associated with breaking such robust bonds.[1] The introduction of transition metals into this area has given new opportunities, and there has been a massive effort to achieve selective C−H bond activation by transition metal complexes.[2]

Activation of aromatic C−H bonds by *ortho*-metalation is a promising example of synthetically applicable catalytic systems.[3] In most cases, the direct use of aromatic compounds in synthesis relies on the presence of a more reactive group C−X (X = Cl, Br, I) than a C−H bond.[4] This chemistry can be very successful, but the manufacture of aryl halides is not an environmentally friendly process. Furthermore, these reactions typically produce halide salts as byproducts. Therefore, the bulk synthesis of aryl derivatives proceeding by such C−H bond activation requires the development of practical catalytic ways to directly activate C−H bonds of arenes. Iron-based catalysts of comparable activity would be desirable owing to their potentially lower cost and lack of toxicity and environmental impact. Despite its advantages, iron was relatively underrepresented in the field of catalysis compared to the other transition metals.[5] Even though strong Lewis acid $FeCl_3$-catalyzed Friedel−Crafts reactions of electron-rich arenes are a well-known process for the formation of new C−C bonds from aromatic C−H bonds, rearrangements can occur to produce a more highly substituted product.[6] There are some well-known iron-based catalysts, for example, the landmark discovery of highly active bis(imino)pyridine iron complexes for ethylene polymerization and α-olefin oligomerization reported by Gibson,[7] DuPont,[8] and Brookhart.[9] Iron dihalide precatalysts are noteworthy in their ability to oligomerize α-olefins.[10] Besides that, there are some very recently reported iron catalysts with N-donor functionality, for example, iron catalyst for the asymmetric hydrogenation of polar bonds by Morris et al.,[11] iron catalysts for olefin hydrogenation by Chirik et al.,[12] and the achiral iron catalyst by Casey and Guan for ketone and imine hydrogenation.[13]

Chart 1



R = C_6H_5 (**1**), $C(CH_3)_3$ (**2**) **4**

Syntheses with catalytic amounts of ruthenium or rhodium, preferentially using an N donor as anchoring group in a substrate molecule, when followed by a coordination of a suitable co-substrate and elimination of the metal, have become an indispensable method of C,C-coupling in organic chemistry.[14] Surprisingly, exploring the coordination chemistry of the postulated [N,C]-cyclometalated intermediates has remained a great challenge to date.[15] Using complexes of low-valent iron (**1**, **2**, and **4**) and cobalt, we have recently conducted cyclometalation reactions that mimic the first steps in the proposed catalytic cycle (Chart 1).[16]

In this paper, the activation and functionalization of C−H bonds by solution-phase iron metal-based systems are presented, with an emphasis on the activation of aromatic C−H bonds. We herein report the synthesis and structural analyses of a series

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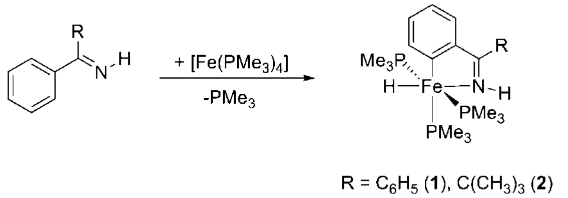
Scheme 1



of *ortho*-metalated hydrido-iron and methyl-iron complexes and their reactivities.

Results and Discussion

1. Reactions of Fe(PMe$_3$)$_4$ with Ketimines, PhRC=NH (R = C$_6$H$_5$, C(CH$_3$)$_3$). The M−H bond plays an important role in organometallic chemistry because metal hydrides can undergo insertion with a wide variety of unsaturated compounds to give stable species or reaction intermediates containing M−C bonds.[17] Not only are these synthetically useful, but many of the catalytic reactions involve hydride insertion as the key step.[18] Fe(PMe$_3$)$_4$ upon reaction with ketimines were transformed to Fe−H complexes under mild reaction conditions.

Stoichiometric amounts of diphenylketimine and *tert*-butylphenylketimine reacted with Fe(PMe$_3$)$_4$ in pentane at −70 °C. During warmup to room temperature, the color of the mixtures changed from dark brown to violet for **1** and to reddish violet for **2** (Scheme 1).[16]

The reaction likely begins with the coordination of the iron adduct to the nitrogen or C=N bond by substituting one of the trimethylphosphines, which brings the metal closer to the *ortho* C−H bond (Scheme 1). This chelation assistance results in an easier and highly selective C−H bond cleavage to give the cyclometalated iron(II) complex.

Compounds **1** and **2** crystallize from pentane at −27 °C as dark violet prisms. While compound **2** is moderately sensitive, compound **1** is extremely hygroscopic. Under 1 bar of argon, the solids decompose at 105−118 °C. IR spectra of the compounds give evidence for hydrido-iron(II) complexes with ν(Fe−H) stretching frequencies at 1730 cm^{-1} for **1** and 1795 cm^{-1} for **2**. ν(N−H) bands are observed with bathochromic shifts between 45 and 70 cm^{-1}, indicating coordination through the N atom. In ^{1}H NMR spectra, Fe−H resonances appear at −16.4 ppm for **1** and −17.5 ppm for **2** as doublets of triplets due to the coupling of the hydride nucleus with *trans*- and *cis*-disposed trimethylphosphines.[19] Both compounds show two sets of anisochronic PMe$_3$ groups, which indicate that the iron centers have an octahedral coordination environment made up of three meridional PMe$_3$ ligands (Figure 1). The presence of the *ortho*-metalated imine complexes is also supported by the ^{13}C{^{1}H} NMR spectra. Compound **1** contains a doublet at 180.2 ppm ($J_{P,C}$ = 10.3 Hz) due to a coupling of the imine carbon with one of the P nuclei and a multiplet at 204.1 ppm assigned to the metalated aromatic carbon. In compound **2**, these resonate as multiplets at 186.1 ppm (C=N) and 200.1 ppm (Fe−C). The ^{31}P{^{1}H} NMR spectra of the two compounds, which are temperature invariant, show two sets of PMe$_3$ groups with couplings of 37 Hz. The PMe$_3$ group *trans* to the metalated carbon gives a triplet with a resonance at around 23 ppm, and the two isochronic *trans* phosphines appear at 18 ppm as doublets in both cases.

The molecular structure of **1** shows a slightly distorted octahedral frame of donor atoms centered by an iron atom that bears three *meridional* PMe$_3$ donor groups (Figure 2). C, N, and H atoms of the metalacycle occupy three remaining ligand positions. The angle P3−Fe1−P1 = 152.878(18) Å shows a significant deviation from 180° because of spatial relaxation. The *ortho*-metalated imine ligand acts with a bite angle of 79.0(6)°, and the sum of internal angle for the five-membered metalacycle (539.90°) approach the ideal value for a planar five-membered ring (540°). The Fe−P distances are in the typical range of 2.18−2.22 Å.[20] The Fe1−P2 distance is lengthened due to the *trans* influence of the carbon donor, while N1−Fe1 and C1−Fe1 distances are also in typical ranges.[21] The C=N bond is lengthened upon coordination from 1.237(3) Å to 1.314(2) Å.[22] The Fe1−H1 1.480(19) Å is in the typical range for molecular iron hydrides.[23]

A view of the molecular geometry of **2** is shown in Figure 3. The X-ray diffraction study on a single crystal of **2** confirms the structure proposed in Scheme 1 and shows the same structural characteristics as **1**.

2. Reactions of Fe(CH$_3$)$_2$(PMe$_3$)$_4$ with Diphenylketimine (Ph$_2$C=NH). The possibility of direct introduction of a new C−C bond via direct C−H bond transformation is a highly attractive synthetic strategy in synthesis owing to the ubiquitous nature of C−H bonds in organic substances, where the range of substrates is virtually unlimited. The activation of C−H bonds and the formation of C−C bonds in a single preparative step combine economy, efficiency, and elegance. The reaction of diphenylketimine with Fe(CH$_3$)$_2$(PMe$_3$)$_4$ afforded a methyl-iron(II) complex with a C,C-coupling between an sp^2 carbon of the aromatic backbone and an sp^3 carbon of the CH$_3$ fragment (Scheme 2). The C,C-coupling in this reaction suggests an unusual reaction pathway. Fe(CH$_3$)$_2$(PMe$_3$)$_4$ reacts first with diphenylketimine to produce a methyl-iron(II) intermediate by elimination of methane. C,C-coupling between methyl and phenyl groups and reductive elimination afford the new aromatic backbone. The Fe(0) complex in solution reinserts into the *ortho* C−H bond of the unsubstituted phenyl ring and forms the hydrido-Fe(II) complex **3**.

IR and NMR data support the structure assigned for **3**. In the IR spectrum, the absorption bands at 3279 and 1761 cm^{-1}, respectively, represent ν(N−H) and ν(Fe−H) vibrations (Table 1 summarizes the properties of complexes **1**−**3**). In the ^{1}H NMR spectrum the new CH$_3$ group formed by C,C-coupling appears as a singlet at 2.21 ppm. The Fe−H group resonates at −17.2 ppm as a doublet of triplets. In ^{13}C{^{1}H} NMR the Ar-CH$_3$ carbon appears as a singlet at 21.1 ppm. The imine carbon atom resonates at 181.2 ppm as a doublet ($^3J_{P,C}$ = 9.8 Hz), and the metalated carbon gives a multiplet at 203.1 ppm. In the ^{31}P{^{1}H} NMR the *trans* PMe$_3$ groups resonate as a multiplet at 15.7 ppm and PMe$_3$ *cis* disposed to H appears as a triplet with a coupling constant $^2J_{P,P}$ of 38.3 Hz. These data support a *mer*-octahedral hydrido-Fe(II) complex with three PMe$_3$ ligands and a coordinated imine backbone.

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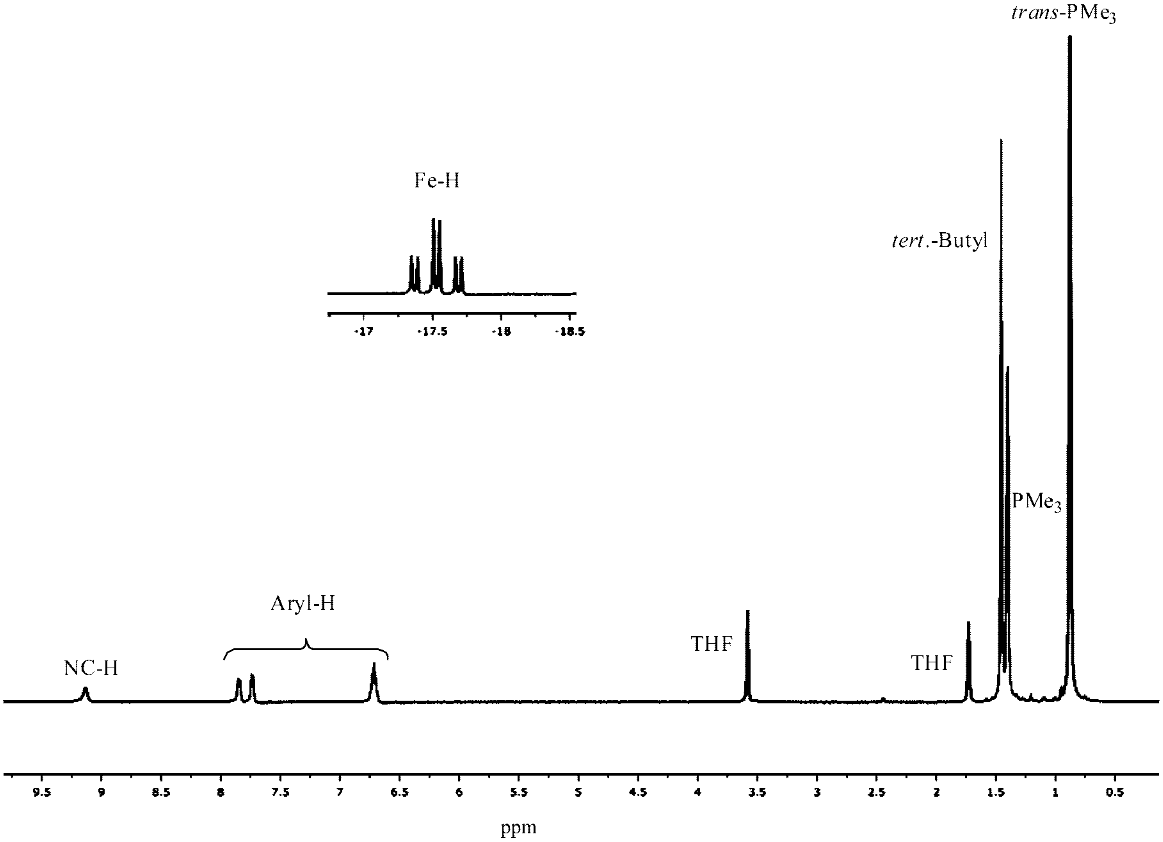


Figure 1. ^{1}H NMR spectra of **2** (500 MHz, d_8-THF, 300 K).

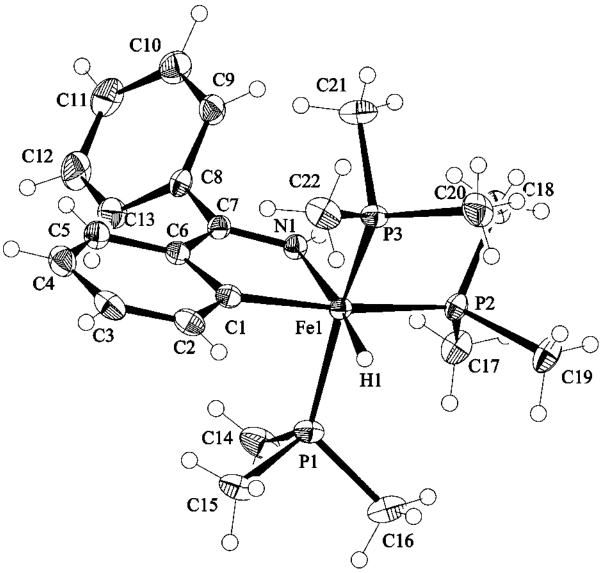


Figure 2. Molecular structure of **1** (ORTEP plot with hydrogen atoms, FeH position indicated).

X-ray diffraction analysis of **3** indicates that the imine reactant binds to iron through the N1 and C1 atoms and forms a five-membered metallacycle with a bite angle N1−Fe1−C1 of 79.52(6)° (Figure 4). The sum of internal angles is that of a planar five-membered ring. An octahedral coordination is formed by three PMe_3 ligands in *meridional* positions and is completed by a hydride ligand in calculated position *trans* to nitrogen. Two trimethylphosphine groups are in opposite positions, P2−Fe1−P3 = 149.64(2)°, and one trimethylphosphine group is *cis* to nitrogen, N1−Fe1−P1 = 87.25(4)°. The most striking feature in the molecular structure of **3** is the methyl substituent (C14) attached to the non-metalated phenyl ring. Table 2 summarizes the structural properties of complexes **1**−**3**.

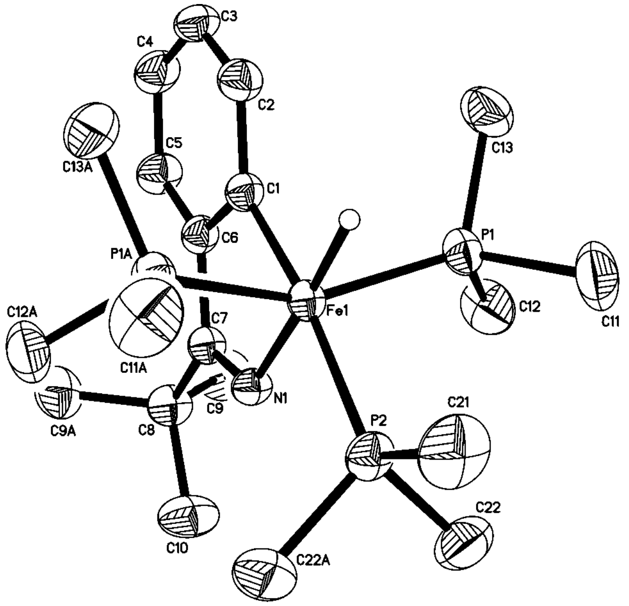


Figure 3. Molecular structure of **2** (ORTEP plot with hydrogen atoms omitted, FeH position indicated).

Because of strong *trans* influence of the aromatic sp^2 carbon, the Fe−P bond length, which is *trans* to the metalated carbon, is clearly longer than the other Fe−P distances in all three structures. They all attain a distorted octahedral geometry, and

Scheme 2

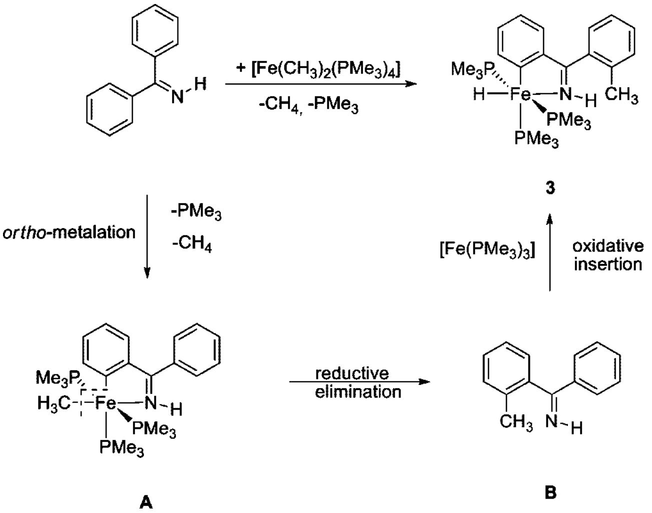


Table 1. Properties of Fe−H Metalacycles 1−3

	yield [%]	color	dec [°C]	$\tilde{\nu}$ [cm^{-1}]
1	78	violet	<105	3281 (N−H), 1730 (Fe−H)
2	48	violet	<118	3335 (N−H), 1795 (Fe−H)
3	74	violet	<104	3279 (N−H), 1761 (Fe−H)

Table 2. Selected Bond Lengths and Angles of Hydrido-Fe(II) Complexes 1−3

	1	2	3
	Bond Lengths [Å]		
Fe−C1	1.9860(15)	1.9660(2)	1.9820(17)
Fe−N1	1.9434(13)	1.9316(19)	1.9438(14)
N1−C7	1.314(2)	1.297(3)	1.306(2)
Fe−P1	2.1874(5)	2.1739(5)	2.1784(5)
Fe−P2	2.2146(5)	2.2146(5)	2.2180(5)
Fe−P3	2.1803(5)	2.1739(5)	2.1751(5)
	Bond Angles [deg]		
C1−Fe−N1	79.60(6)	78.93(9)	79.52(6)
C1−Fe−P1	87.08(4)	86.71(2)	88.23(5)
C1−Fe−P2	167.36(5)	168.96(7)	166.77(5)
C1−Fe−P3	87.59(4)	86.71(2)	87.04(5)
P1−Fe−P3	152.878(18)	153.16(3)	149.64(2)
N1−Fe−P1	102.13(4)	102.105(17)	105.75(5)
N1−Fe−P2	87.76(4)	90.03(6)	87.25(4)
N1−Fe−P3	103.01(4)	102.105(17)	102.82(5)

the iron atom is part of a five-membered metalacycle of a chelating imine ligand.

3. Reactions of $Fe(CH_3)_2(PMe_3)_4$ with Benzylic Imines, PhCH=NR (R = CH_3, $CH(CH_3)_2$, C_6H_5). Cyclometalation reactions of simple imines (R_2C=NR) with basic iron compounds have not been described to date, although such reactions have been carried out with other transition metal complexes and have drawn much attention.[24] Their particular activity is well-known from the palladium *N*-isopropylbenzylidenimine catalyst for the Suzuki reaction, which catalyzes the coupling of aryl bromides and phenylboronic acid with extremely high efficieny.[25]

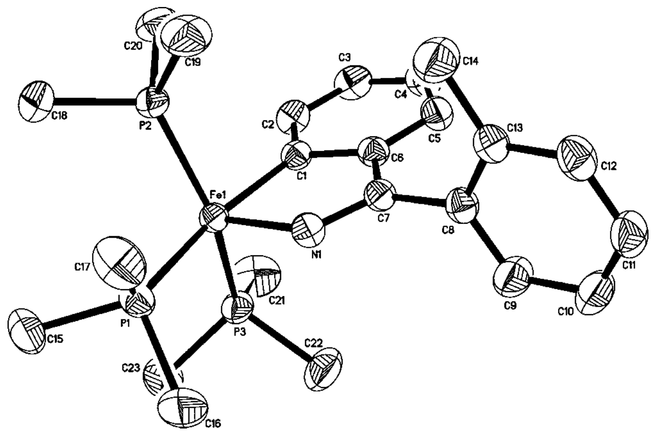
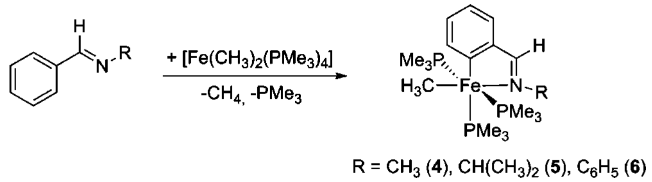


Figure 4. Molecular structure of **3** (ORTEP plot with hydrogen atoms omitted).

Scheme 3



Benzylic imines (*N*-methyl-, *N*-isopropyl-, and *N*-phenylbenzylidenimines) reacted with $Fe(CH_3)_2(PMe_3)_4$ in pentane at −70 °C through the elimination of methane to afford the hexacoordinate iron(II) complexes **4**−**6** (Scheme 3).

While violet solutions of **4** and **5** in pentane deposited violet crystals at −27 °C, petroleum green crystals of **6** deposited at 4 °C. The solids have moderate air-sensitivity and under argon decompose at 115, 116, and 119 °C, respectively. Elemental compositions are consistent with loss of methane and one of the trimethylphosphine groups during the reaction. The infrared spectrum of each compound exhibits an ν(C=N) absorption of the coordinated imine ligand (R = CH_3, 1572 cm^{-1} (m); R = $CH(CH_3)_2$, 1519 cm^{-1} (m); R = C_6H_5, 1543 cm^{-1} (w)), which occurs at significantly lower energies than the free imine C=N stretching absorptions, e.g., ν(C=N) at 1651 cm^{-1} in free PhCHNMe. In all three spectra, δ (Fe−CH_3) absorptions appears at 1180 cm^{-1} (**4**); 1162 cm^{-1} (**5**); and 1193, 1170 cm^{-1} (**6**), although intensities are weak.

The solid state characterization of **4** as an *ortho*-metalated imine complex is derived from an X-ray diffraction experiment on a single crystal (Figure 5). The coordination geometry around the iron atom is octahedral with two P-donor atoms occupying *trans* positions (P1−Fe1−P3 = 168.05(4)°) along the normal of a plane that is defined by the atoms C2 and N1 of the *ortho*-metalated *N*-methylbenzylideneimine (N1−Fe1−C2 = 80.36(13)°), forming a five-membered ring with the iron atom, the P2 atom of the trimethylphosphine group disposed *trans* to C2 (C2−Fe1−P2 = 176.99(10)°), and the CH_3 ligand located in a position opposite the nitrogen atom (N1−Fe1−C1 = 169.89(13)°). The Fe1−N1 bond length of 2.016(3) Å, Fe1−C1 bond length of 2.088(3) Å, and Fe1−C2 bond distance of 1.987(3) Å are typical for Fe−N,[26] Fe−C_{alkyl},[27] and Fe−C_{aryl} single bonds.[28]

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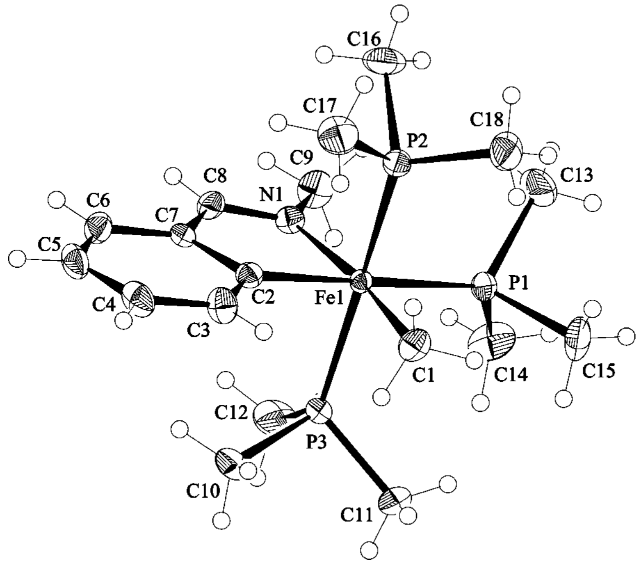


Figure 5. Molecular structure of **4** (ORTEP plot with hydrogen atoms).

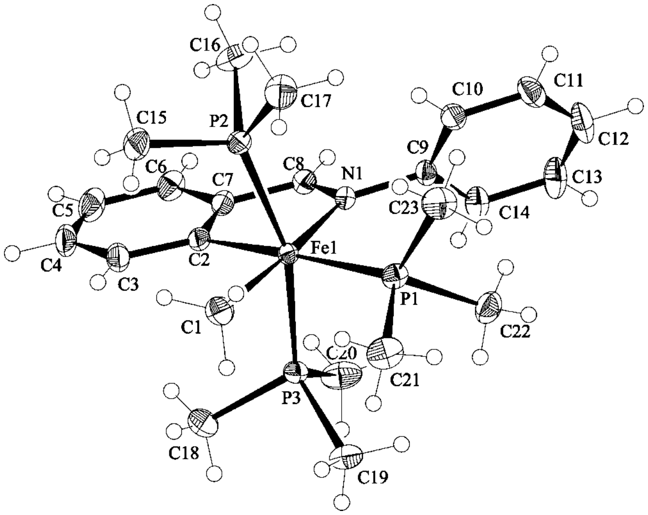


Figure 6. Molecular structure of **6** (ORTEP plot with hydrogen atoms).

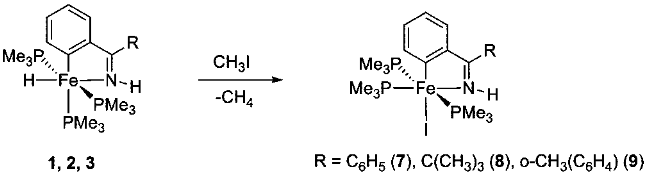
The Fe−P distances are in the range 2.20−2.26 Å and are in agreement with the values previously found in complexes **1**−**3**.

In complex **6**, the configuration about the iron atom is close to octahedral; the principal distortions are related to the angle of 80.11(6)° subtended by the chelating atoms and to a bending along the P2−Fe−P3 positions (Figure 6). The chelate ligand coordinates via Fe−N and M−C σ-bonds in an *ortho* position of the benzylidene phenyl ring that is analogous to compound **5**. At variance with the methyl-iron(II) intermediate of compound **3** (Scheme 2), no reductive C,C-coupling is observed in the formation of compound **6**. On the whole, the configuration of the coordinated imine ligand closely resembles that of free benzylideneimines.[29] The aniline phenyl ring is rotated by 61.2° away from the imine plane in the complex; the corresponding twist in the free ligand is 55°. The other phenyl ring is coplanar with the imine group, forming a dihedral angle of 3.0° with the imine plane, as compared to a value of 10° in the free imine. The C=N bond is lengthened upon coordination from 1.237(3) Å to 1.317(2) Å. The N1−C9 and C7−C8 distances of 1.4436(19) and 1.438(2) Å are both marginally shorter than the corresponding bond lengths of 1.460(3) and 1.496(3) Å in the free imine. The Fe−N (2.0128(13) Å), Fe−C(sp^2) (2.0182(15) Å), and Fe−P distances fall within the literature range and are comparable with compounds **1**−**4**.[30] Table 3 presents selected bond lengths and angles of **4** and **6**.

Table 3. Selected Bond Lengths and Angles of Methyl-Fe(II) Complexes 4 and 6

	4	**6**
	Bond Angles [deg]	
Fe−C(sp^3)	1.987(3)	2.0182(15)
Fe−C(sp^2)	2.088(3)	2.0974(17)
N1−C8	1.289(5)	1.317(2)
Fe−N1	2.016(3)	2.0128(13)
Fe−P1	2.2574(10)	2.2954(5)
Fe−P2	2.2039(11)	2.2500(5)
Fe−P3	2.2242(11)	2.2369(5)
	Bond Lengths [Å]	
C(sp^2)−Fe−N1	80.36(13)	80.11(6)
C(sp^3)−Fe−N1	169.89(13)	175.05(6)
N1−Fe−P_{ax}	93.76(9)	94.67(4)
N1−Fe−P_{ax}	94.51(9)	93.38(4)
C(sp^2)−Fe−P_{trans}	176.99(10)	175.15(4)
P_{trans}−Fe−P	168.05(4)	161.468(18)

Scheme 4



Similar to the hyrido-iron(II) complexes, the reaction is believed to begin with coordination of the iron adduct to the nitrogen or π-bond by substitution of one trimethylphosphine, bringing the metal closer to the *ortho* C−H bond. This chelation assistance facilitates highly selective C−H bond cleavage to give a cyclometalated iron(IV) intermediate. Reductive elimination of CH_4 results in an *ortho*-metalated methyl-iron(II) complex with three trimethylphosphine ligands that is coordinatively saturated, like other alkyl complexes of iron(II) containing Cp and CO ligands.[31] It is the existence of several decomposition pathways that makes many transition metal alkyls unstable. The lack of a β-decomposition pathway due to a Fe-CH_3 group, a blocking imine ligand, and a PMe_3 ligand are in favor of stable compounds **4**−**6**. The principles governing their stability make a useful starting point in order to understand some of the most important organometallic reactions.

4. Iodomethane Reactions of Hydrido-Iron(II) Complexes. The hydrido-iron(II) complexes **1**−**3** are good candidates for oxidative addition reactions. Potential ligands that do not have a lone pair or filled π-type orbitals are still able to interact with transition metal complexes by breaking a σ-bond. Using iodomethane as a substrate, the interesting question arises as to whether attack by the metal would proceed as a regioselective addition or promote ring opening through a subsequent reductive C,C-coupling reaction. Reactions of **1**−**3** in pentane proceed as described in Scheme 4.

When iodomethane is added to the hydrido-iron(II) complexes at −70 °C, evolution of gas is observed during warmup. Compounds **7**−**9** crystallize from pentane at 4 °C. IR spectra

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[29] Burgi, H. B.; Dunitz, J. D. *Helv. Chim. Acta* **1970**, *53*, 1747.

[30] Carthy, A. J.; Mott, G. N.; Taylor, N. J. *J. Organomet. Chem.* **1979**, *182*, C69.

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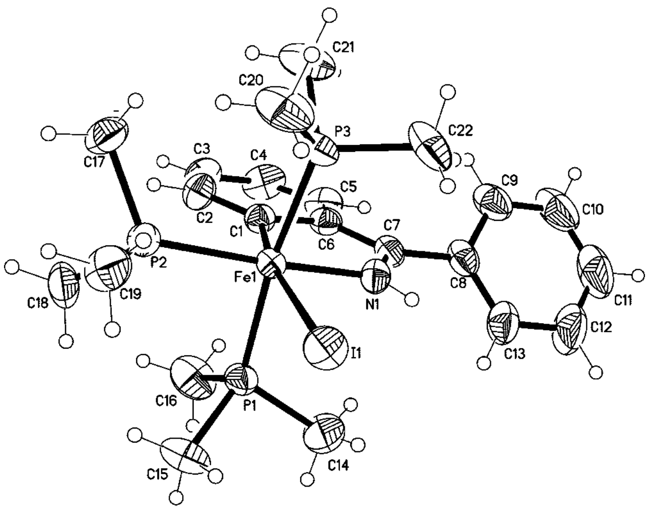


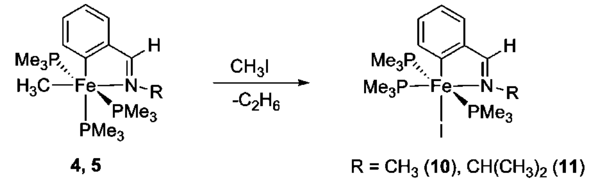
Figure 7. Molecular structure of **7** (ORTEP plot with hydrogen atoms).

give a first clue to the structures of **7**−**9**. Strong stretching vibrations of Fe−H over 1700 cm^{-1} are absent, and there is a bathochromic shift in all characteristic bands. In the ^{1}H NMR spectra, there is no Fe−H resonance at high field and trimethylphosphine resonances are shifted to low field. We can see more clearly the metalated carbons in lower field than in the hydrido-iron(II) compounds. The observed patterns in the ^{31}P{^{1}H} NMR spectra are consistent with a *meridional* arrangement of the three trimethylphoshines. On the basis of chemical shifts, the electron density at the iron nucleus is subject to the σ-electron-withdrawing power of the halides.[32]

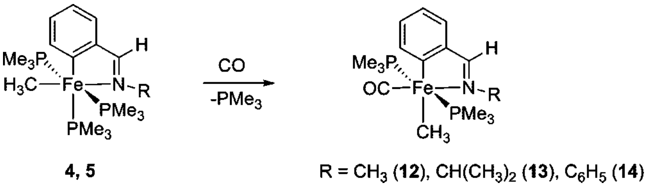
A molecule of the compound **7** is depicted in Figure 7. In an octahedral geometry, a meridional arrangement of the three trimethylphosphines is recognized. The remaining three coordination sites are occupied by an iodide and a chelating imine ligand. The iodide and one trimethylphosphine P-donor are almost coplanar with the metalacycle, forming an angle P2−Fe1−I1 of 97.87(3)°. Because of its weak *trans* influence, the iodide is coordinated *trans* to the metalated carbon (C1−Fe1−I1 166.44(9)°) and the Fe1−C1 distance is 0.029 Å smaller than Fe1−C1 in compound **1**. Complex **7** is less distorted than **1** because the iodo ligand restricts the flexibility of the trimethylphosphine groups. The Fe1−I1 distance (2.7616(5) Å) agrees with the Fe1−I1 distance (2.6646 Å) in the *ortho*-metalated octahedral Fe(II) compound Fe(CO)$_2${P(OPh)$_3$}{(PhO)$_2$POC$_6$H$_4$}(I).[33] The two mutually *trans* trimethylphosphine groups have long Fe−P distances (mean 2.25 Å) compared with the one that is *trans* to the N atom (Fe−P = 2.2350(9) Å) due to a sizable *trans* influence of trialkylphosphines. All bond lengths are well matched with the other structural features.[34]

The resulting iodo-iron(II) complexes are interesting as versatile nucleophiles with applications in organometallic and organic synthesis. The independent reports by Brookhart and Gibson using five-coordinate Fe(II) dihalide complexes as precatalysts for the polymerization of ethylene and α-olefins suggest the idea that iron(II), when in an appropriate coordination environment, may be an active catalyst for C−C and C−H bond forming reactions.[35]

Scheme 5



Scheme 6



5. Iodomethane Reactions of Methyl-Iron(II) Complexes. Similar to the hydrido-iron(II) compounds **1**−**3**, methyl-iron compounds **4** and **5** react with iodomethane to produce iodo-iron(II) compounds **10** and **11** (Scheme 5).

Pink crystals of **10** and light violet crystals of **11** are obtained from pentane at 4 °C. Elemental analysis shows the expected decrease in carbon and hydrogen contents. Thermal stabilities of the solids are improved, as **10** melts at 142 °C and **11** decomposes at 145 °C. IR spectra of **10** and **11** show the absence of characteristic deformation bands (δ_s Fe−CH$_3$) of methyl-iron(II) complexes **4** and **5**. In the ^{1}H NMR spectra, resonances at 1.14 ppm as a singlet in **10** and at 0.84 ppm as a pseudotriplet ($|^2J_{P,H} + {}^4J_{P,H}| = 5.9$ Hz) in **11** are assigned to the trimethylphosphine ligands in mutual *trans* positions. *Cis*-arranged trimethylphosphines resonate at 1.56 ppm as a singlet in **10** and at 1.50 ppm as a doublet ($^2J_{P,H} = 6.4$ Hz) in **11**. Aromatic protons typically appear at 6.7−7.7 ppm. In the ^{13}C{^{1}H} NMR metalated carbon nuclei resonate at 212.7 and 199.7 ppm, respectively. ^{31}P{^{1}H} NMR resonances of **10** and **11** confirm the suggested structures in Scheme 6. Two phosphorus nuclei appear as a doublet at 5.8 ppm ($^2J_{P,P} = 54.3$ Hz, complex **10**) and 28.3 ppm ($^2J_{P,P} = 28.3$ Hz, complex **11**), while the singular phosphorus nuclei form triplets at 14.9 ppm ($^2J_{P,P} = 54.3$ Hz, complex **10**) and 21.8 ppm ($^2J_{P,P} = 28.3$ Hz, complex **11**). This pattern is consistent with a *mer*-octahedral coordination geometry.

An X-ray structural determination was performed on a single crystal of compound **10** grown from pentane (Figure 8). The Fe1−C1 and Fe1−N1 bond lengths (1.949(4) and 2.027(5) Å) fall in the range of values found in the related complexes **7** and **8**. The Fe1−I1 bond length of 2.7974(8) Å lies above the literature value (e.g., the Fe−I distance of 2.61(3) Å in the *cis*,*trans*-Fe(CO)$_2$(PMe$_3$)$_2$(p-C$_6$H$_5$)I complex synthesized by Cardaci) because of the strong *trans* influence of the carbon atom.[36] The acute angle C1−Fe1−N1 (81.2(2)°) reflects the big bite of the *N*-methylbenzylideneimine ligand. The sum of the *cis* angles involving Fe and the atoms C1, N1, I1, and P2 (the equatorial plane) is 359.77°, and the sum of the internal angles in the five-membered metallacycle is 539.80°, consistent with planarity.

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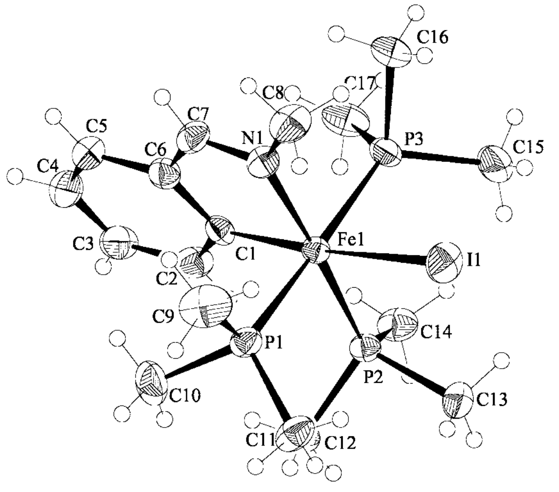

Figure 8. Molecular structure of **10** (ORTEP plot with hydrogen atoms).

Table 4. Selected Bond Lengths and Angles of Iodo-Fe(II) Complexes 7 and 10

	7	10
Bond Lengths [Å]		
Fe−C1	1.957(3)	1.949(4)
Fe−N1	1.940(2)	2.027(5)
Fe−I	2.7616(5)	2.7974(8)
N1−C7	1.294(4)	1.294(7)
Fe−P1	2.2587(9)	2.2629(15)
Fe−P2	2.2350(9)	2.246(3)
Fe−P3	2.2568(9)	2.2490(15)
Bond Angles [deg]		
C1−Fe−N1	80.05(12)	81.2(2)
C1−Fe−I	166.44(9)	171.94(15)
N1−Fe−P2	175.24(9)	175.22(13)
P1−Fe−P3	172.52(4)	175.33(6)

In order to detect the iron(IV) intermediate, the stoichiometric ratios and conditions were modified but resulted in the same products with lower yields. Instead of methane loss, products of oxidative addition reductively eliminate ethane. Like compounds **7−9**, complexes **10** and **11** form thermally stable solids. In contrast to its parent complex, **10** does not decompose in deuterated solvents, and full characterization of its structure confirms that of **5**, also. Table 4 summarizes the crystallographic data of **7** and **10**.

6. Carbon Monoxide Reactions of Methyl-Iron(II) Complexes. Since aromatic imines catalytically react with CO and/or olefins in the presence of $Ru_3(CO)_{12}$ to form new C−C bonds regioselectively in the *ortho* position with respect to the imine substituent, the reaction of the *ortho*-metalated Fe(II) complexes with CO might well serve as model reactions for the initial steps of catalytic C−C bond formation. Under 1 bar of CO, methyl-iron(II) compounds **4−6** in pentane solution form the monocarbonyl complexes **12−14** (Scheme 6). Carbon monoxide substitutes one of the trimethylphosphines, selectively occupying the ligand position opposite the nitrogen atom of the imine group.

12 and **13** form dark pink crystals, and **14** forms light green crystals. When compared with parent methyl-trimethylphosphine complexes, they show increased thermal stability but decompose at 134, 135, and 138 °C, respectively. Elemental analysis confirms the substitution of a trimethylphosphine group by a carbon monoxide ligand. The complexes **12−14** exhibit very strong terminal CO stretching bands at 1869, 1879, and 1870 cm^{-1}, which are at lower energies, reflecting strong back-bonding and weaker C−O bonds. Fe−CH_3 stretching absorption bands are observed at 1153, 1151, and 1193 cm^{-1} for **12−14**, respectively. In contrast to their parent methyl complexes, **13** and **14** do not easily decompose in deuterated solvents. So the spectroscopic characterization of **13** gives the structure solution of **5**. In the ^1H NMR spectra metal-coordinated CH_3 groups show triplets at −0.67 ppm ($^3J_{P,H} = 6.8$ Hz for **12**), −0.59 ppm ($^3J_{P,H} = 7.3$ Hz for **13**), and −0.71 ppm ($^3J_{P,H} = 8.1$ Hz for **14**). For compound **14**, we can observe the expected pseudotriplet at 0.93 ppm ($|^2J_{P,H} + {}^4J_{P,H}| = 4.7$ Hz), while PMe_3 groups in *trans* positions appear as broad singlets around 0.9 ppm for **12** and **13**. The $^{31}P\{^1H\}$ NMR spectra display singlets for *trans*-trimethylphosphine groups. The carbonyl region of the $^{13}C\{^1H\}$ NMR spectra of **13** and **14** comprises triplet resonances consistent with CO groups coupled to two equivalent P nuclei.

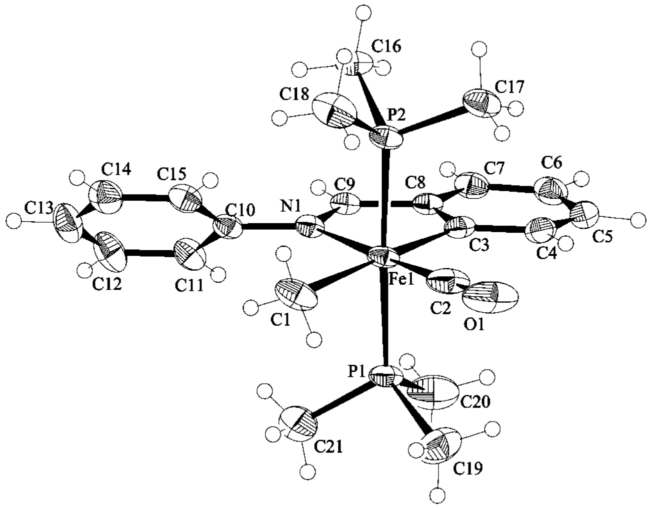

Figure 9. Molecular structure of **14**. Selected bond lengths (Å) and angles (deg): Fe1−C1 2.095(3), Fe1−C2 1.714(3), C2−O1 1.159(4), Fe1−C3 1.971(3), N1−C9 1.303(3), Fe1−N1 2.080(2), Fe1−P1 2.2257(9), Fe1−P2 2.2231(8); C3−Fe1−N1 80.71(10), N1−Fe1−C2 176.95(14), Fe1−C2−O1 178.2(4), C3−Fe1−C1 174.19(11), P2−Fe1−P1 177.29(3), N1−Fe1−P2 91.36(6), C3−Fe1−P1 89.26(8), C1−Fe1−C2 87.87(15), C1−Fe1−P1 86.60(10), C1−Fe1−P2 95.87(10), C2−Fe1−P1 90.47(10), C2−Fe1−P2 88.52(10).

The ORTEP drawing of the molecular structure of **14** is shown in Figure 9. The slight distortions from octahedral geometry may be illustrated by angles for some *trans* arrangements: P2−Fe1−P1 177.29(3)°, N1−Fe1−C2 176.95(14)°, C3−Fe1−C1 174.19(11)°. The main feature of this structure is the five-membered metallacycle derived from *ortho*-metalation of the imine ligand, and the bite angle N1−Fe1−C3 is 80.71(10)°. The constrained bite angle of the chelate ligand is considered to be the ultimate source of the distortions from octahedral geometry exhibited by **14**. The Fe−CH_3, Fe−CO, and C2−O1 bond lengths (2.095(3), 1.714(3), and 1.159(4) Å, respectively) are in literature ranges as compared with isoelectronic benzoyl acetones.[37]

Carbon monoxide reactions of methyl-iron complexes **4−6** afforded monocarbonyl derivatives.[38] Possible insertion reactions of CO into metal−carbon or metal−methyl bonds were not observed. The substitution of one trimethylphosphine ligand and the coordination of the CO stabilize the complexes. **13** and **14**

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do not decompose in deuterated solvents, and their melting points lie above those of their parent complexes. Full characterization of their structure supports the molecular structure of **5** derived from NMR spectroscopic data.

Summary

Using a C−H bond activation strategy, we have synthesized the first examples of *ortho*-metalated mono-iron complexes of monodentate N-donor functional ligands. Treatment of benzylicimines and ketimines with $Fe(CH_3)_2(PMe_3)_4$ and $Fe(PMe_3)_4$ under mild conditions results in *ortho*-metalated hydrido-iron(II) and methyl-iron(II) complexes in high yields. Besides C−H activation, the reaction of diphenylketimine with $Fe(CH_3)_2(PMe_3)_4$ presented a noteworthy hydrido-iron(II) complex with a C,C-coupling between an sp^2 carbon of the aromatic backbone and an sp^3 carbon of the CH_3 fragment. Iodomethane reactions of hydrido-iron(II) and methyl-iron(II) compounds give thermally stable iodo-iron(II) compounds, which are interesting versatile nucleophiles in organometallic and organic chemistry. Carbon monoxide reactions of methyl-iron complexes afford monocarbonyl derivatives, where possible insertion reactions of CO into the Fe−C or $Fe-CH_3$ bonds were not observed.

Experimental Section

General Remarks. All air-sensitive and volatile materials were handled using standard vacuum techniques.[39] Syntheses, transport, and storages of chemicals were done under an atmosphere of purified argon (BTS-Catalyst).[40] Solvents were dried according to known procedures and freshly distilled prior to use. All reagents were used as purchased (Aldrich, Acros, Alfa Aesar) without further purification. Literature methods were applied for the preparation of $[Fe(PMe_3)_4]$,[41] $[Fe(CH_3)_2(PMe_3)_4]$,[42] and *tert*-butylphenylketimine.[43] Trimethylphosphine was synthesized in diethyl ether from methylmagnesium chloride and triphenylphosphite according to a modified procedure given by Wolfsberger and Schmidbaur, which allows a convenient synthesis in yields from 85 to 92%.[44]

Air-sensitive samples were provided in capillaries sealed under vacuum and were analyzed by H. Kolbe Microanalytical Laboratory, Mülheim/Ruhr, FRG. C, H, N analytical identification of air-stable substances was performed in the microanalysis laboratory of Clemens-Schöpf-Institut for Organic Chemistry and Biochemistry at TU-Darmstadt using Perkin-Elmer CHN 240 A and CHN 240 B devices. The melting and decomposition points were measured on a Büchi 510 melting point apparatus and are uncorrected. Air-sensitive substances were sealed in capillaries under 1 bar of argon.

IR spectra were obtained as Nujol mulls between KBr plates using a Bruker FRA 106 spectrophotometer and recorded in the range 4000−400 cm^{-1}. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra (500, 125, and 202 MHz, respectively) were recorded on a Bruker DRX 500 spectrometer at the Organic Chemistry Institute of TU Darmstadt. ^1H and ^{13} C NMR chemical shifts were referenced to external TMS, and $^{31}P\{^1H\}$ chemical shifts were referenced to external 85% H_3PO_4. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ resonances were obtained with broadband proton decoupling. Magnetic suscepitbility data were obtained by the Faraday method using a Cahn D 200 torsion balance (Bruker) at 1.5 T.

General Procedure for the Preparation of Iron Complexes. $Fe(PMe_3)_4$ or $Fe(CH_3)_2(PMe_3)_4$ in pentane solution was combined with stoichiometric amounts of ligands (imines) at −70 °C. The mixture was warmed to 20 °C and kept stirring for 16 h. The volatiles were then removed in vacuo, and the residue was extracted with pentane. Combined solutions were cooled to afford crystalline material.

Synthesis of Hydrido[2-[(imino-*κN*)phenylmethyl]phenyl-*κC*]tris(trimethylphosphine)iron(II) (1). $Fe(PMe_3)_4$ (1.44 g, 3.99 mmol) in pentane was combined with 0.72 g (3.99 mmol) of diphenylketimine to afford violet crystals of **1**, which crystallize in pentane at −27 °C. Yield: 1.451 g (78%). Mp: 105−107 °C. Anal. Calcd for $C_{22}H_{38}FeNP_3$: C, 56.79; H, 8.23; N, 3.01; P, 19.79. Found: C, 57,06; H, 7.58; N, 2.96; P, 20.09. IR (Nujol, cm^{-1}): 3281 w (ν H−N=C); 3068 vw, 3043 vw, 3020 w (ν H−C=C); 1730 vs (ν Fe−H); 1598 m, 1567 m (ν C=C); 1500 m (ν C=N); 1449 vw; 1427 m (δ_{as} PCH_3); 1392 s; 1293 m, 1273 s (δ_s PCH_3); 1229 w; 1191 vw; 1176 vw; 1143 m; 1099 vw; 1072 vw; 1028 w; 1010 vw; 994 w; 936 vs (ρ_1 PCH_3); 849 s (ρ_2 PCH_3); 834 vw; 812 m; 777 s, 758 w, 737 vw, 729 m (γ $C-H_{arom}$); 709 vw, 698 s (ν_{as} PC_3); 657 s (ν_s PC_3); 622 vw; 587 s; 512 m (ν Fe−C); 463 w, 433 m. ^1H NMR (d_8-THF, 300 K, ppm): −16.4 (dt, $^2J_{P,H} = 22.8$ Hz, $^2J_{P,H} = 81.3$ Hz, 1H, Fe−H); 0.94 (s, 18H, PCH_3); 1.42 (d, $^2J_{P,H} = 4.7$ Hz, 9H, PCH_3); 6.72 (t, $^3J_{H,H} = 7.0$ Hz, 1H, Ar−H); 6.82 (t, $^3J_{H,H} = 7.1$ Hz, 1H, Ar−H); 7.30 (t, $^3J_{H,H} = 7.1$ Hz, 1H, Ar−H); 7.38 (t, $^3J_{H,H} = 7.2$ Hz, 2H, Ar−H); 7.47 (t, $^3J_{H,H} = 7.8$ Hz, 3H, Ar−H); 7.89 (d, $^3J_{H,H} = 6.4$ Hz, 1H, Ar−H); 9.40 (s, 1H, N−H). $^{13}C\{^1H\}$ NMR (d_8-THF, 300 K, ppm): 22.5 (dt′, $|^1J_{P,C} + {}^3J_{P,C}| = 12.1$ Hz, $^3J_{P,C} = 3.2$ Hz, PCH_3); 22.3 (td, $^1J_{P,C} = 13.7$ Hz, $^3J_{P,C} = 2.3$ Hz, PCH_3); 118.6 (s, CH); 123.0 (d, $^4J_{P,C} = 1.7$ Hz, CH); 125.9 (s, CH); 127.9 (s, CH); 128.1 (s, CH); 129.4 (s, CH); 142.1 (s, C); 146 (s, C); 152.3 (s, CH); 180.2 (d, $^3J_{P,C} = 10.3$ Hz, C=N); 204.1 (m, Fe−C). $^{31}P\{^1H\}$ NMR (d_8-THF, 296 K, ppm): 18.2 (d, $^2J_{P,P} = 37.4$ Hz, 2P, PCH_3), 22.5 (t, $^2J_{P,P} = 37.4$ Hz, 1P, PCH_3).

Synthesis of Hydrido[2-[(imino-*κN*)phenylmethyl]-1,1-dimethylethyl-*κC*]tris (trimethylphosphine)iron(II) (2). $Fe(PMe_3)_4$ (1.27 g, 3.53 mmol) in pentane was combined with 0.57 g (3.53 mmol) of *tert*-butylphenylketimine to afford reddish-violet crystals of **2**, which crystallize at 4 °C. Yield: 0.753 g (48%). Mp: 118−120 °C. Anal. Calcd for $C_{20}H_{42}FeNP_3$: C, 53.94; H, 9.51; N, 3.15; P, 20.87. Found: C, 53,89; H, 9.35; N, 3.61; P, 19.03. IR (Nujol, cm^{-1}): 3335 m (ν H−N=C); 3060 m, 3026 m (ν H−C=C); 1795 m_{br} (ν Fe−H); 1565 m (ν C=C); 1433 s (δ_{as} PCH_3); 1389 s; 1357 m; 1293 m, 1270 s (δ_s PCH_3); 1194 w; 1173 w; 1149 w; 999 vw; 940 vs (ρ_1 PCH_3); 852 m, 843 m (ρ_2 PCH_3); 813 w; 770 w, 730 s (γ $C-H_{arom}$); 698 m (ν_{as} PC_3); 656 s (ν_s PC_3); 618 vw; 506 vw; 409 s. ^1H NMR (d_8-THF, 300 K, ppm): −17.5 (dt, $^2J_{P,H} = 21.8$ Hz, $^2J_{P,H} = 80.0$ Hz, 1H, Fe−H); 0.88 (s, 18H; PCH_3), 1.40 (d, $^2J_{P,H} = 4.5$ Hz, 9H, PCH_3); 1.46 (s, 9H; $C(CH_3)_3$); 6.71 (dd, $^3J_{H,H} = 6.5$ Hz, $^3J_{H,H} = 7.6$ Hz, 2H, Ar−H); 7.74 (d, $^3J_{H,H} = 7.4$ Hz, 1H, Ar−H); 7.85 (d, $^3J_{H,H} = 6.5$ Hz, 1H; Ar−H); 9.13 (s, 1H, N−H). $^{13}C\{^1H\}$ NMR (d_8-THF, 300 K, ppm): 22.3 (dt, $^3J_{P,C} = 2.6$ Hz, $^1J_{P,C} = 12.8$ Hz, PCH_3); 23.3 (td, $^1J_{P,C} = 12.8$ Hz, $^3J_{P,C} = 2.6$ Hz, PCH_3); 29.8 (s, $C(CH_3)_3$); 40.1 (s, $C(CH_3)_3$); 117.6 (s, CH); 122.4 (s, CH); 126.5 (s, CH); 144.8 (s, C); 152.9 (s, CH); 186.1 (m; C=N), 200.1 (m; Fe−C). $^{31}P\{^1H\}$ NMR (d_8-THF, 300 K, ppm): 18.2 (d, $^2J_{P,P} = 36.5$ Hz, 2P, PCH_3); 23.7 (t, $^2J_{P,P} = 36.5$ Hz, 1P, PCH_3).

Synthesis of Hydrido[2-[(imino-*κN*)phenylmethyl]-2-methylphenyl-*κC*]tris (trimethylphosphine)iron(II) (3). $Fe(CH_3)_2(PMe_3)_4$ (0.94 g, 2.41mmol) in pentane was combined with 0.44 g (2.41 mmol) of diphenylketimine to afford violet crystals of **3**, which crystallize at −27 °C. Yield: 0.740 g (74%). Mp: 108−110 °C. Anal. Calcd for $C_{23}H_{40}FeNP_3$: C, 57.63; H, 8.41; N, 2.92; P, 19.39. Found: C, 58.01; H, 8.43; N, 2.92; P, 18.99. IR (Nujol, cm^{-1}): 3279 vw (ν H−N=C); 3063 vw, 3021 vw (ν H−C=C); 1761 s (ν Fe−H); 1570 w (ν C=C), 1500 w (ν C=N); 1439 w, 1420 vw (δ_{as} PCH_3);

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1396 m; 1293 m, 1268 m (δ_s PCH$_3$), 1277 vw; 1152 vw; 1111 vw; 1091 vw; 1042 vw; 993 vw; 955 w, 935 vs (ρ_1 PCH$_3$); 845 m (ρ_2 PCH$_3$); 802 vw; 764 m, 729 s (γ C−H$_{arom}$); 707 s, 681 w (ν_{as} PC$_3$); 660 m, 650 m (νs PC$_3$); 598 m, 505 w (ν Fe−C); 482 w. ^{1}H NMR (d_8-THF, 300 K, ppm): −17.2 (dt, $^2J_{P,H}$ = 22.5 Hz, $^2J_{P,H}$ = 82.3 Hz, 1H, Fe−H); 0.99 (s, 18H, PCH$_3$); 1.41 (d, $^2J_{P,H}$ = 3.3 Hz, 9H, PCH$_3$); 2.21 (s, 3H, Ar−CH$_3$); 6.65 (t, $^3J_{H,H}$ = 6.0 Hz, 1H, Ar−H); 6.79 (t, $^3J_{H,H}$ = 6.1 Hz, 1H, Ar−H); 7.02 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, Ar−H); 7.10 (t, $^3J_{H,H}$ = 6.1 Hz, 1H, Ar−H); 7.16 (t, $^3J_{H,H}$ = 6.9 Hz, 1H, Ar−H); 7.23 (m, 2H, Ar−H); 7.89 (s, 1H, Ar−H); 9.25 (s, 1H, N−H). ^{13}C NMR (d_8-THF, 300 K, ppm): 21.1 (s, Ar−CH$_3$); 23.2 (m, PCH$_3$); 118.2 (s, CH); 122.8 (s, CH); 126.4(d, $^3J_{P,C}$ = 8.1 Hz, CH), 128.5 (s, CH); 129.4 (s, CH); 131.2 (s; C); 136.6 (s, C); 142.6 (s, C); 147.3 (s, CH); 152.1 (s, CH); 181.2 (d, $^3J_{P,C}$ = 9.8 Hz, *C*=N); 203.1 (m, Fe−C). ^{31}P NMR (d_8-THF, 296 K, ppm): 15.7 (m, 2P, PCH$_3$); 21.2 (t, $^2J_{P,P}$ = 38.3 Hz, 1P, PCH$_3$).

Synthesis of Methyl[2-[(methylimino-*κN*)methyl]phenyl-*κC*]tris(trimethylphosphine)iron(II) (4). Fe(CH$_3$)$_2$(PMe$_3$)$_4$ (1.0 g, 2.56 mmol) was combined with 0.31 g (2.56 mmol) of *N*-methylbenzylidenimine in pentane to afford violet crystals of **4**, which crystallize at 4 °C. Yield: 0.753 g (65%). Mp: 115−117 °C (dec). Anal. Calcd for $C_{18}H_{38}FeNP_3$: C, 51.81; H, 9.18; N, 3.36; P, 22.27. Found: C, 51.52; H, 9.38; N, 3.37; P, 22.27. IR (Nujol, cm^{-1}): 3053 vw, 3034 vw (ν H−C=C); 1572 m (ν C=C); 1521 m (ν C=N); 1416 w (δ_{as} PCH$_3$); 1294 m, 1276 s (δ_s PCH$_3$); 1221 w; 1180 w (δ_s Fe−CH$_3$); 1118 w; 1020 w; 996 w; 937 vs (ρ_1 PCH$_3$); 844 m (ρ_2 PCH$_3$); 746 w, 730 m (γ C−H$_{arom}$); 712 vw, 702 w (ν_{as} PC$_3$); 677 w, 658 w (ν_s PC$_3$); 646 vw. ^{1}H NMR (d_8-THF, 298 K, ppm): −1.38 (s$_{br}$, 3H, Fe−CH$_3$); 0.71 (s$_{br}$, 18H, PCH$_3$); 1.49 (s$_{br}$, 9H, PCH$_3$); 3.65 (s, 3H, N−CH$_3$); 6.74 (s, 1H, Ar−H); 6.85 (s, 1H, Ar−H); 7.30 (s, 1H, Ar−H); 7.87 (s, 1H, Ar−H); 8.48 (s, 1H, N=C−H). ^{13}C{^{1}H} NMR (d_8-THF, 298 K, ppm): −16.6 (dt, $^2J_{P,C}$ = 25.6 Hz, $^2J_{P,C}$ = 8.2 Hz, Fe−CH$_3$); 16.9 (dt′ $|^1J_{P,C} + {}^3J_{PC}|$ = 9.3 Hz, $^3J_{PC}$ = 2.3 Hz, PCH$_3$); 24.0 (d, $^1J_{P,C}$ = 12.5 Hz, PCH$_3$), 54.8 (d, $^3J_{P,C}$ = 3.6 Hz, N−CH$_3$); 119.1 (s, CH); 124.7 (s, CH); 126.0 (s, CH); 143.5 (s, CH); 149.5 (s, C); 174.4 (d, $^3J_{P,C}$ = 5.5 Hz, C=N), 206.6 (dt, $^2J_{P,C}$ = 26.2 Hz, $^2J_{P,C}$ = 6.2 Hz, Fe−C). ^{31}P{^{1}H} NMR (d_8-THF, 296 K, ppm): 7.6 (t, $^2J_{P,P}$ = 35.6 Hz, 1P, PCH$_3$), 16.7 (d, $^2J_{P,P}$ = 35.6 Hz, 2P, PCH$_3$).

Synthesis of Methyl[2-[[(1-methylethyl)imino]methyl]phenyl-*κC*]tris(trimethylphosphine)iron(II) (5). Fe(CH$_3$)$_2$(PMe$_3$)$_4$ (1.06 g, 2.72 mmol) in pentane was combined with 0.39 g (2.72 mmol) of *N*-(1-methylethyl)benzylidenimine to afford violet crystals of **5**, which crystallize at −27 °C. Yield: 0.840 g (69%). Mp: 116−118 °C. Anal. Calcd for $C_{20}H_{42}FeNP_3$: C, 53.94; H, 9.51; N, 3.15; P, 20.87. Found: C, 54.09; H, 8.54; N, 2.88; P, 19.75. IR (Nujol, cm^{-1}): 3037 vw (ν H−C=C); 1571 m, 1561 m (ν C=C); 1519 m (ν C=N); 1415 s (δ_{as} PCH$_3$); 1360 w; 1292 s, 1272 s (δ_s PCH$_3$); 1222 m; 1162 m (δ_s Fe−CH$_3$); 1148 m; 1107 m; 1031 m; 941 vs (ρ_1 PCH$_3$); 868 w; 846 m (ρ_2 PCH$_3$); 748 s, 729 s (γ C−H$_{arom}$); 708 m, 695 s (ν_{as} PC$_3$); 658 s (ν_s PC$_3$); 636 w; 567 vw; 537 vw; 451 vw. ^{1}H NMR (d_8-THF, 298 K, ppm): −1.06 (s$_{br}$, 3H, Fe−CH$_3$); 0.91 (s$_{br}$, 18H, PCH$_3$); 1.16 (s$_{br}$, 9H, PCH$_3$); 1.33 (d, $^3J_{H,H}$ = 6.7 Hz, 6H, CH−CH$_3$); 3.44−3.48 (m, 1H, NC*H*(CH$_3$); 6.96 (s, 1H, Ar−H); 7.20 (s, 1H, Ar−H); 7.52 (s, 1H, Ar−H); 7.83 (s, 1H, Ar−H); 8.36 (s, 1H, N=C−H). ^{13}C{^{1}H} NMR (d_8-THF, 298 K, ppm): −14.2 (dt, $^2J_{P,C}$ = 25.4 Hz, $^2J_{P,C}$ = 8.1 Hz, Fe−CH$_3$); 15.7 (dt′ $|^1J_{P,C} + {}^3J_{PC}|$ = 9.1 Hz, $^3J_{PC}$ = 2.1 Hz, PCH$_3$); 22.1 (d, $^1J_{P,C}$ = 12.5 Hz, PCH$_3$), 25.4 (s, CH−*C*H$_3$); 54.8 (d, $^3J_{P,C}$ = 4.0 Hz, N−*C*H−CH$_3$); 121.1 (s, CH); 128.7 (s, CH); 129.2 (s, CH); 139.6 (s, CH); 149.5 (s, C); 169.7 (d, $^3J_{P,C}$ = 5.5 Hz, C=N), 200.7 (dt, $^2J_{P,C}$ = 20.2 Hz, $^2J_{P,C}$ = 7.2 Hz, Fe−C). ^{31}P{^{1}H} NMR (d_8-THF, 296 K, ppm): 7.1 (t, $^2J_{P,P}$ = 31.0 Hz, 1P, PCH$_3$), 15.6 (d, $^2J_{P,P}$ = 33.6 Hz, 2P, PCH$_3$).

Synthesis of Methyl[2-[(phenylimino-*κN*)methyl]phenyl-*κC*]tris(trimethylphosphine)iron(II) (6). Fe(CH$_3$)$_2$(PMe$_3$)$_4$ (1.40 g, 3.58 mmol) in pentane was combined with 0.65 g (3.58 mmol) of *N*-phenylbenzylidenimine to give petroleum green crystals of **6**, which crystallize at 4 °C. Yield: 1.480 g (73%). Mp: 119−121 °C. Anal. Calcd for $C_{23}H_{40}FeNP_3$: C, 57.63; H, 8.41; N, 2.92; P, 19.39. Found: C, 57.80; H, 8.10; N, 2.95; P, 19.32. IR (Nujol, cm^{-1}): 3038 vw (ν H−C=C); 1594 w, 1571 w (ν C=C); 1543 w (ν C=N); 1422 m, 1412 w (δ_{as} PCH$_3$); 1333 m; 1295 m, 1277 m (δ_s PCH$_3$); 1223 vw; 1193 w, 1170 w (δ_s Fe−CH$_3$); 1149 w; 1072 vw; 1026 vw; 993 vw; 942 vs (ρ_1 PCH$_3$); 886 w; 852 m (ρ_2 PCH$_3$); 765 s, 750 m (γ C−H$_{arom}$); 727 s, 701 s (ν_{as} PC$_3$); 659 w (ν_s PC$_3$); 636 vw; 572 w; 537 vw. ^{1}H NMR (d_8-THF, 300 K, ppm): −0.96 (s$_{br}$, 3H, Fe−CH$_3$); 1.11 (s, 18H, PCH$_3$); 1.42 (d, $^2J_{P,H}$ = 4.5 Hz, 9H, PCH$_3$); 6.82−7.06 (m, 2H, Ar−H); 7.14−7.26 (m, 3H; Ar−H); 7.33 (t, $^3J_{H,H}$ = 7.0 Hz, 1H, Ar−H); 7.41 (t, $^3J_{H,H}$ = 7.1 Hz, 1H, Ar−H); 7.50 (t, $^3J_{H,H}$ = 7.1 Hz, 1H, Ar−H); 7.83 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, Ar−H); 8.38 (s, 1H, H−C=N). ^{13}C{^{1}H} NMR (d_8-THF, 300 K, ppm): −13.8 (dt, $^2J_{P,C}$ = 25.6 Hz, $^2J_{P,C}$ = 8.2 Hz, Fe−CH$_3$); 14.2 (dt′ $|^1J_{P,C} + {}^3J_{PC}|$ = 9.3 Hz, $^3J_{P,C}$ = 2.3 Hz, PCH$_3$); 22.0 (d, $^1J_{P,C}$ = 12.5 Hz, PCH$_3$); 119.0 (s, CH); 122.1 (s, CH); 127.0(s, CH); 128.1 (s, CH); 129.0(s, CH); 129.3 (s, CH); 131.0 (s, CH); 153.2 (s, C); 169.7 (s, C); 171.7 (d, $^3J_{P,C}$ = 5.5 Hz, C=N), 203.7 (dt, $^2J_{P,C}$ = 22.2 Hz, $^2J_{P,C}$ = 5.5 Hz, Fe−C$_m$). ^{31}P{^{1}H} NMR (d_8-THF, 296 K, ppm): 8.2 (t, $^2J_{P,P}$ = 37.4 Hz, 1P, PCH$_3$), 19.1 (d, $^2J_{P,P}$ = 37.4 Hz, 2P, PCH$_3$).

General Procedure for Iodomethane Reactions. Iodomethane was added to a sample of cyclometalated complex in pentane at −70 °C, and the mixture was allowed to warm to 20 °C. After 5 h stirring, the mixture was filtered and the solution was kept at 4 °C to afford crystals.

Synthesis of Iodo[2-[(imino-*κN*)phenylmethyl]phenyl-*κC*]tris(trimethylphosphine)iron(II) (7). **1** (610 mg, 1.31 mmol) was combined with 186 mg (0.82 mL, 1.31 mmol) of CH$_3$I in pentane to afford reddish-pink crystals of **7**, which crystallize at 4 °C. Yield: 0.597 g (77%). Mp: 143−145 °C. Anal. Calcd for $C_{22}H_{37}FeINP_3$: C, 44.69; H, 6.31; N, 2.37; P, 15.72. Found: C, 44.68; H, 6.67; N, 2.31; P, 15.64. IR (Nujol, cm^{-1}): 3287 w (ν H−N=C); 3055 w (ν H−C=C); 1597 vw, 1572 m, 1513 m (ν C=C); 1489 vw (ν C=N); 1407 m (δ_{as} PCH$_3$); 1298 m, 1271 m (δ_s PCH$_3$); 1236 w; 1213 w; 1157 w; 1099 vw; 1077 vw; 995 w; 945 vs (ρ_1 PCH$_3$); 847 s (ρ_2 PCH$_3$); 783 s, 755 w, 727 s (γ C−H$_{arom}$); 700 vs (ν_{as} PC$_3$); 664 m (ν_s PC$_3$); 589 w; 513 w (ν Fe−C); 463 vw. ^{1}H NMR (d_8-THF, 300 K, ppm): 1.09 (t′, $|^2J_{P,H} + {}^4J_{P,H}|$ = 6.6 Hz, 18H, PCH$_3$); 1.66 (d, $^2J_{P,H}$ = 6.6 Hz, 9H, PCH$_3$); 6.67 (t, $^3J_{H,H}$ = 7.3 Hz, 1H, Ar−H); 6.79 (dt, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, Ar−H); 7.43 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 0.9 Hz, 1H, Ar−H); 7.47 (td, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, Ar−H); 7.49−7.53 (m, 2H, Ar−H); 7.57−7.59 (t, $^3J_{H,H}$ = 7.8 Hz, 3H, Ar−H); 7.61 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, Ar−H); 9.49 (s$_{br}$, 1H, N−H). ^{13}C{^{1}H} NMR (d_8-THF, 300 K, ppm): 19.1 (t′, $|^1J_{P,C} + {}^3J_{P,C}|$ = 22.3 Hz, PCH$_3$); 24.2 (d, $^1J_{P,C}$ = 18.8 Hz, PCH$_3$); 119.1 (s, CH); 127.1 (s, CH); 128.3 (s, CH); 129.7 (s, CH), 129.9 (s, CH); 149.4 (d, $^4J_{P,C}$ = 4.8 Hz, C); 181.9 (m, C=N), 208.1 (m, Fe−C). ^{31}P{^{1}H} NMR (d_8-THF, 296 K, ppm): 11.3 (d, $^2J_{P,P}$ = 57.0 Hz, 2P, PCH$_3$), 17.7 (t, $^2J_{P,P}$ = 57.0 Hz, 1P, PCH$_3$).

Synthesis of Iodo[2-[(imino-*κN*)phenylmethyl]-1,1-dimethylethyl-*κC*]tris(trimethylphosphine)iron(II) (8). **2** (774 mg, 1.74 mmol) was combined with 247 mg (1.09 mL, 1.74 mmol) of CH$_3$I in pentane to afford reddish-pink crystals of **8**, which crystallize at 4 °C. Yield: 0.745 g (75%). Mp: 160−162 °C (dec). Anal. Calcd for $C_{20}H_{41}FeINP_3$: C, 42.05; H, 7.23; N, 2.45; P, 16.27. Found: C, 41.85; H, 6.95; N, 2.20; P, 16.55. IR (Nujol, cm^{-1}): 3320 w (ν H−N=C); 3070 vw, 3042 vw, 3012 vw (ν H−C=C), 1565 m (ν H−C=C); 1565 m, 1556 w (ν C=C); 1525 vw (ν C=N); 1406 m (δ_{as} PCH$_3$); 1353 w; 1297 m, 1281 m (δ_s PCH$_3$); 1231 m; 1205 vw; 1176 vw; 1152 vw; 1107 w; 1016 w; 999 w; 941 vs (ρ_1 PCH$_3$); 868 vw; 851 m (ρ_2 PCH$_3$); 815 w; 776 w, 738 s (γ C−H$_{arom}$); 716 s, 692 w (ν_{as} PC$_3$); 660 m (ν_s PC$_3$); 648 vw; 507 vw. ^{1}H NMR (d_8-THF, 300 K, ppm): 1.06 (s, 18H, PCH$_3$), 1.51 (s, 9H, C(CH$_3$)$_3$); 1.61 (d, $^2J_{P,H}$ = 5.9 Hz, PCH$_3$); 6.69 (m, 2H, Ar−H); 7.51 (d,$^4J_{P,H}$

Table 5. Crystal Data for Compounds 1−4 and 6

	1	2	3	4	6
empirical formula	$C_{22}H_{38}FeNP_3$	$C_{20}H_{42}FeNP_3$	$C_{23}H_{40}FeNP_3$	$C_{18}H_{38}FeNP_3$	$C_{23}H_{40}FeNP_3$
molecular mass	465.29	445.31	479.32	417.25	479.32
cryst size [mm]	0.12 × 0.10 × 0.08	0.40 × 0.20 × 0.18	0.45 × 0.30 × 0.20	0.15 × 0.10 × 0.10	0.12 × 0.10 × 0.08
cryst syst	triclinic	orthorhombic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	*Pnma*	$P\bar{1}$	$P\bar{1}$	$P21/n$
a [Å]	9.2765(12)	9.6581(7)	9.2537(4)	8.6470(14)	8.6450(6)
b[Å]	11.4028(13)	13.5905(10)	9.3794(4)	14.882(4)	17.2303(9)
c [Å]	13.4638(16)	18.7569(14)	14.8576(6)	17.814(3)	17.5171(12)
α [deg]	65.433(9)	90	94.603(1)	103.140(16)	90
β [°deg]	78.456(10)	90	90.404(1)	95.330(13)	102.068(6)
γ [deg]	74.456(10)	90	93.928(1)	90.060(17)	90
V [Å^3]	1243.2(3)	2462.0(3)	1282.27(9)	2222.1(7)	2551.6(3)
Z	2	4	2	4	4
D_{calcd} [g/cm^3]	1.243	1.201	1.241	1.247	1.248
μ(Mo Kα) [mm^{-1}]	0.807	0.812	0.784	0.895	0.788
temperature [K]	150(2)	298(2)	298(2)	150	150(2)
θ range [deg]	$1.67 \leq \theta \leq 26.92$	$1.85 \leq \theta \leq 28.20$	$2.18 \leq \theta \leq 28.24$	$1.62 \leq \theta \leq 26.86$	$1.68 \leq \theta \leq 26.85$
h	$-11 \leq h \leq 11$	$-11 \leq h \leq 12$	$-12 \leq h \leq 12$	$-10 \leq h \leq 10$	$-10 \leq h \leq 10$
k	$-14 \leq k \leq 14$	$-18 \leq k \leq 18$	$-12 \leq k \leq 12$	$-18 \leq k \leq 18$	$-21 \leq k \leq 21$
l	$-17 \leq l \leq 17$	$-24 \leq l \leq 24$	$-19 \leq l \leq 18$	$-22 \leq l \leq 22$	$-22 \leq l \leq 22$
no. reflns measd	18 486	29 358	16 331	26 214	35 729
no. unique data	5253 [$R_{\mathrm{int}} = 0.0990$]	3145 [$R_{\mathrm{int}} = 0.0486$]	6316 [$R_{\mathrm{int}} = 0.0194$]	9308 [$R_{\mathrm{int}} = 0.0727$]	5410 [$R_{\mathrm{int}} = 0.0562$]
no. params	396	143	263	437	253
no. restraints	0	0	0	0	0
GoF on F^2	1.109	0.997	1.067	1.056	1.080
R_1 [$I \geq 2\sigma(I)$]	0.0294	0.0378	0.0365	0.0525	0.0290
wR_2 (all data)	0.0791	0.1098	0.1048	0.1266	0.0737

= 7.4 Hz, 1H, Ar−H); 7.76 (d, $^3J_{\mathrm{H,H}}$ = 6.7 Hz, 1H, Ar−H); 9.50 (s_{br}, 1H, N−H). ^{13}C{^{1}H} NMR (d_8-THF, 300 K, ppm): 18.9 (t′, $|^1J_{\mathrm{P,C}} + {}^3J_{\mathrm{P,C}}|$ = 22.1 Hz, PCH_3); 24.3 (td, $^1J_{\mathrm{P,C}}$ = 18.5 Hz, $^3J_{\mathrm{P,C}}$ = 2.2 Hz, PCH_3); 29.3(s, $\mathrm{C\underline{C}H_3}$); 39.8 (s, $\mathrm{\underline{C}CH_3}$); 118.3 (s, CH); 126.2 (s, CH); 129.3 (s, CH); 146.1 (d, $^3J_{\mathrm{P,C}}$ = 7.9 Hz, CH); 148.3 (d, $^4J_{\mathrm{P,C}}$ = 4.6 Hz, C); 187.8 (t, $^3J_{\mathrm{P,C}}$ = 8.6 Hz, C═N); 208.4 (m, Fe−C). ^{31}P{^{1}H} NMR (d_8-THF, 300 K, ppm): 13.1 (d, $^2J_{\mathrm{P,P}}$ = 55.9 Hz, 2P, PCH_3); 19.9 (t, $^2J_{\mathrm{P,P}}$ = 55.9 Hz, 1P, PCH_3).

Synthesis of Iodo[2-[(imino-κ*N*)phenylmethyl]-2-methylphenyl-κ*C*]tris (trimethylphosphine)iron(II) (9). 3 (598 mg, 1.25 mmol) in pentane was combined with 177 mg (0.78 mL, 1.25 mmol) of CH_3I to afford reddish-pink crystals of **9**, which crystallize at 4 °C. Yield: 544 mg (72%). Mp: 146−148 °C (dec). Anal. Calcd for $C_{23}H_{39}FeINP_3$: C, 45.64; H, 6.49; N, 2.31; P, 15.35. Found: C, 45.17; H, 5.38; N, 1.80; P, 16.28. IR (Nujol, cm^{-1}): 3289 vw (ν H−N═C); 3050 w, 3019 vw (ν H−C═C); 1570 m (ν C═C); 1514 w (ν C═N); 1408 m (δ_{as} PCH_3); 1297 w, 1280 w (δ_{s} PCH_3), 1231 vw; 1152 vw; 993 vw; 940 vs (ρ_1 PCH_3); 850 m (ρ_2 PCH_3); 782 w, 760 m (γ C−H_{arom}); 738 s, 719 m (ν_{as} PC_3); 658 m (ν_{s} PC_3); 596 w; 500 vw. ^{1}H NMR (d_8-THF, 300 K, ppm): 1.17 (t′ $|^2J_{\mathrm{P,H}} + {}^4J_{\mathrm{P,H}}|$ = 6.4 Hz, 18H, PCH_3); 1.67 (d, $^2J_{\mathrm{P,H}}$ = 6.4 Hz, 9H, PCH_3); 2.17 (s, 3H, Ar−CH_3); 6.61 (t, $^3J_{\mathrm{H,H}}$ = 7.3 Hz, 1H, Ar−H); 6.75 (dt, $^3J_{\mathrm{H,H}}$ = 8.1 Hz, $^4J_{\mathrm{H,H}}$ = 1.4 Hz, 1H, Ar−H); 7.01 (d, $^3J_{\mathrm{H,H}}$ = 8.1 Hz, 1H, Ar−H); 7.31 (t, $^3J_{\mathrm{H,H}}$ = 7.8 Hz, 2H, Ar−H); 7.40 (dt, $^3J_{\mathrm{H,H}}$ = 7.4 Hz, $^4J_{\mathrm{H,H}}$ = 1.4 Hz, 1H, Ar−H); 7.42 (dd, $^3J_{\mathrm{H,H}}$ = 6.5 Hz, $^4J_{\mathrm{H,H}}$ = 1.2 Hz, 1H, Ar−H); 7.62 (d, $^3J_{\mathrm{H,H}}$ = 7.8 Hz 1H, Ar−H); 9.42 (s, 1H, N−H). ^{13}C{^{1}H} NMR (d_8-THF, 300 K, ppm): 19.5 (t′ $|^1J_{\mathrm{P,H}} + {}^3J_{\mathrm{P,H}}|$ = 22.5 Hz, PCH_3); 21.8 (s, Ar−CH_3); 24.1 (d, $^1J_{\mathrm{P,C}}$ = 18.8 Hz, PCH_3); 118.9 (s, CH); 126.7 (s, CH); 127.4(s, CH), 128.3 (s, C); 129.4 (s, CH); 130.1 (d; $^3J_{\mathrm{P,C}}$ = 16.9 Hz, CH); 131.8 (s, C); 136.1 (s, C); 145.7 (d, $^4J_{\mathrm{P,C}}$ = 7.1 Hz, CH); 182.9 (m, C═N); 228.4 (m, Fe−C). ^{31}P{^{1}H} NMR (d_8-THF, 300 K, ppm): 10.8 (d, $^2J_{\mathrm{P,P}}$ = 57.5 Hz, 2P, PCH_3); 19.2 (t, $^2J_{\mathrm{P,P}}$ = 57.5, 1P, PCH_3.

Synthesis of Iodo[2-[(methylimino-κ*N*)methyl]phenyl-κ*C*]tris(trimethylphosphine)iron(II) (10). 4 (623 mg, 1.49 mmol) was combined with 211 mg (0.93 mL, 1.49 mmol) of CH_3I in pentane to afford rose crystals of **10**, which crystallize at 4 °C. Yield: 426 mg (72%). Mp: 142−144 °C. Anal. Calcd for $C_{17}H_{35}FeINP_3$: C, 38.59; H, 6.67; N, 2.65; P, 17.56. Found: C, 38.86; H, 6.53; N, 2.60; P, 17.58. IR (Nujol, cm^{-1}): 3056 vw (ν H−C═C); 1591 s, 1572 s (ν C═C); 1529 m (ν C═N); 1421 s (δ_{as} PCH_3); 1296 s, 1280 s, 1273 s (δ_{s} PCH_3); 1236 w; 1219 w; 1156 w; 1124w; 1105 w; 1038 vw; 1008 w; 997 w; 939 vs (ρ_1 PCH_3); 856 m (ρ_2 PCH_3); 753 m, 746 m (γ C−H_{arom}); 727 s, 713 s (ν_{as} PC_3); 694 vw; 663 m (ν_{s} PC_3); 642 vw; 537 vw, 471 vw. ^{1}H NMR (d_8-THF, 298 K, ppm): 1.14 (s, 18H, PCH_3); 1.56 (s, 9H, PCH_3); 3.83 (s, 3H, N−CH_3); 6.70 (m, 2H, Ar−H); 7.27 (s, 1H, Ar−H); 7.54 (s, 1H, Ar−H); 8.43 (s, 1H, N═C−H). ^{13}C{^{1}H} NMR (d_8-THF, 298 K, ppm): 18.9 (t′ $|^1J_{\mathrm{P,C}} + {}^3J_{\mathrm{P,C}}|$ = 21.3 Hz, PCH_3); 24.5 (d, $^1J_{\mathrm{P,C}}$ = 20.9 Hz, PCH_3); 55.3 (s, N-CH_3); 119.3 (s, CH); 126.7 (m, CH); 128.3 (s, CH); 146.3 (s, C); 162.4 (s, CH); 174.7 (s, C═N), 212.7 (s, Fe−C). ^{31}P{^{1}H} NMR (d_8-THF, 296 K, ppm): 5.8 (d, $^2J_{\mathrm{P,P}}$ = 54.3 Hz, 2P, PCH_3); 14.9 (t, $^2J_{\mathrm{P,P}}$ = 54.3 Hz, 1P, PCH_3).

Synthesis of Iodo[2-[[(1-methylethyl)imino-κ*N*]methyl]phenyl-κ*C*]tris (trimethylphosphine)iron(II) (11). 5 (1.02 g, 2.29 mmol) was combined with 0.33 g (0.93 mL, 1.43 mmol) of CH_3I in pentane to afford light violet crystals of **11**, which crystallize at 4 °C. Yield: 0.88 g (69%). Mp: 145−147 °C. Anal. Calcd for $C_{19}H_{39}FeINP_3$: C, 40.96; H, 7.05; N, 2.51; P, 16.68. Found: C, 40.94; H, 7.15; N, 2.46; P, 16.47. IR (Nujol, cm^{-1}): 3088 w (ν H−C═C); 1594 m, 1572 m (ν C═C); 1533 w (ν C═N); 1423 m (δ_{as} PCH_3); 1313 w; 1298 s, 1273 m (δ_{s} PCH_3); 1236 w; 1221 w; 1163 w; 1121w; 1108 w; 1005 w; 944 vs (ρ_1 PCH_3); 870 w; 844 w (ρ_2 PCH_3); 746 m (γ C−H_{arom}); 728 s, 714 m (ν_{as} PC_3); 660 m (ν_{s} PC_3). ^{1}H NMR (d_8-THF, 298 K, ppm): 0.84 (t′, $|^2J_{\mathrm{P,H}} + {}^4J_{\mathrm{P,H}}|$ = 5.9 Hz, 18H, PCH_3); 1.69 (d, $^2J_{\mathrm{P,H}}$ = 6.4 Hz, 6H, $\mathrm{CH(C\underline{H}_3)_2}$); 1.50 (d, $^2J_{\mathrm{P,H}}$ = 6.4 Hz, 9H, PCH_3); 5.38 (sep, $^2J_{\mathrm{H,H}}$ = 6.2 Hz, 1H, $\mathrm{C\underline{H}(CH_3)_2}$); 7.11 (m, 1H, Ar−H); 7.17 (m, 1H, Ar−H); 7.51 (m, 1H, Ar−H); 7.65 (m, 1H, Ar−H), 8.29 (s, 1H, N═C−H). ^{13}C{^{1}H} NMR (d_8-THF, 298 K, ppm): 12.3 (t′ $|^1J_{\mathrm{P,C}} + {}^3J_{\mathrm{P,C}}|$ = 28.7 Hz, PCH_3); 15.8 (d, $^1J_{\mathrm{P,C}}$ = 20.3 Hz, PCH_3); 19.2 (s, $\mathrm{CH(\underline{C}H_3)_2}$); 49.5 (d, $^3J_{\mathrm{P,C}}$ = 13.9 ppm, $\mathrm{\underline{C}H(CH_3)_2}$); 129.1 (s, CH); 129.6 (d, $^4J_{\mathrm{P,C}}$ = 4.4 Hz, CH); 130.1 (s, CH); 131.2 (s, CH); 158.9 (s, C); 160.4 (s, C═N); 199.7 (s, Fe−C). ^{31}P{^{1}H} NMR (d_8-THF, 296 K, ppm): 28.3 (d, $^2J_{\mathrm{P,P}}$ = 28.3 Hz, 2P, PCH_3); 21.8 (t, $^2J_{\mathrm{P,P}}$ = 28.3 Hz, 1P, PCH_3).

General Procedure for Carbon Monoxide Reactions. A sample of cyclometalated complex was stirred under 1 bar of CO for 10 h. Upon filtration, the solution was cooled to 4 °C to afford crystals.

Synthesis of Methyl[2-[(methylimino-*κN*)methyl]phenyl-*κC*](carbonyl)bis(trimethylphosphine)iron(II) (12). A sample of **4** (770 mg, 1.84 mmol) in pentane was stirred under 1 bar of CO to provide reddish-pink crystals of **12**, which crystallize at −27 °C. Yield: 450 mg (66%). Mp: 134−136 °C. Anal. Calcd for $C_{16}H_{29}FeNOP_2$: C, 52.05; H, 7.92; N, 3.79; P, 16.78. Found: C, 52.30; H, 7.91; N, 3.10; P, 17.32. IR (Nujol, cm^{-1}): 3068 vw, 3028 vw (ν H−C═C); 1869 vs (ν C≡O); 1595 m, 1573 w (ν C═C); 1531 w (ν C═N); 1420 m (δ_{as} PCH_3); 1298 w, 1281 m (δ_s PCH_3); 1240 w; 1218 w; 1153 w (δ Fe−CH_3); 1036 vw; 1008 vw; 946 vs (ρ_1 PCH_3); 854 m (ρ_2 PCH_3); 751 m (γ C−H_{arom}); 722 s (ν_{as} PC_3); 668 m (ν_s PC_3); 646 w; 620 w, 607 w. ^1H NMR (d_8-THF, 298 K, ppm): −0.67 (t, $^3J_{P,H}$ = 6.8 Hz, 3H, Fe−CH_3); 0.89 (s, 18H, PCH_3); 3.34 (s, 3H, N−CH_3); 6.72 (t, $^3J_{H,H}$ = 6.0 Hz 1H, Ar−H); 6.79 (t, $^3J_{H,H}$ = 6.0 Hz, 1H, Ar−H); 7.34 (d, $^3J_{H,H}$ = 6.0 Hz, 1H, Ar−H); 7.96 (d, $^3J_{P,H}$ = 5.4 Hz, 1H, Ar−H); 8.33 (s, 1H, N═C−H). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, ppm): −11.5 (t, $^2J_{P,C}$ = 18.4 Hz, Fe−CH_3); 15.0 (t′ $|^1J_{P,C} + {}^3J_{PC}|$ = 23.0 Hz, PCH_3); 46.8 (s, N−CH_3); 120.0 (s, CH); 126.9 (s, CH); 128.1 (s, CH); 143.5 (s, CH); 148.9 (s, C); 174.3 (t, $^3J_{P,C}$ = 4.4 Hz, C═N), 211.6 (m, Fe−C); 224.2 (s, Fe−CO) ppm. $^{31}P\{^1H\}$ NMR (d_8-THF, 296 K, ppm): 19.1 (s, PCH_3) ppm.

Synthesis of Methyl[2-[[(1-methylethyl)imino-*κN*]methyl]phenyl-*κC*(carbonyl)bis(trimethylphosphine)iron(II) (13). A sample of **5** (650 mg, 1.46 mmol) in pentane was stirred under 1 bar of CO to provide reddish-pink crystals of **13**, which crystallize at −27 °C. Yield: 336 mg (58%). Mp: 131−133 °C. Anal. Calcd for $C_{18}H_{33}FeNOP_2$: C, 54.42; H, 8.37; N, 3.53; P, 15.59. Found: C, 54.46; H, 8.43; N, 3.53; P, 16.54. IR (Nujol, cm^{-1}): 3075 vw, 3040 w (ν H−C═C); 1879 vs (ν C≡O); 1591 m, 1573 w (ν C═C); 1532 w (ν C═N); 1420 m (δ_{as} PCH_3); 1299 w, 1279 m (δ_s PCH_3); 1239 vw; 1219 vw; 1151 vw (δ_s Fe−CH_3); 1126 vw; 1113 vw; 1032 vw; 1010 vw; 941 vs (ρ_1 PCH_3); 850 m (ρ_2 PCH_3); 754 m (γ C−H_{arom}); 721 s (ν_{as} PC_3); 667 (ν_s PC_3); 646 m; 629 w; 599 m. ^1H NMR (d_8-THF, 298 K, ppm): −0.59 (t, $^3J_{P,H}$ = 7.3 Hz, 3H, Fe−CH_3); 0.90 (s_{br}, 18H, PCH_3); 1.29 (d, $^3J_{H,H}$ = 6.5 Hz, 6H, $CH(\underline{CH_3})_2$); 4.08 (sep, $^3J_{H,H}$ = 6.5 Hz, 1H, $C\underline{H}(CH_3)_2$); 6.75 (t, $^3J_{H,H}$ = 6.9 Hz 1H, Ar−H); 6.82 (t, $^3J_{H,H}$ = 6.9 Hz 1H, Ar−H); 7.40 (d, $^3J_{H,H}$ = 7.2 Hz, 1H, Ar−H); 7.91 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, Ar−H); 8.49 (m, 1H, H−C═N). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, ppm): −13.2 (t, $^2J_{P,C}$ = 17.2 Hz, Fe−CH_3); 13.2 (t′, $|^1J_{P,C} + {}^3J_{PC}|$ = 11.2 Hz, PCH_3); 22.4 (s, $CH(\underline{C}H_3)_2$); 51.4 (s, $\underline{C}H(CH_3)_2$); 118.1 (s, CH); 124.9 (s, CH); 126.4 (s, CH); 141.4 (s, CH); 148.7 (s, C); 168.0 (t, $^3J_{P,C}$ = 3.6 Hz, CN); 207.3 (t, $^2J_{P,C}$ = 21.8 Hz, Fe−C); 222.6 (t, $^2J_{P,C}$ = 35.6 Hz, Fe−CO). $^{31}P\{^1H\}$ NMR (d_8-THF, 296 K, ppm): 18.7 (s, 2P, PCH_3).

Synthesis of Methyl[2-[(phenylimino-*κN*)methyl]phenyl-*κC*](carbonyl)bis (trimethylphosphine)iron(II) (14). A sample of **6** (490 mg, 1.02 mmol) in pentane was stirred under 1 bar of CO to provide reddish-pink crystals of **14**, which crystallize at −27 °C. Yield: 347 mg (73%). Mp: 137−139 °C (dec). Anal. Calcd for $C_{24}H_{29}FeNOP_2$: C, 58.48; H, 7.25; N, 3.25; P, 14.36. Found: C, 58.85; H, 6.81; N, 3.24; P, 14.35. IR (Nujol, cm^{-1}): 3075 vw, 3063 w, 3012 vw (ν H−C═C); 1870 vs (ν Fe−C≡O); 1576 m (ν C═C), 1514 m (ν C═N); 1350 vw (δ_{as} PCH_3); 1302 w, 1280 m (δ_s PCH_3); 1230 vw; 1193 m (δ_s Fe−CH_3); 1107 m_{br}; 1008 vw; 944 vs (ρ_1 PCH_3); 852 m (ρ_2 PCH_3); 768 m, 748 m (γ C−H_{arom}); 722 s, 701 m (ν_{as} PC_3); 670 w (ν_s PC_3); 645 w; 628 w; 600 m; 566 w. ^1H NMR (d_8-THF, 298 K, ppm): −0.71 (t, $^3J_{P,H}$ = 8.1 Hz, 3H, Fe−CH_3); 0.93 (t′ $|^2J_{P,H} + {}^4J_{P,H}|$ = 7.3 Hz, 18H, PCH_3); 6.83 (t, $^3J_{H,H}$ = 7.2 Hz 1H, Ar−H); 6.89 (t, $^3J_{H,H}$ = 7.2 Hz 1H, Ar−H); 7.02 (d, $^3J_{H,H}$ = 7.8 Hz, 2H, Ar−H); 7.19 (t, $^3J_{H,H}$ = 7.3 Hz, 1H, Ar−H); 7.33 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, Ar−H); 7.57 (d, $^3J_{H,H}$ = 7.4 Hz, 1H, Ar−H); 8.08 (d, $^3J_{H,H}$ = 7.3 Hz, 1H, Ar−H); 8.49 (t, $^4J_{P,H}$ = 4.2 Hz, 1H, N═C−H). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K, ppm): −7.1 (t, $^2J_{P,C}$ = 17.2 Hz, Fe−CH_3); 15.4 (t′ $|^1J_{P,C} + {}^3J_{PC}|$ = 23.2 Hz, PCH_3); 120.7 (s, CH); 125.3 (s, CH); 129.2 (s, CH); 130.8 (s, CH); 144.1 (s, CH); 150.5 (s, C); 152.9 (s, C); 175.8 (t, $^3J_{P,C}$ = 4.5 Hz, C═N), 215.8 (m, Fe−C); 224.9 (t, $^2J_{P,C}$ = 35.6 Hz, Fe−CO). $^{31}P\{^1H\}$ NMR (d_8-THF, 296 K, ppm): 18.3 (s, PCH_3).

In Situ Observation of Methane/Ethane. To detect gaseous products, we repeated the reactions of $Fe(PMe_3)_4$ and $Fe(CH_3)_2(PMe_3)_4$ with diphenylketimine and complex **4** with CH_3I in NMR Schlenk tubes by condensing 0.8 mL of d_8-THF to the starting materials. Under vacuum, the solutions were frozen to −196 °C, and the NMR tubes were sealed. The reactions were immediately monitored at room temperature by ^1H NMR spectroscopy for 2 h. Together with the all characteristic signals of expected products, CH_4 (0.22 ppm) and C_2H_6 (0.84 ppm) resonances were recorded in the high-field region.

General Comments on X-ray Diffraction Studies. Single crystals were sealed under argon in glass capillaries, whereas air-stable crystals were glued on a glass fiber. Data collections were performed on a STOE IPDSII image detector and on a Bruker AXS SMART APEX diffractometer using Mo Kα radiation (λ = 0.71019 Å). Details of the crystal structure are given in Table 5. Data collection:[45] Stoe X-AREA, Bruker SMART. Data reduction:[45] Stoe X-RED, Bruker SAINT. The structures were solved by direct methods using SHELXS-97, and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97.[46] Hydrogen atoms on C were placed at idealized positions (C−H = 0.93, 0.96 Å for methyl groups) and were allowed to ride on the parent atom [U_{iso}(H) = 1.2U(C) for CH groups and U_{iso}(H) = 1.5U(C) for methyl groups].

Supporting Information Available: . Structure determination summaries and listings of final atomic coordinates, thermal parameters, bond lengths, and bond angles for compounds **1**−**4**, **6**, **7**, **10**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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