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C_2-Symmetric Iron(II) Diphosphine−Dialkoxide Dicarbonyl and Related Complexes

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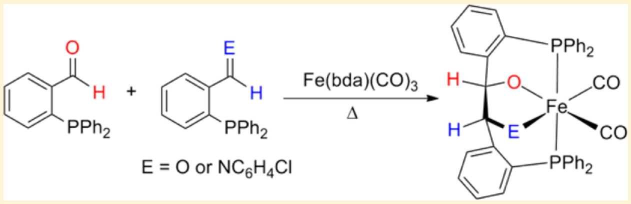
S *Supporting Information*



ABSTRACT: Reaction of Fe(bda)(CO)$_3$ (bda = benzylideneacetone) and Ph$_2$P-2-C$_6$H$_4$CHO (PCHO) affords the bisphosphine bisalkoxide complex Fe[(Ph$_2$PC$_6$H$_4$)$_2$C$_2$H$_2$O$_2$](CO)$_2$ (**1**) arising from the head-to-head coupling of two formyl groups concomitant with oxidation of Fe(0) to Fe(II). Crystallographic studies show that **1** features *cis* alkoxide ligands that are *trans* to CO; the two phosphine groups are mutually *trans* with a P−Fe−P angle of 167.44(4)°. The pathway leading to **1** was examined, starting with the adduct Fe(PCHO)(CO)$_4$ (**2**), which was obtained by addition of PCHO to Fe$_2$(CO)$_9$. Compound **2** decarbonylates to give tricarbonyl Fe(κ^1,η^2-PCHO)(CO)$_3$ (**3**), which features a π-bonded aldehyde. Photolysis of **2** gives a mixture of **3** and isomeric hydride HFe(κ^2-PCO)(CO)$_3$. Complex **3** reacts with an additional equivalent of PCHO to afford **1**, whereas treatment with PPh$_3$ afforded the substituted product Fe(κ^1,η^2-PCHO)(PPh$_3$)(CO)$_2$ (**4**). In **4**, the phosphine ligands are *trans* and the aldehyde is π-bonded. The geometry around Fe is pseudo trigonal bipyramidal. To gain insights into the mechanism and scope of the C−C coupling reaction, complexes were prepared with the imine Ph$_2$PC$_6$H$_4$CH═NC$_6$H$_4$Cl (abbreviated as PCHNAr), derived by condensation of 4-chloroaniline and PCHO. PCHNAr reacts with Fe$_2$(CO)$_9$ and with Fe(bda)(CO)$_3$ to afford the tetra- and tricarbonyl compounds Fe(PCHNAr)(CO)$_4$ (**5**) and Fe(PCHNAr)(CO)$_3$ (**6**), respectively. Treatment of **6** with PCHO gave the unsymmetrical C−C coupling complex Fe[(Ph$_2$PC$_6$H$_4$)$_2$CH(O)CH(NAr)](CO)$_2$ (**7**). Compound **7** was also prepared by the reaction of **3** and PCHNAr. The solid-state structure of **7**, as established by X-ray crystallography, is similar to that of **1** but with an amido group in place of one alkoxide. The deuterium-labeled phosphine aldehyde PCDO was prepared by the reaction of *ortho*-lithiated phosphine Ph$_2$PC$_6$H$_4$-2-Li with DMF-d_7. Reaction of **6** with PCDO gave **7**-d_1 with no scrambling of the deuterium label. Attempted oxidation of **1** with FcBF$_4$ (Fc$^+$ = ferrocenium) gave the adduct Fe[(Ph$_2$PC$_6$H$_4$)$_2$C$_2$H$_2$O$_2$(BF$_3$)$_2$](CO)$_2$ (**8**). The structures of **1** and **8** are almost identical. Compound **8** was independently synthesized by treating **1** with BF$_3$OEt$_2$ via the intermediacy of the 1:1 adduct, which was detected spectroscopically. Qualitative tests showed that **1** also reversibly protonates with HOSO$_2$CF$_3$ and binds TiCl$_4$.

■ INTRODUCTION

C_2-Symmetric tetradentate ligands represent an important class of reagents.[1] Their complexes are useful catalysts in various asymmetric catalytic transformations. For example, tetradentate bis(phenolate) ligands have been considered as feasible alternatives to the C_2-symmetric *ansa*-metallocene found in olefin polymerization catalysts.[2] Group 4 metal catalysts bearing such bis(phenolate) ligands with various additional neutral donors (such as N,[3] S,[4] or P[5]) have been heavily investigated. The binding mode of the bis(phenolate) ligands usually depends on the nature of the additional donors, the size of the metal ion, and the ligand framework.

Discovered more than 150 years ago, pinacol coupling remains a versatile tool for chemists to construct C−C bonds.[6] Numerous reagents have been developed for both stoichiometric and catalytic pinacol coupling reactions. More recently, stereoselection has been achieved using specifically designed metal complexes.[7] Among these metal reagents, reports of Fe-promoted pinacol coupling are rather limited. Pinacol coupling reactions have been studied in the presence of Fe(0) carbonyls and pyridine, and it was proposed that [Fe$_2$(CO)$_8$]$^{2-}$ is an important reactive intermediate in the process.[8] Combinations of FeCl$_3$/^{n}BuLi or (Bu$_4$N)$_2$[Fe$_4$S$_4$(SPh)$_4$]/^{n}BuLi have been shown to mediate the couplings of aromatic ketones and aldehydes in moderate yields.[9] Recently, an Fe(I) dinitrogen complex LFeNNFeL (L = β-diketiminato ligand) was shown to reduce acetophenone to afford the *rac*-diastereomer of the pinacolate.[10]

The discoveries reported in this paper grew from our work on phosphine-acyl chelates of Fe(II),[11] which represent structural models for the pyridinol-acyl chelates found in the hydrogenase Hmd.[12] This work led us to examine the addition of Ph$_2$PC$_6$H$_4$-2-CHO (abbreviated PCHO) to Fe(0) carbonyls. The coordination chemistry of PCHO with other metals is already well established, although mainly with second- and third-row metals.[13] Aside from forming simple κ^1-P adducts, PCHO has been shown to give κ^2-P,O chelate rings involving σ-bonding from the carbonyl oxygen, e.g., Re(CO)$_3$Cl(PCHO)[14] and RuCl$_2$(PCHO)$_2$.[15] In some complexes, the

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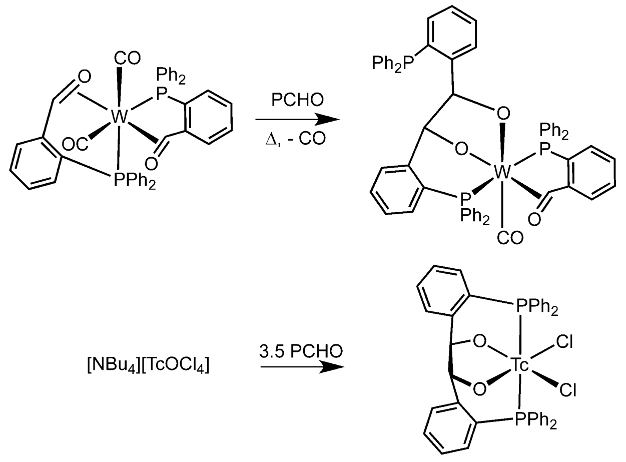
formyl group forms π-bonds to the metal, as illustrated by Cp*Co(PCHO)[16] and some W[17] and Mo[18] complexes. The addition of PCHO to electron-rich late transition metals, such as Rh(I),[19] Ir(I),[20] Pt(0),[21] and Co(I),[22] frequently results in chelate-assisted C−H bond activation to give phosphine acyl η^2-P-acyl derivatives. In two examples, pairs of PCHO ligands undergo C−C coupling to afford complexes of the glycolate ligand $[(Ph_2PC_6H_4)_2C_2H_2O_2]^{2-}$. The formation of the same P_2O_2 ligand can be templated on a Tc center.[23] Insights into the coupling process were obtained when starting with W(0) precursors,[17] which gives both κ^3- and κ^4-derivatives (Scheme 1), albeit in low yields.

Scheme 1. C−C Coupling Reactions of Ph_2P-2-C_6H_4CHO on W and Tc Templates



■ RESULTS AND DISCUSSION

Synthesis and Structure of $Fe[(Ph_2PC_6H_4)_2C_2H_2O_2]$-$(CO)_2$. Heating a THF solution of $Fe(bda)(CO)_3$ (bda = benzylideneacetone) in the presence of 2 equiv of PCHO gave an 89% yield of the yellow compound $Fe[(Ph_2PC_6H_4)_2C_2H_2O_2](CO)_2$ (**1**) (eq 1).

$$Fe(bda)(CO)_3 + 2Ph_2PC_6H_4CHO \rightarrow \underset{\mathbf{1}}{Fe[(Ph_2PC_6H_4)_2C_2H_2O_2](CO)_2} + bda + CO \tag{1}$$

The same product was also obtained in slightly lower yield by the reaction of PCHO with $Fe_2(CO)_9$ at 60 °C in THF. The solution IR spectrum of **1** featured a pair of comparably intense CO bands at 1965 and 2025 cm^{-1}. The ^{31}P NMR spectrum consisted of a singlet at δ 21.1. Aside from the phenyl signals, the ^1H NMR spectrum features a singlet at δ 4.49 that integrated in a 1:14 ratio relative to the phenyl signals.

Single-crystal X-ray diffraction confirmed that **1** is a ferrous complex of a bisphosphine glycolate ligand. The ligand results from the apparent head-to-head coupling of two formyl groups, which was confirmed by the distance between the two aliphatic carbon atoms (C(19)−C(26) = 1.549(4) Å). The *cis* alkoxide ligands are *trans* to CO, and the two phosphine groups are mutually *trans* with a P−Fe−P angle of 167.44(4)°. Few ferrous alkoxides are known, and fewer still with CO ligands.[24]

Studies on the C−C Coupling Pathway. We investigated the pathway for the formation of **1** starting with the adduct $Fe(PCHO)(CO)_4$ (**2**) (Scheme 2). This tetracarbonyl was obtained in good yield by addition of PCHO to $Fe_2(CO)_9$ at room temperature, with the concomitant formation of a small portion of tricarbonyl complex $Fe(PCHO)(CO)_3$ (**3**). Complex **2** displays an IR spectrum typical of phosphine adducts of the type $Fe(PR_3)(CO)_4$.[25] Photolysis of a toluene solution of **2** at room temperature resulted in decarbonylation to give a mixture of mainly two isomeric tricarbonyls as well as some **1**, which could be removed by hexane extraction of the two tricarbonyls. The initially formed tricarbonyls, assigned the formula $Fe(\kappa^1,\eta^2$-$PCHO)(CO)_3$ (**3**), feature the π-bonded

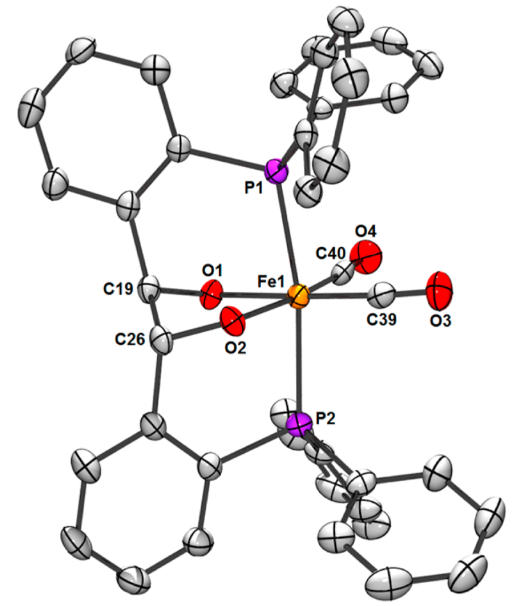
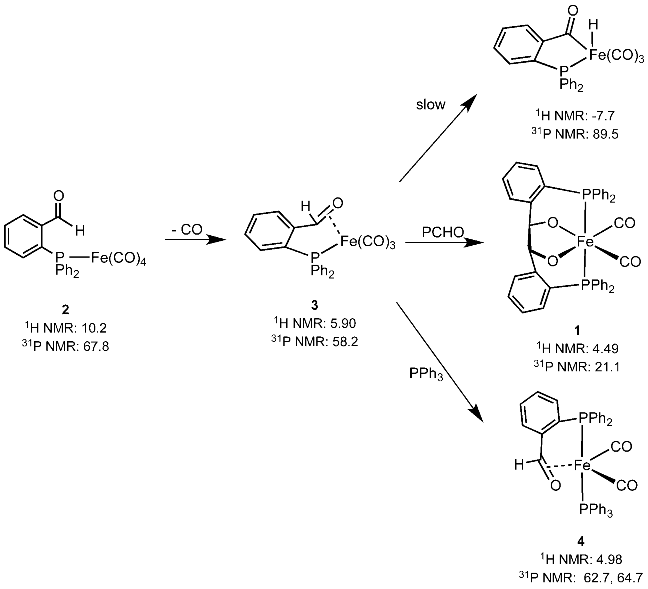


Figure 1. Molecular structure of $Fe[(Ph_2PC_6H_4)_2C_2H_2O_2](CO)_2$ (**1**) with hydrogen atoms omitted for clarity. The thermal ellipsoids are shown at 50% probability with Fe, orange; P, purple; C, gray; O, red. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1) 2.2496(9), Fe(1)−P(2) 2.2395(10), Fe(1)−O(1) 1.945(2), Fe(1)−O(2) 1.954(2), Fe(1)−C(39) 1.774(3), Fe(1)−C(40) 1.754(3), C(19)−C(26) 1.549(4), C(40)−Fe(1)−C(39) 92.64(14), C(40)−Fe(1)−O(1) 96.01(12), C(39)−Fe(1)−O(2) 86.26(12), O(1)−Fe(1)−O(2) 85.07(8), P(2)−Fe(1)−P(1) 167.44(4).

Scheme 2. Pathway for Formation of 1 and Related Reactions and Selected NMR Data



aldehyde, as evidenced by an ^{1}H NMR signal of δ 5.90. A similar chemical shift of δ 6.28 was observed for the π-bonded aldehyde group in $W(CO)_3(\eta^1\text{-PCHO})(\kappa^1,\eta^2\text{-PCHO})$.[17] Reaction of $Fe(bda)(CO)_3$ with 1 equiv of PCHO at room temperature afforded a mixture of complexes **3** and **1**. Samples of **3** were always contaminated by small amounts of the isomeric acyl hydride $HFe(\kappa^2\text{-PCO})(CO)_3$. This species is characterized by doublets at δ −7.7 and at δ 89.5 in the ^{1}H and ^{31}P NMR spectra, respectively.

Although **3** was not obtained in analytical purity, the crude product can be used to test steps in the formation of **1**. Complex **3** reacts with an additional equiv of PCHO to afford **1** in good yield over the course of a week. When this conversion was monitored by ^{31}P NMR spectroscopy, no intermediates were detected. Slightly more quickly than the reaction with PCHO, **3** underwent substitution with PPh_3 to give $Fe(PCHO)(PPh_3)(CO)_2$ (**4**), analogous to the intermediate proposed for the reaction of **3** and PCHO. The ^{31}P NMR spectrum of this heterodisubstituted compound shows an AB quartet with large ^{31}P−^{31}P coupling constant (169 Hz), suggesting that the phosphines are mutually *trans*. The ^{1}H NMR spectrum exhibits a doublet at δ 4.98 indicative of a π-bonded formyl group. The solid-state structure of **4** was confirmed by X-ray crystallography (Figure 2). Although many examples of π-bonded aldehyde metal complexes are known, only a few feature first-row metals.[13] The compounds $Fe(PR_3)_2(R'CHO)(CO)_2$ (R = Et, R′ = Ph; R = OMe, R′ = H) represent the only structurally characterized iron-aldehyde complexes.[26]

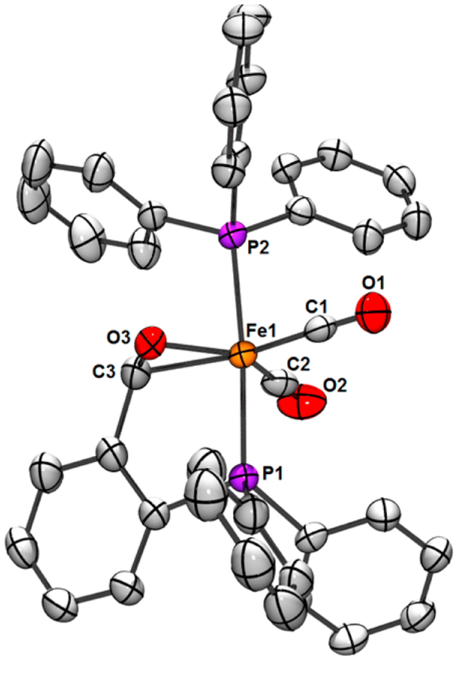


Figure 2. Molecular structure of $Fe(\kappa^1,\eta^2\text{-PCHO})(PPh_3)(CO)_2$ (**4**) with hydrogen atoms omitted for clarity. The thermal ellipsoids are shown at 50% probability with Fe, orange; P, purple; C, gray; O, red. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1) 2.2314(10), Fe(1)−P(2) 2.2613(10), Fe(1)−C(1) 1.791(3), Fe(1)−C(2) 1.762(4), Fe(1)−C(3) 2.026(3), Fe(1)−O(3) 1.974(2), C(1)−Fe(1)−C(2) 104.49(15), C(2)−Fe(1)−C(3) 105.25(15), C(3)−Fe(1)−O(3) 39.88(13), O(3)−Fe(1)−C(1) 110.28(12), P(1)−Fe(1)−P(2) 175.27(3).

Crystallographic analysis of **4** revealed that the Fe center is coordinated to two P atoms from the phosphine ligands, two carbonyl groups, and a π-bonded formyl group. The two phosphine groups are mutually *trans*, with an almost linear P(1)−Fe(1)−P(2) angle (175.27(3)°). The *cis*-CO groups and the π-bonded formyl group are almost planar (sum of interligand angles equals 359.9°). The geometry around Fe is thus pseudo trigonal bipyramidal. Most of the geometric parameters in **4** resemble those of $Fe(PR_3)_2(R'CHO)(CO)_2$; however, the C═O bond (1.365(4) Å) in **4** is much longer than the corresponding values (1.29(2) Å, R = Et, R′ = Ph; 1.32(2) Å, R = OMe, R′ = H).[26] Indeed, this value is much closer to the value of a C−O single bond (~1.45 Å) than that of a C═O bond (~1.20 Å). This indicates strong π-donation toward the Fe center and significant weakening of the C═O bond, which might be crucial for the subsequent formation of the Fe−O and C−C bonds. The coordination geometry around the Fe atoms in **4** and **1** are quite similar, reinforcing the view that **4** is a good model for an intermediate in the formation of **1**. One interesting feature is the short distance (1.974(2) Å) between the Fe(1) atom and O(3) of the formyl group. This distance is almost the same as the Fe−O distances in **1**.

Imine-Formyl Cross-Coupling. Analogous to the pinacol coupling that gives **1** is the corresponding imine-formyl cross-coupling. This process was investigated using the imine $Ph_2PC_6H_4CHNC_6H_4Cl$ (abbreviated as PCHNAr), derived by condensation of 4-chloroaniline and PCHO.[27] PCHNAr reacts with $Fe_2(CO)_9$ at room temperature to afford the monophospine adduct $Fe(PCHNAr)(CO)_4$ (**5**). In addition, treatment of $Fe(bda)(CO)_3$ with PCHNAr affords the expected chelate complex $Fe(PCHNAr)(CO)_3$ (**6**), which is green. Alternatively, compound **6** could be generated by photolysis of **5**. Treatment of complex **6** with PCHO gave good yields of the unsymmetrical C−C coupling complex $Fe[(Ph_2PC_6H_4)_2CH(O)CH(NAr)](CO)_2$ (**7**). The IR spectrum in the CO region shows a pair of CO bands at 1959 and 2022 cm^{-1}. In contrast to **1**, the methine groups give rise to two ^{1}H NMR signals, at δ 4.69 and 4.14, corresponding to the OC*H* and NC*H* groups, respectively. The ^{31}P NMR spectrum of **7** features an AB quartet with a large ^{31}P−^{31}P coupling constant (301 Hz). Compound **7** could also be prepared by the reaction of **3** and PCHNAr, although traces of compound **1** also formed. Attempted coupling of PCHNAr and **6** failed to afford the diamido complex.

The solid-state structure of compound **7** was established by X-ray crystallography (Figure 3). The molecular structure of **7** is similar to that of **1**: the Fe center is pseudo-octahedral. The coordination sphere is completed by two mutually *cis* carbonyl ligands, two mutually *trans* phosphine groups, and the amido-alkoxo ligand. The large difference between the C(1)−Fe(1)−N(1) (100.38(8)°) angle and the C(2)−Fe(1)−O(3) (87.85(8)°) angle may be the consequence of the bulky aryl substituent on the amido nitrogen atom.

Isotopic Labeling Experiment. The imine-formyl cross-coupling reaction was further examined by studies on the reaction of **6** with deuterium-labeled phosphinealdehyde $Ph_2P\text{-}2\text{-}C_6H_4CDO$ (abbreviated as PCDO). A toluene solution of **6** and PCDO was heated at 50 °C, and the ^{1}H and ^{31}P NMR spectra were monitored (Scheme 3). After 2 h, the AB quartet shown in the ^{31}P NMR spectrum clearly indicated the formation of the cross-coupled product. In the ^{1}H NMR spectrum, however, only the C*H*NR signal was detected (δ

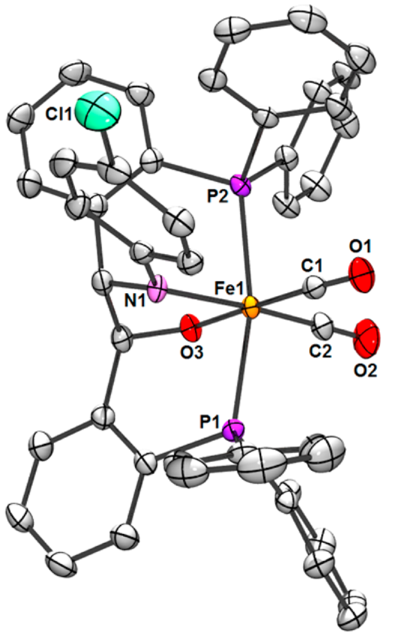
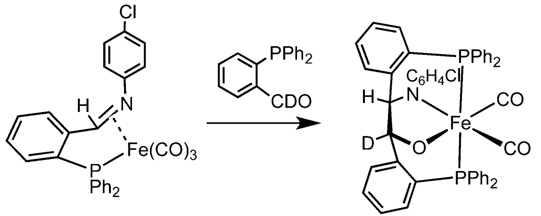


Figure 3. Molecular structure of Fe[$(Ph_2PC_6H_4)_2$CH(O)CH(NAr)]-$(CO)_2$ (**7**) with hydrogen atoms omitted for clarity. The thermal ellipsoids are shown at 50% probability with Fe, orange; P, purple; N, pink; Cl, green; C, gray; O, red. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1) 2.2651(6), Fe(1)−P(2) 2.2656(6), Fe(1)−O(3) 1.9622(13), Fe(1)−N(1) 2.0184(15), Fe(1)−C(1) 1.781(2), Fe(1)−C(2) 1.781(2), C(1)−Fe(1)−C(2) 87.92(9), C(1)−Fe(1)−N(1) 100.38(8), C(2)−Fe(1)−O(3) 87.85(8), N(1)−Fe(1)−O(3) 83.85(6), P(1)−Fe(1)−P(2) 166.55(2).

Scheme 3. Reaction of Ph_2P-2-C_6H_4CDO with 6



6 **7**-d_1

4.26). No scrambling was observed. Only one signal (δ 4.91) was observed in the ^{2}H NMR spectrum.

Reactions of 1 with Lewis Acids. Expecting that the alkoxide ligands would stabilize ferric derivatives, we attempted to oxidize **1** with $FcBF_4$ (Fc^+ = ferrocenium). Instead of oxidation, this reaction resulted in about 50% yield of Fe[$(Ph_2PC_6H_4)_2C_2H_2O_2(BF_3)_2$]$(CO)_2$ (**8**). The fate of the fluoride lost from the BF_4^- was not determined, but the stoichiometry of this reaction would be consistent with the formation of a ferrous fluoride species. Compound **8** was characterized by single-crystal X-ray diffraction (Figure 4). The product contains BF_3 bound to the two alkoxide centers. The coordination at Fe is relatively unchanged compared with **1**. A small expansion of the P−Fe−P angle from 167.44(4)° to 171.81(4)° was observed.

Compound **8** was independently synthesized by the reaction of **1** and 2 equiv of BF_3OEt_2 in CH_2Cl_2 (eq 2). The product features a pair of CO bands at 2023 and 2066 cm^{-1} in the IR spectrum. When instead 1 equiv of BF_3OEt_2 was used in the reaction, the 1:1 adduct could be detected (ν_{CO} = 1995, 2048 cm^{-1}), the ^{31}P NMR spectrum of which indicates nonequivalent phosphines (δ 28.1, 25.4, J = 245 Hz). The difference in ν_{CO} of the two adducts (28 and 18 cm^{-1}) is just lower than half of the overall ν_{CO} change from **1** to **8** (58 and 41 cm^{-1}).

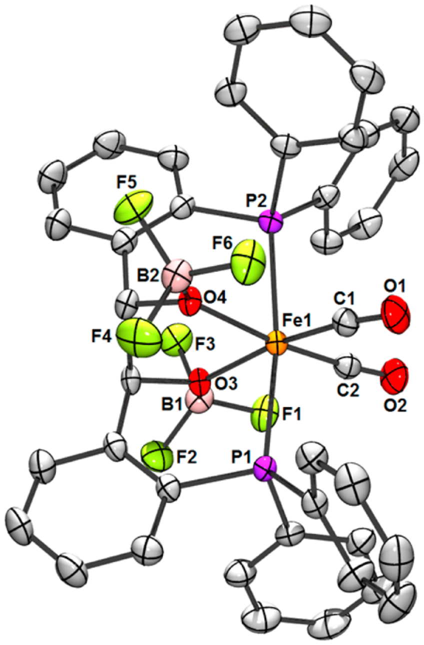


Figure 4. Molecular structure of Fe[$(Ph_2PC_6H_4)_2C_2H_2O_2(BF_3)_2$]-$(CO)_2$ (**8**) with hydrogen atoms omitted for clarity. The thermal ellipsoids are shown at 50% probability with Fe, orange; P, purple; C, gray; O, red; B, pink; F, green. Selected bond lengths (Å) and angles (deg): Fe(1)−P(1) 2.3136(11), Fe(1)−P(2) 2.3119(11), Fe(1)−O(3) 2.011(3), Fe(1)−O(4) 2.016(3), Fe(1)−C(1) 1.782(4), Fe(1)−C(2) 1.777(4), C(1)−Fe(1)−C(2) 85.59(18), C(1)−Fe(1)−O(4) 96.95(15), C(2)−Fe(1)−O(3) 98.20(15), O(3)−Fe(1)−O(4) 80.84(10), P(2)−Fe(1)−P(1) 171.81(4).

$$\underset{\mathbf{1}}{\mathrm{Fe[(Ph_2PC_6H_4)_2C_2H_2O_2](CO)_2}} + 2\mathrm{BF_3} \rightarrow \underset{\mathbf{8}}{\mathrm{Fe[(Ph_2PC_6H_4)_2C_2H_2O_2(BF_3)_2](CO)_2}} \qquad (2)$$

The generality of the binding of Lewis acids to the alkoxide ligands in **1** was further tested qualitatively with 1 and 2 equiv of HOTf (OTf = CF_3SO_3), MeOTf, and $TiCl_4$. Formation of 1:1 or 1:2 derivatives with these electrophiles was confirmed by the IR spectra (Table 1). Protonation and methylation induce the most significant change in ν_{CO}, indicating the stronger Lewis acidity of H^+ and Me^+ compared to BF_3 and $TiCl_4$.[28] However, double methylation was slow.

Table 1. IR Measurements (CH_2Cl_2 solutions, ν_{CO}, cm^{-1}) of the Derivatives Formed from 1 and Various Electrophiles

Lewis acids	1:1 adduct	1:2 adduct
BF_3	1995, 2048	2023, 2066
H^+	2001, 2050	2036, 2075
Me^+	2002, 2051	2030, 2070
$TiCl_4$	2000, 2050	2025, 2068

■ CONCLUSIONS

The ferrous complex of an unusual diphosphine dialkoxide ligand was prepared in high yields by the pinacol-like coupling of 2 equiv of a phosphine aldehyde. Routes to this ligand involved the use of an exotic metal (Tc)[23] or proceeded in low yields (W).[17] Our studies point to the intermediacy of a π-aldehyde complex, which undergoes substitution by a second phosphine aldehyde followed rapidly by C−C coupling. The two phosphine ligands in the proposed Fe(0) intermediate would be *trans,* as seen for Fe(κ^1,η^2-PCHO)(PPh_3)$(CO)_2$ and as observed in the coupled product. Isotopic labeling studies using PCDO are consistent with this mechanism.

The new diphosphineglycolate platform offers scope for further work, especially in view of their efficient formation of the iron complex. The discovery of the imine-formyl cross-coupling expands the range of these tetradentate ligands because so many iminophosphines are known.[29] The new iron dialkoxide was shown to bind a variety of Lewis acids through the alkoxide centers to afford 1:1 or 1:2 adducts. Investigations aimed at liberating the diphosphine-glycol and its application to other metal systems are currently under way.

■ EXPERIMENTAL SECTION

General Considerations. Unless otherwise indicated, reactions were conducted using standard Schlenk techniques under an Ar atmosphere at room temperature with stirring. $Ph_2PC_6H_4$-2-CHO,[30] $Ph_2PC_6H_4$-2-Li$(OEt_2)_{0.74}$,[31] and Fe(bda)$(CO)_3$[32] were synthesized according to literature preparations. $Fe_2(CO)_9$ (Strem Chemicals), 1 M $TiCl_4$ in CH_2Cl_2 (Aldrich), and BF_3OEt_2 (Aldrich) were used as received. $FcBF_4$ was obtained from Aldrich and recrystallized prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were acquired on Varian UNITY INOVA 500NB and UNITY 500 NB instruments. ^{2}H NMR spectra were acquired on a Varian UNITY INOVA 600 instrument. Elemental analyses were performed by the School of Chemical Sciences Microanalysis Laboratory utilizing a model CE 440 CHN analyzer. A Spectroline model MB 100 lamp (λ = 365 nm) was used for experiments requiring UV irradiation.

*Fe[$(Ph_2PC_6H_4)_2C_2H_2O_2$]$(CO)_2$ (**1**).* A solution of 0.991 g (3.47 mmol) of Fe(bda)$(CO)_3$ and 2.012 g (6.93 mmol) of PCHO in 30 mL of THF was heated to 60 °C for 4 h. The reaction was followed by solution IR spectroscopy, and after 2 h, the signals for Fe(bda)$(CO)_3$ were no longer apparent. A large amount of bright yellow precipitate formed. The slurry was concentrated to 15 mL under reduced pressure and filtered, leaving bda in the filtrate. The solid was washed with an additional 5 mL of THF followed by 3 × 10 mL of hexanes and then left under reduced pressure overnight. ^{1}H NMR analysis confirmed that the crystalline product contains 0.5 equiv of THF. The crystalline yellow solid was collected in a drybox. Yield: 2.26 g (89%). Redissolving the solid in CH_2Cl_2 followed by removal of solvent under reduced pressure afforded a yellow powder containing 1 equiv of CH_2Cl_2, which was confirmed by ^{1}H NMR spectroscopy and elemental analysis. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 4.49 (s, 2H, OC*H*), 7.10−7.64 (m, 24H, phenyl-H), 8.06 (s, 4H, phenyl-H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 211.7 (t, CO, J_{CP} = 21 Hz), 155.2, 136.1, 135.3, 134.5, 133.5, 132.9, 130.9, 130.8, 130.3, 128.8, 128.6, 127.4, 127.3, 123.9, 87.0 (s, OCH). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 21.1 (s). IR spectrum (CH_2Cl_2): ν_{CO} 1965, 2025 cm^{-1}. Anal. Calcd for $C_{41}H_{32}Cl_2FeO_4P_2$ (found): C, 63.35 (63.21); H, 4.15 (4.06); N, 0.00 (0.33).

*Fe(PCHO)$(CO)_4$ (**2**).* A solution of 1.00 g (3.44 mmol) of PCHO in 50 mL of THF was transferred via cannula onto 1.25 g (3.44 mmol) of solid $Fe_2(CO)_9$. The mixture was stirred at 23 °C until all solids dissolved (40 min). ^{31}P NMR spectroscopy confirmed the consumption of the PCHO. The solvent and most $Fe(CO)_5$ were removed under reduced pressure. The yellow residue was extracted into 2 × 50 mL of hexanes, and the solvent was removed under reduced pressure to give a yellow powder. Yield: 0.768 g (49%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.17−8.07 (m, 14H, phenyl-H), 10.18 (s, 1H, C*H*O). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 213.6 (d, CO, J_{CP} = 18 Hz), 189.8 (d, CHO, J_{CP} = 8 Hz), 138.0, 137.2, 134.9, 134.2, 133.7, 133.5, 132.0, 131.8, 130.5, 129.5. ^{31}P NMR (202 MHz, CD_2Cl_2): δ 67.8 (s). IR spectrum (CH_2Cl_2): ν_{CO} 1944, 1978, 2052 cm^{-1}. Anal. Calcd for $C_{23}H_{15}FeO_5P$ (found): C, 60.29 (60.03); H, 3.30 (3.18); N, 0.00 (0.28).

*Fe(κ^1,η^2-PCHO)$(CO)_3$ (**3**).* A solution of 1.022 g (2.23 mmol) of **2** in 20 mL of CH_2Cl_2 was irradiated, while monitoring the progress of the reaction by ^{31}P NMR spectroscopy. After the ^{31}P NMR signal for **2** was no longer apparent (ca. 30 h), the solution was concentrated to 10 mL and then diluted with 40 mL of hexanes. The red precipitate was collected. The filtrate was further concentrated and then stored at −20 °C for several days to afford additional product, and the sequence of concentrating followed by cooling was repeated. Several recrystallizations removed most of the less soluble components, affording a sample of **3** with >70% purity. The sample was used for the preparation of **4** without further purification. ^{1}H NMR (500 MHz, toluene-d_8): δ 5.90 (s, C*H*O). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 90.2 (s, CHO). ^{31}P NMR (202 MHz, toluene-d_8): δ 58.2 (s). IR spectrum (CH_2Cl_2): ν_{CO} 1957, 1989, 2051 cm^{-1}.

*Fe(κ^1,η^2-PCHO)(PPh_3)$(CO)_2$ (**4**).* A solution of 0.198 g (0.46 mmol) of **3** and 0.127 g (0.48 mmol) of PPh_3 in 20 mL of toluene was heated at 50 °C for 6 h. The orange solution was evacuated to dryness under vacuum. The residue was washed with 3 × 10 mL of hexanes, and an orange solid was obtained. The solid was dissolved in CH_2Cl_2 (5 mL), and this solution was layered with pentane (15 mL). Slow diffusion overnight at room temperature yielded orange crystals. Yield: 0.099 g (32%). ^{1}H NMR (500 MHz, toluene-d_8): δ 4.98 (d, 1H, C*H*O), 6.76−8.20 (m, 29H, phenyl-H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 218.8 (dd, CO, J_{CP} = 24, 26 Hz), 213.9 (dd, CO, J_{CP} = 24, 28 Hz), 159.1, 134.2, 134.0, 133.8, 132.0, 131.6, 130.8, 130.5, 130.4, 128.8, 128.7, 128.5, 126.8, 126.1, 91.6 (d, CHO, J_{CP} = 4 Hz). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 62.7, 64.7 (AB quartet, J_{PP} = 169 Hz). IR spectrum (CH_2Cl_2): ν_{CO} 1900, 1967 cm^{-1}. Anal. Calcd for $C_{39}H_{30}FeO_3P_2$ (found): C, 70.50 (69.70); H, 4.55 (4.32); N, 0.00 (0.36).

$Ph_2PC_6H_4CHNC_6H_4Cl$ (PCHNAr). This ligand was prepared following a modification of the literature procedure.[27] A solution of 0.679 g (2.34 mmol) of PCHO and 0.304 g (2.38 mmol) of 4-chloroaniline in 20 mL of toluene was refluxed for 16 h in the presence of molecular sieves. The solution was cooled to room temperature and filtered. Solvent was removed under vacuum, and the residue was washed with 2 × 2 mL of Et_2O. The yellow powder was dried under vacuum. Yield: 0.763 g (82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (d, 2H, phenyl-H), 6.93 (m, 1H, phenyl-H), 7.22−7.36 (m, 13H, phenyl-H), 7.46 (t, 1H, phenyl-H), 8.17 (m, 1H, phenyl-H), 9.01 (d, 1H, C*H*N). ^{31}P NMR (202 MHz, $CDCl_3$): δ −12.4 (s).

*Fe(PCHNAr)$(CO)_4$ (**5**).* A solution of 0.897 g (2.46 mmol) of $Fe_2(CO)_9$ and 0.986 g (2.46 mmol) of PCHNAr in 30 mL of THF was stirred at room temperature for 2 h. All solvents were evaporated under vacuum, and the residue was extracted with 60 mL of hexanes. The solution was filtered and concentrated to 10 mL. After the solution was stored at −20 °C overnight, a yellow powder was obtained and dried under vacuum. Yield: 0.657 g (47%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.48 (dt, 2H, phenyl-H), 7.12 (dt, 2H, phenyl-H), 7.30 (ddd, 1H, phenyl-H), 7.44−7.52 (m, 7H, phenyl-H), 7.59−7.66 (m, 5H, phenyl-H), 8.40 (ddd, 1H, phenyl-H), 8.51 (s, 1H, C*H*N). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 213.6 (d, CO, J_{CP} = 18 Hz), 158.6 (d, CHN, J_{CP} = 6 Hz), 149.9, 138.1, 135.1, 134.9, 134.2, 133.8, 131.9, 131.8, 131.6, 131.1, 129.5, 129.4, 129.2, 122.8. ^{31}P NMR (202 MHz, $CDCl_3$): δ 68.5 (s). IR spectrum (hexanes): ν_{CO} 1948, 1981, 2053 cm^{-1}. Anal. Calcd for $C_{29}H_{19}ClFeNO_4P$ (found): C, 61.35 (61.50); H, 3.37 (3.35); N, 2.47 (2.59).

*Fe(PCHNAr)$(CO)_3$ (**6**).* A solution of 0.224 g (0.78 mmol) of Fe(bda)$(CO)_3$ and 0.296 g (0.74 mmol) of PCHNAr in 30 mL of toluene was heated at 45 °C overnight. The reaction was followed by ^{31}P NMR spectroscopy. After ca. 24 h, the ^{31}P NMR signals for PCHNAr fully disappeared, indicating the completion of the reaction. Solvents were removed under reduced pressure, and the obtained solid contains the desired product with bda as impurity. The mixture can be used for the preparation of **7** without further purification. Alternatively, compound **6** could be generated by photolysis of **5** in a NMR tube. However, the photolysis is not efficient enough for large-scale preparation. ^{1}H NMR (500 MHz, toluene-d_8): δ 6.65−7.86 (m, 18H, phenyl-H), 4.94 (s, br, 1H, C*H*N). ^{31}P NMR (202 MHz, toluene-d_8): δ 62.8 (s). IR spectrum (hexanes): ν_{CO} = 1962, 1989, 2046 cm^{-1}.

*Fe[(Ph$_2$PC$_6$H$_4$)$_2$CH(O)CH(NAr)](CO)$_2$ (**7**).* A mixture of crude compound **6** (prepared from 0.224 g (0.78 mmol) of Fe(bda)(CO)$_3$ and 0.296 g (0.74 mmol) of PCHNAr) and 0.218 g (0.75 mmol) of Ph$_2$PC$_6$H$_4$CHO was dissolved in 20 mL of toluene. The solution was heated at 50 °C for 2 h. The greenish-brown solution was filtered off from the cold reaction mixture, and the dark purple precipitate was washed with about 10 mL of hexanes. The solid was dried under reduced pressure. Yield: 0.433 g (72%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.99 (t, 2H, phenyl-H), 7.83 (m, 2H, phenyl-H), 7.59 (m, 3H, phenyl-H), 7.53 (t, 1H, phenyl-H), 7.35−7.42 (m, 9H, phenyl-H), 7.28 (t, 2H, phenyl-H), 7.22 (t, 1H, phenyl-H), 7.14 (m, 3H, phenyl-H), 7.05 (t, 2H, phenyl-H), 6.93 (t, 1H, phenyl-H), 6.87 (t, 2H, phenyl-H), 6.21 (d, 2H, phenyl-H), 5.90 (d, 2H, phenyl-H), 4.69 (d, 1H, OC*H*), 4.14 (dd, 1H, NC*H*). ^{13}C NMR (126 MHz, CD$_2$Cl$_2$): δ 212.6 (CO), 211.3 (CO), 157.7, 154.4, 154.0, 136.4, 136.2, 134.3, 134.2, 133.7, 133.6, 133.0, 132.9, 132.6, 132.5, 131.6, 130.8, 130.6, 130.5, 129.8, 129.6, 129.5, 128.9, 128.8, 128.7, 128.6, 128.1, 128.0, 127.7, 127.6, 127.4, 127.1, 125.3, 124.4, 119.4, 115.8, 86.7 (s, OCH), 74.7 (s, NCH). ^{31}P NMR (202 MHz, CD$_2$Cl$_2$): δ 26.6, 25.1, 22.2, 20.7 (AB quartet, J_{PP} = 301 Hz). IR spectrum (CH$_2$Cl$_2$): ν_{CO} 1959, 2022 cm^{-1}. Anal. Calcd for C$_{46}$H$_{34}$ClFeNO$_3$P$_2$ (found): C, 68.89 (68.40); H, 4.27 (4.26); N, 1.75 (2.01).

Ph$_2$PC$_6$H$_4$CDO (PCDO). Our procedure was adapted from the literature reaction of DMF and the lithiated phosphine.[33] A solution of 1.02 g (3.16 mmol) of Ph$_2$PC$_6$H$_4$Li(OEt$_2$)$_{0.74}$ and 1.0 mL (12.8 mmol) of DMF-d_7 in 20 mL of ether was stirred overnight. The reaction mixture was treated with 10 mL of 3 M HCl and then extracted with CH$_2$Cl$_2$ (20 mL × 3). The organic phase was dried with Na$_2$SO$_4$ and evaporated under vacuum. The crude product was washed with 10 mL of methanol and 10 mL of pentane and then dried under reduced pressure. Yield: 0.448 g (49%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.98 (m, 1H, phenyl-H), 7.45−7.52 (m, 2H, phenyl-H), 7.33−7.37 (m, 6H, phenyl-H), 7.27−7.31 (m, 4H, phenyl-H), 6.98 (m, 1H, phenyl-H). ^{2}H NMR (92 MHz, CHCl$_3$/CDCl$_3$): δ 10.53 (s, C*D*O). ^{31}P NMR (202 MHz, CDCl$_3$): δ −11.0 (s).

*Reaction of PCDO with **6** to give **7**-d_1.* A NMR tube was charged with 5.1 mg (0.018 mmol) of Fe(bda)(CO)$_3$, 7.9 mg (0.020 mmol) of PCHNAr, and 0.5 mL of toluene-d_8. The mixture was heated at 45 °C overnight and then treated with 5.4 mg (0.018 mmol) of PCDO. NMR spectra were recorded after heating at 50 °C for 2 h. ^{1}H NMR (500 MHz, toluene-d_8): δ 8.23 (m, 2H, phenyl-H), 7.97 (t, 2H, phenyl-H), 7.60 (t, 2H, phenyl-H), 6.78−7.24 (m, 22H, phenyl-H), 6.46 (m, 2H, phenyl-H), 6.12 (d, 2H, phenyl-H), 4.26 (s, 1H, NC*H*). ^{2}H NMR (92 MHz, C$_7$H$_8$/C$_7$D$_8$): δ 4.91 (s, OC*D*). ^{31}P NMR (202 MHz, toluene-d_8): δ 26.4, 24.9, 21.6, 20.1 (AB quartet, J_{PP} = 305 Hz).

*Fe[(Ph$_2$PC$_6$H$_4$)$_2$C$_2$H$_2$O$_2$(BF$_3$)$_2$](CO)$_2$ (**8**).* A solution of 0.563 g (0.813 mmol) of **1** in 20 mL of CH$_2$Cl$_2$ was treated with 0.20 mL (1.63 mmol) of BF$_3$OEt$_2$ added dropwise via syringe. The solution was stirred for 1 h, before the solvent was removed under reduced pressure. The yellow powder was recrystallized from CH$_2$Cl$_2$/hexanes. Residual solvent was removed under reduced pressure overnight. The product was obtained as a microcrystalline yellow solid. Yield: 0.673 g (95%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 5.05 (s, 2H, OC*H*), 7.02 (q, 2H, phenyl-H), 7.36 (m, 6H, phenyl-H), 7.47 (m, 9H, phenyl-H), 7.57 (m, 4H, phenyl-H), 7.66 (t, 3H, phenyl-H), 7.92 (q, 4H, phenyl-H). ^{19}F NMR (470 MHz, CD$_2$Cl$_2$): δ −146 (s). ^{31}P NMR (202 MHz, CD$_2$Cl$_2$): δ 31.5 (s). IR spectrum (CH$_2$Cl$_2$): ν_{CO} 2023, 2066 cm^{-1}. Anal. Calcd for C$_{40}$H$_{30}$B$_2$F$_6$FeO$_4$P$_2$ (found): C, 58.02 (57.62); H, 3.65 (3.58); N, 0.00 (0.27).

Reactions of 1 with Electrophiles. *TiCl$_4$.* A solution IR spectrum of 0.100 g (0.137 mmol) of **1** in 30 mL of CH$_2$Cl$_2$ was obtained. A 1 M solution of TiCl$_4$ in CH$_2$Cl$_2$ (0.15 mL, 0.148 mmol) was added dropwise, giving a yellow precipitate. An IR spectrum of the yellow solution was obtained (ν_{CO} = immediate: 2068, 2025 cm^{-1}). Upon stirring 10 min, the solids dissolved to give a homogeneous solution (ν_{CO} = 2050, 2000 cm^{-1}). The solution IR was obtained. The solution was allowed to stir at 23 °C over 24 h with no noticeable change in the solution IR spectrum.

HOTf. A solution of 10.6 mg of **1** (0.015 mmol) in CH$_2$Cl$_2$ was treated with 0.15 mL of CH$_2$Cl$_2$ solution of HOTf (v_{CH2Cl2}:v_{HOTf} = 100:1), and the IR spectrum was obtained. Two CO bands at 2001 and 2050 cm^{-1} were observed. Another 0.15 mL of HOTf solution was added, and the mixture was stirred for 20 min. The IR spectrum was taken, and CO bands at 2036 and 2075 cm^{-1} were obtained.

MeOTf. A solution of 18.7 mg of **1** (0.027 mmol) in CH$_2$Cl$_2$ was treated with 0.3 mL of a CH$_2$Cl$_2$ solution of MeOTf (v_{CH2Cl2}:v_{MeOTf} = 100:1), and the IR spectrum was obtained. Two CO bands at 2002 and 2051 cm^{-1} were observed. With additional MeOTf, we detected bands at 2030 and 2070 cm^{-1} assigned to the dication.

Detection of Intermediates in Formation of 1. A solution of 9.5 mg (0.02 mmol) of **2** in 0.8 mL of toluene-d_8 was prepared in a J. Young NMR tube. The tube was sealed, and ^{1}H and ^{31}P NMR spectra were obtained. The tube was then irradiated, and ^{1}H and ^{31}P NMR spectra were collected periodically over the course of 2 h. After 2 h, a large quantity of the hydride product was detected with **1** also formed.

In Situ Detection of Hydride HFe(κ^2-PCO)(CO)$_3$. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ −7.7 (d, 47.5 Hz, 1 H, Fe−H). ^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$): δ 89.5 (s, P−Fe−H). ^{31}P NMR (202 MHz, CD$_2$Cl$_2$): δ 89.5 (d, 47.5 Hz, P−Fe−H).

*In Situ Detection of **3**.* ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 5.91 (s 1 H, Fe-(C*H*O)). ^{31}P NMR (202 MHz, CD$_2$Cl$_2$): δ 58.2 (s, P−Fe).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR, ^{31}P NMR, and IR spectra for **1**−**8** and CIF files including X-ray crystallographic data for the structures of **1**, **4**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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