Tuning a Phosphine-Substituted Diimine Ligand to Afford an Iron Monocarbonyl Complex

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Dedicated to Peter T. Wolczanski on the occasion of his 70th birthday.

KEYWORDS

Ligand Design, Substitution, Carbonyl Compounds, Bromide Compounds, Earth-Abundant Metal

ABSTRACT

A series of low-valent iron complexes that feature a phosphine-substituted α-diimine (DI) ligand have been synthesized. Reduction of (^{Ph_2PPr}DI)FeBr$_2$ with an excess of Na/Hg in the presence of carbon monoxide afforded the corresponding dicarbonyl complex, (^{Ph_2PPr}DI)Fe(CO)$_2$. Through multinuclear NMR and single crystal X-ray diffraction analysis, this complex was found to possess a 3-coordinate DI ligand. Upon heating for 10 days at 110 °C while applying intermittent vacuum, (^{Ph_2PPr}DI)Fe(CO)$_2$ was successfully converted to the corresponding monocarbonyl complex, (^{Ph_2PPr}DI)Fe(CO), which was found to feature a tetradentate chelate. Similar reactivity was explored using the analogous bis(*tert*-butyl)phosphine-substituted ligand, ^{tBu_2PPr}DI. Addition of this chelate to FeBr$_2$ afforded (^{tBu_2PPr}DI)FeBr$_2$, and subsequent reduction yielded (^{tBu_2PPr}DI)FeBr, which was found to possess a tridentate DI ligand by single crystal X-ray diffraction. Performing the reduction of (^{tBu_2PPr}DI)FeBr$_2$ in the presence of CO afforded the corresponding dicarbonyl complex, (^{tBu_2PPr}DI)Fe(CO)$_2$. Like aryl-substituted (^{Ph_2PPr}DI)Fe(CO)$_2$, alkyl-substituted (^{tBu_2PPr}DI)Fe(CO)$_2$ was found to feature a pendant phosphine arm. However, heating (^{tBu_2PPr}DI)Fe(CO)$_2$ under vacuum did not allow for phosphine substitution and conversion to the corresponding monocarbonyl complex, highlighting the importance of phosphine π-acidity for substitution and the stabilization of low-valent iron.

INTRODUCTION

The synthesis and reactivity of iron carbonyl compounds has captured the attention of coordination chemists for generations. Following their seminal synthesis of $Ni(CO)_4$ in 1890,[1] Mond and co-workers remained interested in preparing homoleptic carbonyl complexes,[2] and they were ultimately successful in isolating $Fe(CO)_5$ as a viscous liquid.[3] While $Fe(CO)_5$ remains an important industrial precursor for powder metallurgy and metal injection molding,[4] it can also be photolyzed to generate $Fe_2(CO)_9$.[5] These compounds, along with $Fe_3(CO)_{12}$, have been used in thermal and light-promoted substitution reactions to prepare compounds of the formula, $(CO)_{5-n}Fe(L)_n$.[6] In the 1980's, researchers became interested in the reactivity of α-diimine (DI) iron tricarbonyl complexes, $(DI)Fe(CO)_3$,[7] due to their propensity to undergo CO substitution with a single phosphine,[8,9] pyridine,[9] isocyanide,[9] or alkene ligand[10] to generate the corresponding $(DI)Fe(CO)_2(L)$ complexes.

A more recent approach to synthesize DI iron compounds that feature fewer than three CO ligands relies on extended chelate denticity. In 2013, Huang and co-workers prepared (^{tBu}PNN^{iPr})$Fe(CO)_2$ (**A**, Figure 1) by adding 2 equivalents of $NaEt_3BH$ to the corresponding dichloride in the presence of CO.[11] Subsequently, Milstein used phosphine-substituted bipyridine ligands to prepare (^{R}PNN)$Fe(CO)_2$ (**B**, where R = tBu, iPr, Ph) complexes either by reduction under 1 atm of CO or upon substitution of $Fe(CO)_5$ in dioxane at 95 °C.[12] The (imino)pyridine variant of this ligand featuring bis(*tert*-butyl)phosphine-substitution was subsequently used to prepare an iron dicarbonyl complex (**C**),[13] which was converted into an iron hydride catalyst for ketone hydrogenation upon HBF_4 addition.[14] The Chirik Group prepared iron dicarbonyl complexes featuring PNN ligands derived from acenaphthenequinone (**D**) to compare the π-acidity of these chelates to related pincer ligands.[15] By both direct substitution of $(benzylideneacetone)Fe(CO)_3$ and $NaBEt_3H$ addition to the bromide precursor, Rauchfuss demonstrated that phosphine-substituted imino(pyridine) ligands support the formation of iron dicarbonyl complexes (**E**).[16] While these studies allowed for iron dicarbonyl synthesis, their phosphine-substituted imino(pyridine), bipyridine, and diimine ligands lack a fourth σ-donating group that could promote the isolation of an iron monocarbonyl complex.

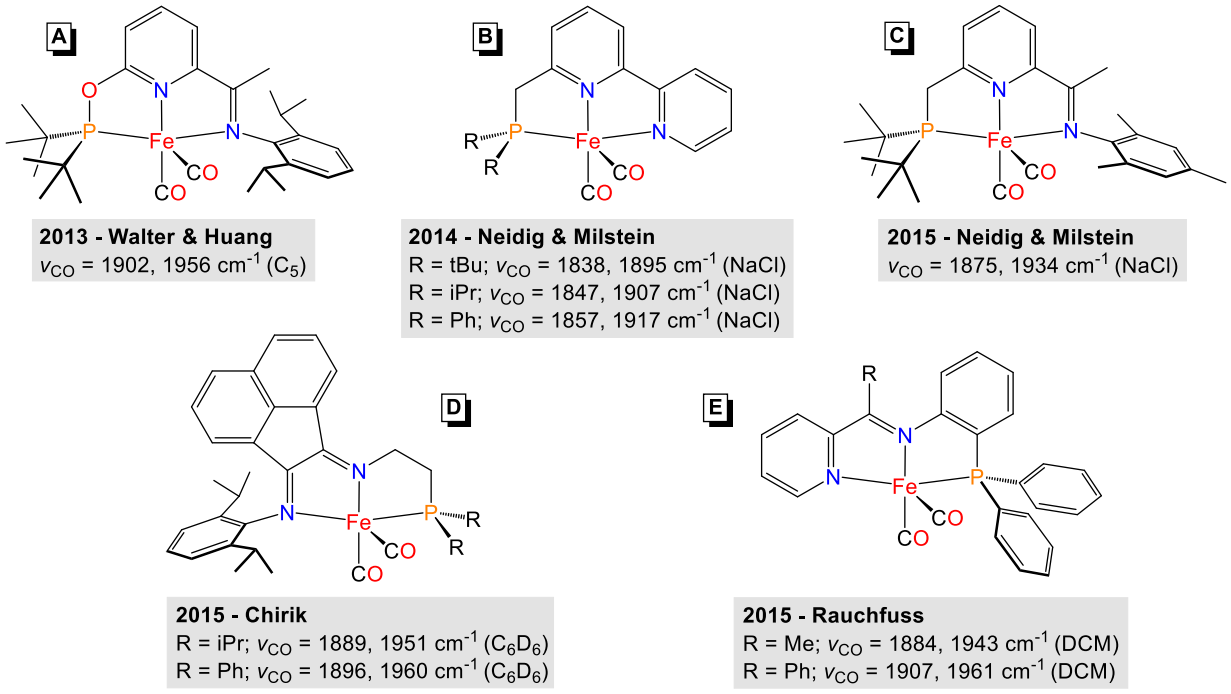

Figure 1. Phosphine-substituted imino(pyridine), bipyridine, and diimine ligands that support iron dicarbonyl complex formation.

In 2016, we metallated the diphenylphosphine-substituted DI ligand, ^{Ph_2PPr}DI,[17] with anhydrous $FeBr_2$ to prepare (^{Ph_2PPr}DI)$FeBr_2$ (Figure 2, **1**).[18] This compound was characterized by single crystal X-ray diffraction and was found to possess a tetradentate DI ligand and *cis*-bromide ligands. Moreover, **1** was found to have an unreduced DI chelate and a high-spin Fe(II) center. Reduction of this compound under a nitrogen atmosphere afforded the corresponding dinitrogen complex, (^{Ph_2PPr}DI)Fe(N_2) (Figure 2, **2**). This complex was found to have a distorted square pyramidal geometry in the solid state, a singly reduced DI ligand that is antiferromagnetically coupled to a low-spin Fe(I) center, and a weakly activated N_2 ligand as judged by single crystal X-ray diffraction [N–N bond distance of 1.117(3) Å] and IR spectroscopy [ν_{NN} of 2011 cm^{-1} in KBr].[18]

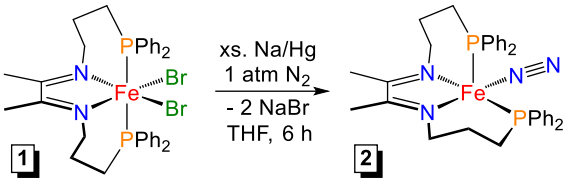

Figure 2. Reduction of **1** under nitrogen atmosphere to generate **2**.

In this contribution, we sought to prepare an isostructural monocarbonyl complex through the reduction of **1** and its bis(*tert*-butyl)phosphine-substituted counterpart under CO. In both cases dicarbonyl products are initially obtained; however, we have found that increased phosphine π-acidity can drive carbonyl ligand substitution. For each product, Wolczanski's charge distribution via reporters (CDVR) method[19] is applied to assess the charge distribution among the carbonyl ligands without the need for computation. Through the process of elimination, this approach allows for a complementary, non-crystallographic assessment of electron density stored within the redox non-innocent DI ligand π-system. Moreover, the phosphine hemilability observed throughout this study adds to existing findings which have highlighted its importance for DI-supported catalysis.[20-22]

RESULTS

With **1** in hand,[18] its reduction using excess sodium amalgam under an atmosphere of CO was explored. After stirring at room temperature for 24 h in THF, this reduction yielded a diamagnetic crimson red product. Analysis of its ^{1}H NMR spectrum revealed two distinct resonances for the backbone methyl groups at 1.43 and 1.73 ppm, which is indicative of a non-C_2-symmetric compound. Additionally, the ^{31}P NMR spectrum collected for this product revealed resonances at 67.40 and -16.37 ppm, suggesting that one chelate phosphine moiety is coordinated to iron while the other is not (the free ligand ^{31}P shift in benzene-d_6 is -16.61 ppm).[17] The infrared spectrum of this compound in KBr was found to possess CO stretching frequencies at 1938 and 1874 cm^{-1}, which is consistent with the coordination of two CO ligands. Taken together, our spectroscopic data suggested the formation of (^{Ph_2PPr}DI)Fe(CO)$_2$ (Figure 3, **3**), which features a tridentate DI chelate.

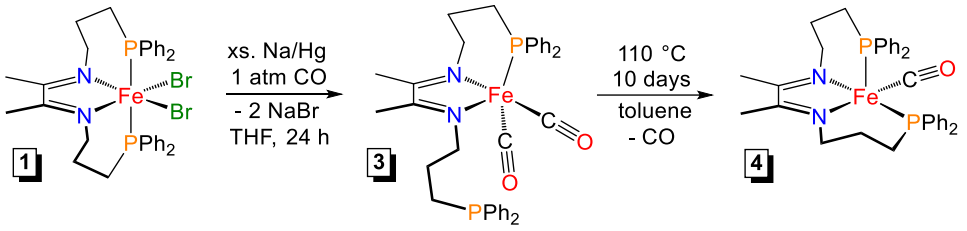

Figure 3. Preparation of dicarbonyl **3** and its conversion to monocarbonyl **4**.

To confirm this coordination environment, crystals of **3** were grown from a concentrated diethyl ether solution at -35 °C and analyzed by single crystal X-ray diffraction. The solid-state structure of **3** revealed a distorted trigonal bipyramidal coordination environment in which one imine and one CO ligand occupy the axial positions, with an N(1)-Fe(1)-C(35) angle of 174.15(17) °. The remaining imine, CO, and phosphine ligands occupy the equatorial positions with N(2)-Fe(1)-P(1), P(1)-Fe(1)-C(36), and C(36)-Fe(1)-N(2) angles of 124.35(9), 101.26(12), and 133.68(15) °, respectively. As expected for carbonyl ligands bound to a low-valent metal center, the C(35)-O(1) and C(36)-O(2) distances of 1.156(4) and 1.159(4) Å are consistent with considerable backbonding from iron. Diimine ligands are well known to behave in a redox non-innocent fashion when coordinated to low-valent first-row metals[23,24] and it must be pointed out that the N(1)-C(2) and N(2)-C(3) distances of 1.333(4) and 1.344(4) Å are consistent with the presence of a singly-reduced ^{Ph_2PPr}DI chelate.[25] The C(2)-C(3) distance of 1.408(5) Å determined for **3** is also significantly contracted from the neutral ligand value of 1.47 Å.[25] While many would assume that **3** features a DI radical anion because of its metrical parameters, Neidig and Milstein nicely determined that related compounds **B** and **C** (Figure 1) feature considerable covalency, and that a competition for backbonding across the ligand set discourages electron transfer to the chelate, rendering the most appropriate assignment Fe(0) with neutral ligands.[12,13]

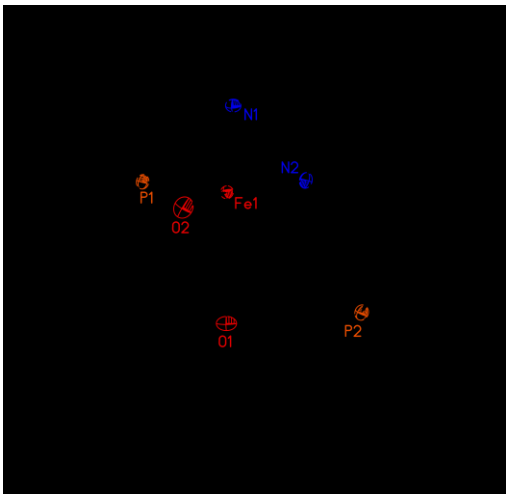

Figure 4. The solid-state structure of **3** shown with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 1. Bond lengths (Å) and angles (˚) determined for **3** and **4**.

	3	**4**
Fe(1)-N(1)	1.920(3)	1.919(2)
Fe(1)-N(2)	1.903(3)	1.921(2)
Fe(1)-P(1)	2.1886(10)	2.1770(9)
Fe(1)-P(2)	-	2.1787(9)
Fe(1)-C(35)	1.758(3)	1.740(3)
Fe(1)-C(36)	1.767(4)	-
C(35)-O(1)	1.156(4)	1.164(3)
C(36)-O(2)	1.159(4)	-
N(1)-Fe(1)-N(2)	79.79(12)	80.33(9)
N(1)-Fe(1)-P(1)	89.66(9)	90.95(7)
N(2)-Fe(1)-P(1)	124.35(9)	114.66(7)
N(1)-Fe(1)-C(35)	174.15(17)	92.28(12)
N(2)-Fe(1)-C(35)	94.56(16)	148.98(12)
P(1)-Fe(1)-P(2)	-	105.19(3)
C(35)-Fe(1)-C(36)	90.92(17)	-

In instances like this, where a definitive electronic structure assignment is challenging to make, it is perhaps more convenient to apply Wolczanski's charge distribution via reporters (CDVR) method[19] to gauge the amount of electron density that is being accepted by each ligand.

According to this method, the Fe center is assigned a constant charge of +2.0 and the partial charge of each reporting CO ligand (c_{CO}) can be obtained according to equation 1:

$$c_{CO} = \{\nu(CO) - 2207\}\ cm^{-1} / 475\ cm^{-1} \qquad (1)$$

where ν(CO) is the average CO stretching frequency. For **3**, an average CO stretching frequency of 1906 cm^{-1} gives rise to a charge of -0.63 on each CO ligand, for a total of -1.26. The CDVR method treats phosphine ligands as non-reporting ligands, with values ranging from -0.3 to 0 for trialkylphosphines and -0.4 to -0.1 for triarylphosphines. Therefore, the bound diarylphosphine moiety of ^{Ph_2PPr}DI is estimated to have a charge of -0.22, which represents 2/3 of the difference between the range midpoints. Through elimination, the charge held by the α-diimine moiety of **3** is estimated to be -0.52. In other words, this method indicates that less than one electron worth of density is being transferred from the Fe center to the chelate π-system.

Heating **3** in toluene at 110 °C gradually resulted in a change of color from crimson red to burgundy. Liberated CO gas was removed under vacuum every 2 days and repeated 5 times. After 10 days of heating at 110 °C with intermittent gas removal, the product was found to possess a single ^{1}H NMR backbone methyl resonance at 1.76 ppm and a single ^{31}P NMR resonance at 69.33 ppm. Moreover, IR spectroscopic analysis revealed one CO stretching frequency at 1846 cm^{-1}. These observations are consistent with the substitution of one carbonyl ligand with the second chelate phosphine group to prepare the monocarbonyl compound, (^{Ph_2PPr}DI)Fe(CO) (Figure 3, **4**), which features C_2-symmetry in solution at ambient temperature.

The structure of **4** was confirmed by X-ray diffraction analysis of a single crystal grown from a concentrated diethyl ether solution at -35 °C (Figure 5). This complex was found to feature a distorted square pyramidal geometry, with P(1) occupying the apical position. The C(35)-O(1) bond distance of 1.164(3) Å is longer than the C–O distances observed for **3** [1.156(4) and 1.159(4)], which is consistent with the heightened degree of backbonding inferred from IR spectroscopy. The N(1)-C(2) and N(2)-C(3) distances of 1.351(3) and 1.360(3) Å, respectively, along with the C(2)-C(3) distance of 1.396(4) Å, are consistent with a more reduced ^{Ph_2PPr}DI chelate in **4** relative to **3**. The application of Wolczanski's CDVR method[19] reveals a carbonyl ligand charge density of -0.76. Assuming that the coordinated phosphine moieties carry a charge of -0.22 each, the diimine portion of ^{Ph_2PPr}DI is found to be more reduced, featuring an overall charge of -0.80.

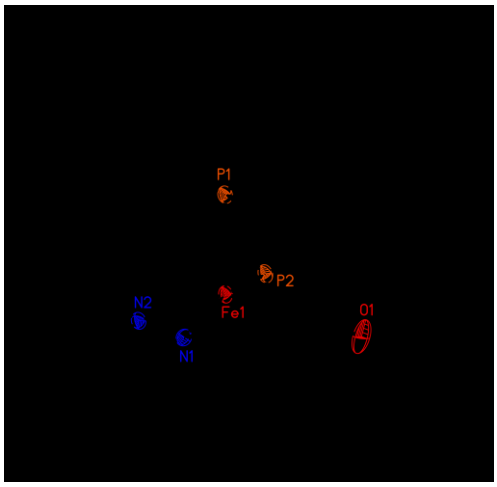

Figure 5. The solid-state structure of **4** shown with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

While surveying the literature, a few examples of DI-supported iron monocarbonyl compounds were identified. The most studied examples are dications supported by the macrocyclic bis(diimine) ligand, TIM (2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-tetraene), which features two propylene bridges that tie together two diimine moieties. This ligand framework has allowed for the preparation of $[(TIM)Fe(CO)(L)]^{2+}$, where L = OH_2,[26-29] NCMe,[30-33] or DMSO.[34] In 2005, Kubas and co-workers calculated the structure of $[(^{Me_2NPr}DI)Fe(CO)(Cl)]^{+}$, to rationalize why they could not prepare complexes of this type by adding CO in the presence or absence of silver salts to $(^{Me_2NPr}DI)FeCl_2$.[35] Examples of neutral (DI)Fe monocarbonyl complexes are fairly rare. Heindirk tom Dieck and co-workers spectroscopically observed the alkyl- and aryl-substituted bis(diimine) Fe^0 monocarbonyl complexes, $(^{R}DI)_2Fe(CO)$,[36-37] and substituted butadienes have been used in place of one of the DI ligands.[38-40] We suspect that **4** is the first $(DI)Fe^0$ monocarbonyl complex to be supported by a tetradentate ligand.

In prior work, we utilized the bis(*tert*-butyl)phosphine substituted DI ligand, $^{tBu_2PPr}DI$, to support Ni mediated carbonyl hydrosilylation.[20] With this chelate in hand, we sought to explore whether $^{tBu_2PPr}DI$ could also be used to prepare a $(DI)Fe^0$ monocarbonyl complex. The addition of $^{tBu_2PPr}DI$ to $FeBr_2$ in THF solution resulted in an immediate color change and the formation of a blue product after stirring for 24 h at 25 °C, removing the solvent under vacuum, and washing with pentane. The ^1H NMR spectrum of this compound in chloroform-*d* featured

paramagnetically shifted and broadened peaks over a 250 ppm sweep width, and its magnetic susceptibility was determined to be 5.43 (± 0.20) μ_B at 25 °C. The solubility of this product, its physical appearance, its ^{1}H NMR spectrum, and magnetic moment are analogous to the same properties reported for structurally characterized **1**,[18] allowing assignment of this compound as (^{tBu_2PPr}DI)FeBr$_2$ (Figure 6, **5**).

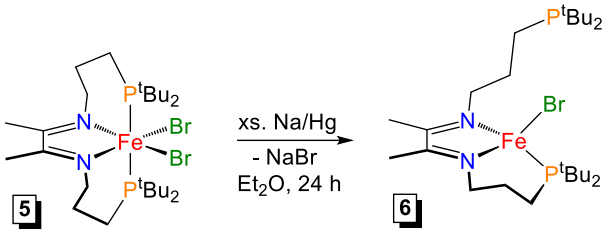

Figure 6. Reduction of **5** to **6**.

In the absence of CO, the reduction of **5** with an excess of sodium amalgam was performed in THF and a color change from blue to green was observed over the course of 2 h. After 24 h, the solution was filtered through Celite and the solvent was removed under vacuum to afford a green product. This compound was found to feature ^{1}H NMR resonances over 260 ppm, and surprisingly, ^{31}P NMR spectroscopy revealed resonances at 26.04 and 3.35 ppm, which are consistent with uncoordinated (matching the free ligand value)[20] and coordinated phosphine environments, respectively. The magnetic susceptibility of this product was found to be 3.66 (± 0.20) μ_B at 25 °C. Taken together, this data suggests the formation of partially-reduced (^{tBu_2PPr}DI)FeBr (Figure 6, **6**), which features a coordinated and uncoordinated phosphine arm.

Single crystal X-ray diffraction analysis was then employed to confirm the identity of **6**, and the solid-state structure revealed a pseudo-tetrahedral geometry with N(1)-Fe(1)-N(2) and Br(1)-Fe(1)-P(1) angles of 79.7(2) and 116.46(6) Å, respectively (Figure 7). Inspection of the metrical parameters (Table 2) reveals that the Fe(1)-P(1) distance of 2.3842(19) Å and the Fe(1)-Br(1) distance of 2.3925(11) Å are nearly identical, even though the covalent radius of P (1.07) is much smaller than the covalent radius of Br (1.20).[41] This suggests considerable π-donation from Br and minimal π-backbonding into P due to the lower π-acidity of trialkylphosphines. The N(1)-C(2) and N(2)-C(3) distances of 1.331(8) and 1.344(7) Å, respectively are longer than the

unreduced imine distance of 1.29 Å, while the C(2)-C(3) distance of 1.424(8) Å is shorter than the distance of 1.47 Å expected for an unreduced DI chelate.[25] Considering that **6** lacks π-accepting carbonyl ligands, we propose that it features an intermediate-spin Fe(II) center that exhibits antiferromagnetic coupling to a DI radical anion.

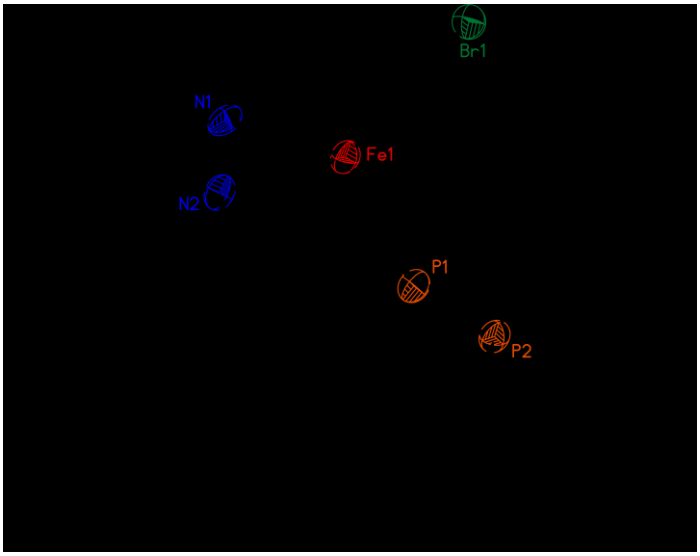

Figure 7. The solid-state structure of **6** shown with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 2. Bond lengths (Å) and angles (˚) determined for **6**.

Bond Lengths		**Bond Angles**	
Fe(1)-N(1)	2.015(5)	N(1)-Fe(1)-N(2)	79.7(2)
Fe(1)-N(2)	1.972(5)	N(1)-Fe(1)-P(1)	90.37(15)
Fe(1)-P(1)	2.3842(19)	N(2)-Fe(1)-P(1)	120.10(16)
Fe(1)-Br(1)	2.3925(11)	N(1)-Fe(1)-Br(1)	120.88(15)
N(1)-C(2)	1.331(8)	N(2)-Fe(1)-Br(1)	119.13(15)
N(2)-C(3)	1.344(7)	P(1)-Fe(1)-Br(1)	116.46(6)
C(2)-C(3)	1.424(8)		

The reduction of **5** using an excess of sodium amalgam was then repeated under an atmosphere of CO. Upon stirring the reduction for 24 h and removing the excess CO gas, filtration and solvent removal afforded an orange solid. The ^{1}H NMR spectrum of this product was found to feature inequivalent backbone methyl resonances at 1.61 and 1.91 ppm, while the

^{31}P NMR spectrum revealed the presence of a coordinated phosphine arm (91.56 ppm) along with an uncoordinated phosphine (27.95 ppm). These observations are consistent with those made during the characterization of dicarbonyl **3**, allowing us to identify the product as (^{tBu_2PPr}DI)Fe(CO)$_2$ (Figure 8, **7**). Notably, the IR spectrum of **7** was found to feature carbonyl stretching frequencies at 1932 and 1868 cm^{-1} in KBr, values that are lower those observed for **3** (1938 and 1874 cm^{-1}) and which are consistent with additional CO π-backdonation due to weaker phosphine π-backdonation. Assuming that the coordinated trialkylphosphine carries a charge of -0.12 (slightly less negative than the midpoint of the range due to ^{t}Bu substitution), Wolczanski's CDVR method[19] reveals carbonyl ligand charge densities of -0.65 and an overall charge on the DI ligand of -0.58 for **7**, which are slightly reduced relative to the same ligands of **3**. Using the CDVR method to access the charge density of **C** (Figure 1) reveals charges of -0.64 for the carbonyl ligands, and -0.60 for the imino(pyridine) portion of the chelate. Since **C** was shown by Neidig and Milstein to feature an Fe(0) center and neutral chelate,[13] CDVR analysis suggests that **3** (with a DI ligand charge of -0.52) and **7** possess the same electronic structure since they feature less reduced diimine functionalities.

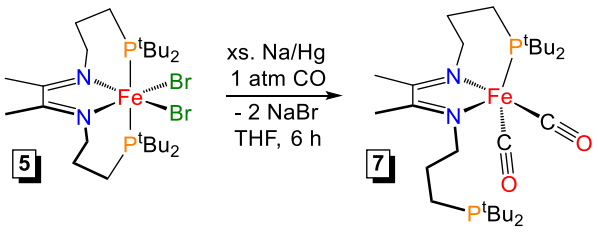

Figure 8. The solid-state structure of **7** shown with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Finally, attempts were made to convert **7** into the corresponding monocarbonyl complex upon heating to 110 °C and intermittently applying vacuum over the course of 10 days. Under these conditions, the conversion of **7** to a monocarbonyl complex was not observed. This lack of phosphine for carbonyl substitution can be rationalized through the electronic differences between the diphenylalkylphosphines of ^{Ph_2PPr}DI and the trialkylphosphines of ^{tBu_2PPr}DI. Importantly, the trialkylphosphines of ^{tBu_2PPr}DI are better σ-donors and poorer π-acceptors, which

results in greater M-CO backbonding and a lower propensity for CO dissociation at the formally 18-electron Fe center.

CONCLUSIONS

Upon reducing (^{Ph_2PPr}DI)FeBr$_2$ in the presence of CO to obtain (^{Ph_2PPr}DI)Fe(CO)$_2$, heating under vacuum was found to afford the first zerovalent Fe monocarbonyl compound to feature a tetradentate chelate, (^{Ph_2PPr}DI)Fe(CO). Although it was not fully appreciated at the outset, the choice of ligand for achieving this substitution reaction was fortuitous considering that the same transformation could not be achieved using the trialkylphosphine-substituted variant, ^{tBu_2PPr}DI. In the process of preparing these carbonyl compounds, Wolczanski's charge distribution via reporters (CDVR) method was applied to estimate the amount of electron density being transferred to the redox non-innocent portion of the chelate. For (^{Ph_2PPr}DI)Fe(CO)$_2$ and (^{tBu_2PPr}DI)Fe(CO)$_2$, this method afforded diimine charges of -0.52 and -0.58, respectively, an early indication that both compounds feature an Fe(0) center and an unreduced chelate.

EXPERIMENTAL DETAILS

General Considerations: All reactions were performed inside an MBraun glovebox under an atmosphere of purified nitrogen or on a high-vacuum manifold. Toluene, tetrahydrofuran, diethyl ether, and pentane were purchased from Sigma-Aldrich, purified using a Pure Process Technology solvent system, and stored in the glovebox over activated 4 Å molecular sieves and potassium prior to use. Chloroform-*d* was purchased from Cambridge Isotope Laboratories and dried over 4Å molecular sieves prior to use. Benzene-d_6 was purchased from Oakwood Chemical and dried over 4Å molecular sieves and potassium prior to use. FeBr$_2$ and 3-(di-t-butylphosphino)propylamine (as a 10% solution in THF) were used as received from Strem. Carbon monoxide was purchased from Sigma-Aldrich. (^{Ph_2PPr}DI)FeBr$_2$[18] and ^{tBu_2PPr}DI[20] were synthesized according to literature procedure.

Solution ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Varian 400 MHz or Avance NEO 500 MHz NMR spectrometer. All ^{1}H NMR and ^{13}C NMR chemical shifts (ppm) are reported relative to SiMe$_4$ using ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standards. ^{31}P NMR data (ppm) is reported relative to H$_3$PO$_4$ as an

external standard or using the absolute ^{1}H NMR frequency of an internal Si(Me)$_4$ standard. Solution state magnetic susceptibility data was obtained at 23 °C using the Evans method, and three trials were performed for each paramagnetic compound. IR spectroscopy was conducted on Bruker VERTEX 70 spectrometer with an MCT detector.

X-ray Crystallography: Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in the glovebox and transferred to a glass fiber with Apiezon N grease, which was then mounted on the goniometer head of a Bruker APEX Diffractometer equipped with Mo Kα radiation (Arizona State University). A hemisphere routine was used for data collection and determination of the lattice constants. The space group was identified and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct method (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix, least square procedures on [F^2] (SHELXL).

Preparation of (^{Ph_2PPr}DI)Fe(CO)$_2$ (3): In a nitrogen filled glove box, a 100 mL Schlenk tube was charged with 6.47 g of Hg^0 (32.37 mmol) followed by freshly cut Na^0 (0.037 g, 1.62 mmol) in approximately 10 mL of THF solvent. The mixture was stirred for 20 min at room temperature until the cloudy grey suspension turned clear. To this Na-Hg mixture, a solution of **1** (0.243 g, 0.324 mmol) in THF (~8 mL) was added. The Schlenk tube was then sealed, taken outside the box, and frozen in liquid nitrogen and degassed. To this reaction mixture, 1 atm of CO gas was introduced using the Schlenk line. After gas addition was completed, the reaction was warmed to room temperature and stirred for 24 h. Excess CO was removed using the Schlenk line and the red reaction mixture was filtered through Celite to remove the byproduct NaBr inside the glove box. The solvent was removed under vacuum to obtain 0.186 g of a fluffy red solid identified as **3** (88%). Single crystals of **3** were grown from a concentrated solution of diethyl ether at -35 °C. ^{1}H NMR (400 MHz, benzene-d_6): δ 7.45 (t, J = 6.8 Hz, 4H, *phenyl*), 7.14–6.89 (m, 16H, *phenyl*), 4.40 (d, J = 13.3 Hz, 2H, CH_2), 4.04 (d, J = 10.2 Hz, 2H, CH_2), 2.05–2.17 (m, 6H, CH_2), 1.73 (d, J = 2.3 Hz, 3H, CH_3), 1.56 (d, J = 25.1 Hz, 2H, CH_2), 1.43 (d, J = 5.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, benzene-d_6): δ 223.35 (d, J_{CP} = 6.0 Hz, *C*O), 145.79 (d, J_{CP} = 2.0 Hz, *C*=N), 145.29 (d, J_{CP} = 5.0 Hz, *C*=N), 139.83 (d, J_{CP} = 15.0 Hz, *phenyl*), 137.47 (d, J_{CP} = 35.5 Hz, *phenyl*), 133.23 (d, J_{CP} = 18.0 Hz, *phenyl*), 132.14 (d, J_{CP} = 11.0 Hz, *phenyl*), 129.46 (d, J_{CP} = 2.0 Hz, *phenyl*), 62.05 (d, J_{CP} = 12.0 Hz, *C*H$_2$), 55.93 (d, J_{CP} = 3.0 Hz, *C*H$_2$), 31.48 (d, J_{CP} = 10.0 Hz,

*C*H$_2$), 29.62 (d, J_{CP} = 7.0 Hz, *C*H$_2$), 28.64 (d, J_{CP} = 23.0 Hz, *C*H$_2$), 25.95 (d, J_{CP} = 3.0 Hz, *C*H$_2$), 15.00 (d, J_{CP} = 3.0 Hz, *C*H$_3$), 14.92 (s, CH$_3$). ^{31}P NMR (162 MHz, benzene-d_6): δ 67.40, -16.37. IR (KBr): ν_{CO} = 1938, 1874 cm^{-1}.

Preparation of (^{Ph_2PPr}DI)Fe(CO) (4): In a nitrogen filled glove box, a 100 mL Schlenk tube was filled with 0.060 g (0.092 mmol) of **3** in approximately 10 mL of toluene. The tube was sealed, taken outside the box, and heated to 110 °C in a pre-heated oil bath. Every 2 days, CO gas was removed on the Schlenk line. After 10 days of heating and CO gas removal, the reaction mixture was filtered through Celite and the solvent was removed under vacuum to obtain of 0.041 mg (71%) of a burgundy solid identified as **4**. Single crystals of **4** were grown from a concentrated solution of diethyl ether at -35 °C. ^{1}H NMR (400 MHz, benzene-d_6): δ 7.33 (t, *J* = 8.3 Hz, 4H, *phenyl*), 6.99–6.93 (m, 6H, *phenyl*), 6.93–6.87 (m, 6H, *phenyl*), 6.84 (t, *J* = 7.2 Hz, 4H, *phenyl*), 4.24–4.19 (m, 2H, C*H*$_2$), 3.76 (d, *J* = 14.0 Hz, 2H, C*H*$_2$), 2.18 (m, 3H, C*H*$_2$), 2.02 (m, 5H, C*H*$_2$), 1.76 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, benzene-d_6): δ 224.18 (s, *C*O), 143.80 (s, *C*=N), 141.59 (d, J_{CP} = 2.0 Hz, *phenyl*), 141.25 (d, J_{CP} = 2.0 Hz, *phenyl*), 138.36 (d, J_{CP} = 30.5 Hz, *phenyl*), 132.89 (d, J_{CP} = 10.0 Hz, *phenyl*), 132.14 (d, J_{CP} = 10.0 Hz, *phenyl*), 55.32 (d, J_{CP} = 5.0 Hz, *C*H$_2$), 28.51 (d, J_{CP} = 20.0 Hz, *C*H$_2$), 27.97 (d, J_{CP} = 52.5 Hz, *C*H$_2$), 16.05 (s, *C*H$_3$). ^{31}P NMR (162 MHz, benzene-d_6): δ 69.33. IR (KBr): ν_{CO} = 1846 cm^{-1}.

Preparation of (^{tBu_2PPr}DI)FeBr$_2$ (5): In a nitrogen filled glove box, a 20 mL scintillation vial was charged with 0.029 g (0.132 mmol) of FeBr$_2$ in approximately 5 mL of THF and stirred for 10 min until the FeBr$_2$ was almost dissolved. To this, a solution of ^{tBu_2PPr}DI (0.075 g, 0.165 mmol) in THF (~5 mL) was added and immediately the solution turned blue in color. The reaction was allowed to stir for 24 h at room temperature to allow for completion, after which it was filtered. The solvent was removed under vacuum and the resulting solid was washed with pentane (3 x 5 mL) and then dried to yield 0.079 g of a blue THF soluble compound identified as **5** (88%). ^{1}H NMR (500 MHz, benzene-d_6): δ 154.49 (1788 Hz), 37.87 (1450 Hz), 9.21 (247 Hz), 7.13 (10 Hz), 3.64 (74 Hz), 3.23 (7 Hz), 2.09 (9 Hz), 1.07 (9 Hz), 0.83 (9 Hz), -88.63 (152 Hz). Magnetic susceptibility (Evans method, 23 °C): μ_{eff} = 5.43 (± 0.20) μ_B.

Preparation of (^{tBu_2PPr}DI)FeBr (6): In a nitrogen filled glove box, a 20 mL scintillation vial was charged with 2.21 g of Hg^0 (11.04 mmol) followed by freshly cut Na^0 (0.013 g, 0.552 mmol) in

approximately 5 mL of Et_2O. The mixture was stirred for 20 min at room temperature until the cloudy grey suspension turned clear. To this Na-Hg mixture, a suspension of **5** (0.074 g, 0.110 mmol) in Et_2O (~8 mL) was added. The color of the reaction mixture changed from blue to green within 15 h. After stirring for 24 h at room temperature, the reaction mixture was filtered through Celite to remove the byproduct NaBr. The solvent was removed under vacuum to obtain 0.039 g (60%) of a green solid identified as **6**. Single crystals of **6** were grown from a concentrated solution of diethyl ether at -35 °C. ^{1}H NMR (400 MHz, benzene-d_6): δ 30.58 (225 Hz), 21.18 (606 Hz), 3.28 (62 Hz), 2.70 (54 Hz), 1.13 (73 Hz), -0.52 (123 Hz), -1.97 (125 Hz), -5.12 (411 Hz), -8.40 (184 Hz), -20.15 (981 Hz), -30.91 (1219 Hz), -56.67 (324 Hz), -124.88 (649 Hz), -223.67 (1060 Hz). ^{13}C NMR (101 MHz, benzene-d_6): δ No resonances observed. ^{31}P NMR (162 MHz, benzene-d_6): δ 26.04, 3.35. Magnetic susceptibility (Evans method, 23 °C): μ_{eff} = 3.66 (± 0.20) μ_B.

Preparation of (^{tBu_2PPr}DI)Fe(CO)$_2$ (7): In a nitrogen filled glove box, a 100 mL Schlenk tube was charged with 1.76 g of Hg^0 (8.84 mmol) followed by freshly cut Na^0 (10.2 mg, 0.412 mmol) in approximately 10 mL of THF solvent. The mixture was stirred for 20 min at room temperature until the cloudy grey suspension turned clear. To this Na-Hg mixture, a solution of **5** (0.059 g, 0.088 mmol) in THF (~8 mL) was added. The Schlenk tube was then sealed, taken outside the box and thawed in liquid nitrogen and degassed. To this reaction mixture, 1 atm of CO gas was introduced on the Schlenk line. After gas addition was completed, the reaction was warmed to room temperature and stirred for another 24 h. Excess CO was removed on the Schlenk line and the orange reaction mixture was filtered through Celite to remove the byproduct NaBr inside the glove box. The solvent was removed under vacuum to obtain 0.030 g (60%) of a fluffy orange solid identified as **7**. ^{1}H NMR (400 MHz, benzene-d_6): δ 4.54 (m, 2H, CH_2), 3.74 (m, 2H, CH_2), 2.31 (m, 2H, CH_2), 1.95 (m, 2H, CH_2), 1.91 (s, 3H, CH_3), 1.67 (m, 2H, CH_2), 1.61 (d, J = 4.0 Hz, 3H, CH_3), 1.25 (m, 2H, CH_2), 1.15 (d, J = 10.6 Hz, 9H, C(CH_3)$_3$), 1.09 (d, J = 7.5 Hz, 9H, C(CH_3)$_3$), 1.04–0.79 (m, 18H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, benzene-d_6): δ 145.57 (d, J_{CP} = 2.0 Hz, *C*=N), 145.35 (d, J_{CP} = 5.0 Hz, *C*=N), 61.87 (d, J_{CP} = 13.0 Hz, *C*H$_2$), 55.44 (d, J_{CP} = 2.0 Hz, *C*H$_2$), 36.14 (d, J_{CP} = 3.0 Hz, *C*(CH$_3$)$_3$), 35.89 (d, J_{CP} = 3.0 Hz, *C*(CH$_3$)$_3$), 31.43 (d, J_{CP} = 23.0 Hz, *C*H$_2$), 30.23 (d, J_{CP} = 6.0 Hz, *C*H$_2$), 29.90 (d, J_{CP} = 13.0 Hz, *C*H$_3$), 29.61 (s, *C*H$_3$),

19.24 (d, J_{CP} = 23.0 Hz, CH_2), 18.29 (d, J_{CP} = 11.0 Hz, CH_2), 15.50 (d, J_{CP} = 3.0 Hz, CH_3), 15.19 (s, CH_3). ^{31}P NMR (162 MHz, benzene-d_6): δ 91.56, 27.95. IR (KBr): ν_{CO} = 1932, 1868 cm^{-1}.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under Grant No. 2154359. We would like to acknowledge Marco Flores for assistance with preparing X-ray crystallographic data.

Appendix A. Supplementary data. Supplementary data for this article can be found online at https://doi.org/10.1016/. CCDC contains the supplementary crystallographic data for 2301321-2301323. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Data availability

Data will be made available on request.

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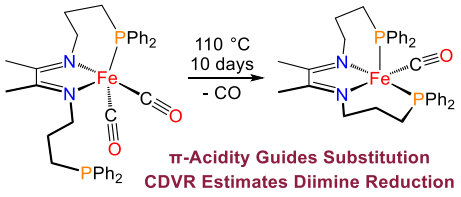

Reduction of (^{Ph_2PPr}DI)FeBr$_2$ or (^{tBu_2PPr}DI)FeBr$_2$ under CO afforded the corresponding dicarbonyl compounds. Relative to the phosphine groups of ^{Ph_2PPr}DI, the trialkylphosphine substituents of ^{tBu_2PPr}DI are weaker π-acceptors, a feature that prevents substitution and formation of the respective monocarbonyl complex upon heating under vacuum.