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Synthesis and Characterization of Iron Complexes based on Bis-Phosphinite PONOP and Bis-Phosphite PONOP Pincer Ligands

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Abstract

A series of bis-phosphinite and bis-phosphite PONOP iron complexes were prepared and characterized by NMR and IR spectroscopy. Bis-phosphinite PONOP iron dichloride complexes ($^R\text{PONOP}$)FeCl₂ ($^R\text{PONOP}$ = 2,6-(R₂PO)₂(C₅H₃N) and R = ⁱPr, ^tBu) were prepared through complexation of the free ligands with FeCl₂ and their solid-state structures were determined. Bis-phosphite PONOP iron complexes ($^{\text{OEt}}\text{PONOP}$)Fe(PMe₃)₂ and ($^{\text{Cat}}\text{PONOP}$)Fe(PMe₃)₂ (Cat = catechol) were synthesized through complexation of the free ligands to Fe(PMe₃)₄. Carbonyl complexes of both bis-phosphinite and bis-phosphite PONOP were prepared and characterized by IR. The monocarbonyl ($^{\text{iPr}}\text{PONOP}$)Fe(CO)Cl₂ was accessed through exposure of ($^{\text{iPr}}\text{PONOP}$)FeCl₂ to an atmosphere of CO and the CO stretching frequency was observed at 1969 cm⁻¹. Dicarbonyl complexes ($^{\text{iPr}}\text{PONOP}$)Fe(CO)₂ and ($^{\text{OEt}}\text{PONOP}$)Fe(CO)₂ were accessed through reduction of the corresponding chloride complexes with sodium amalgam under a CO atmosphere. Carbonyl stretching frequencies for ($^{\text{iPr}}\text{PONOP}$)Fe(CO)₂ and ($^{\text{OEt}}\text{PONOP}$)Fe(CO)₂ were observed at 1824 and 1876 cm⁻¹, and at 1871 and 1927 cm⁻¹ respectively. The bis-phosphite PONOP complexes exhibit a less electron rich metal center than the bis-phosphinite PONOP complexes, as would be expected based on the stronger π -acceptor character of these ligands. The electronic properties of the bis-phosphinite PONOP and bis-phosphite PONOP iron complexes are intermediate between previously reported PNP and PDI iron complexes, with the PONOP ligands exhibiting stronger electron donating ability than PDI ligands, but promoting a less electron rich metal center than found in analogous PNP iron complexes.

Keywords

Iron pincer complexes; Bis-phosphite pyridine ligands; Bis-phosphinite pyridine ligands

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Appendix A. Supplementary material

CCDC 1016572, 839105 and 1016573 contain the supplementary crystallographic data for complexes **1**, **2**, and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at ...

1. Introduction

Research on pincer ligands has increased dramatically since the late 1990's. These tridentate ligands promote highly stabilized metal centers and their modularity allows for systematic variation of the ligand's steric and electronic properties.^{1–3} Similarly, the development of iron homogeneous catalysts has greatly intensified in recent years.^{4–16} Iron complexes stabilized by pincer ligands have emerged as one of the important sources of catalytically active species.^{17–20} Some of the most promising examples of iron pincer catalysts belong to the family of iron complexes stabilized by the NNN aryl-substituted pyridine diimine (^{Ar}PDI) ligands [^{Ar}PDI = (2,6-ArN=C(Me))₂(C₅H₃N); Ar = 2,6-C₆H₃(ⁱPr)₂, 2,6-C₆H₃(Me)₂, 2-C₆H₄(^tBu)]. The dihalide iron PDI complexes were independently introduced by the Gibson and Brookhart groups as precatalysts for ethylene polymerization.^{17,18} Brookhart reported that the active catalysts could be prepared *in situ* by adding modified methylalumoxane to the precatalysts in the presence of ethylene. The iron systems are robust and offer high activity on par with the best Ziegler-Natta polymerization systems. The ^{Ar}PDI iron complexes have since been developed extensively by the Chirik group, which reported reduced dinitrogen iron PDI complexes [(^{Ar}PDI)Fe(N₂)₂] and their use as olefin hydrogenation and hydrosilation catalysts.^{19–21}

More recently, the Chirik group prepared iron alkylidene complexes by reacting dinuclear PDI iron complexes [(^{Me}PDI)Fe(N₂)₂](μ₂-N₂) and [(^{Et}PDI)Fe(N₂)₂](μ₂-N₂) with diazoalkanes.²² Notably, only a diphenyl-substituted diazoalkane reagent provided enough steric hindrance to stabilize the alkylidene against subsequent side reactions.²² Similar results have been reported for iron alkylidenes stabilized by porphyrin-style ligands.^{23,24} Klose reported that an iron-carbene stabilized by a tetramethyldibenzo-tetraazaannulene ligand was stable at room temperature when prepared with Ph₂CN₂ whereas use of PhCHN₂ led to a carbene which decomposed at room temperature.²³ These results suggest that steric factors within the coordination pocket of these iron complexes are crucial to stabilization of an iron alkylidene species.

Other examples of pincer ligands coordinated to iron include those with phosphine arms. The ^RPNP iron dihalide complexes [^RPNP = 2,6-(R₂PCH₂)₂(C₅H₃N); R = ⁱPr, ^tBu] have been utilized by Chirik and Milstein as precursors to hydrido iron complexes.^{12,25} The Chirik group accessed the dihydride ⁱPrPNPFeH₂(N₂) and the related silyl hydride ⁱPrPNPFeH(Si)N₂. Both structures exhibited modest hydrogenation and hydrosilylation activity with simple olefins.²⁵ Milstein and coworkers were able to prepare ⁱPrPNPFeH(CO)Br which they demonstrated to be an efficient catalyst for ketone hydrogenation.¹²

Iron compounds bearing modifications of the PNP ligands have been reported as well. For example, the Milstein group prepared an iron dichloride complex supported by the hybrid ligand ^RPNN [^RPNN = 2-(R₂PCH₂)-6-(Et₂NCH₂)(C₅H₃N); R = ^tBu], in which one phosphine group has been substituted with a diethylamino group.²⁶ There also have been reports of ^RPNNNP iron complexes [^RPNNNP = 2,6-(R₂PNH)₂(C₅H₃N); R = ⁱPr], which exhibit intermolecular hydrogen bonding and the formation of supramolecular solid state structures.²⁷ Also notable are the bis-phosphinite ^RPOCOP [^RPOCOP = 2,6-(R₂PO)₂(C₆H₃);

R = ⁱPr, Ph] iron systems. These ligands present an additional challenge as metallation requires activation of the C-H bond. As a result, there are few reports of these ligands on iron. Bhattacharya and coworkers reported the successful synthesis of a ^RPOCOP iron structure using Fe(PMe₃)₄ as a starting material.²⁸ These structures catalyzed the hydrosilylation of aldehydes and ketones.

The bis-phosphinite ^RPONOP ligands [^RPONOP = 2,6-(R₂PO)₂(C₅H₃N); R = ⁱPr, ^tBu] were introduced by Salem and coworkers in 2009 on ruthenium.²⁹ They reported preparation of a *trans*-dihydride ruthenium complex with reactivity toward water and electrophiles. PONOP has since been coordinated to group 9 and 10 metals.^{30–32} The iridium and rhodium structures have been used to study C-H bond activation.^{30–31} The group 10 metals formed unusual hydrido structures after use of the superhydride LiEt₃BH led to removal of the para proton of the pyridine ring and loss of aromaticity.³² The nickel analogues have catalyzed hydrosilylation of aldehyde. To date, there have been no reports of PONOP iron complexes.

To our knowledge, there has been only one report of pyridine centered bisphosphite pincer complexes to date. In 2012, Rubio and coworkers reported rhodium and iridium complexes of bis-phosphite PONOP with biphenyl substituents on the phosphorus. The iridium chloride analogue was found to be active as a catalyst precursor for the hydrogenation of 2-methyl-quinoline and 2-methylquinoxaline.³³

In light of these developments, we became interested in exploring the coordination chemistry and reactivity of iron complexes stabilized by bis-phosphinite and bis-phosphite PONOP ligands.

2. Experimental Section

2.1. General procedures

All manipulations of air- and moisture-sensitive compounds were performed using standard cannula and Schlenk techniques under argon or in glove boxes containing either a purified argon or nitrogen atmosphere. Solvents in air- and moisture-sensitive reactions were purified with a Vacuum Atmospheres solvent purification system, degassed by sparging with argon or by the freeze-pump-thaw method, and stored over molecular sieves under inert atmosphere. Deuterated solvents were purchased from Cambridge Isotopes and dried over molecular sieves. CD₂Cl₂ was freeze-pump-thawed prior to use. Carbon monoxide (99.995%) was purchased from AirGas. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 in ATR mode. Elemental analysis was performed at ALS Environmental in Tucson, AZ. ¹H, ¹³C and ³¹P NMR spectra were recorded on a Varian 400 MHz spectrometer at 25 °C and all chemical shifts are reported in parts per million values. ¹H and ¹³C chemical shift values are reported relative to the residual solvent peak. Abbreviations used to describe NMR data are as follows: bs, broad singlet; d, doublet; m, multiplet; q, quartet; s, singlet; sept, septet; t, triplet; vt, virtual triplet. The bis-phosphinite PONOP ligands²⁹ and Fe(PMe₃)₄³⁴ were prepared according to literature procedures.

2.2. X-ray structure determinations

Single crystals of complexes **1** and **3** were analyzed on a Bruker Apex-II CCD while a single crystal of complex **2** was analyzed on a Bruker Smart 1000. All X-ray data collections were carried out using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K. The structures of complexes **1** and **3** were solved by dual space methods while the structure of complex **2** was solved by direct methods. All structures were refined using the full-matrix least-squares on F^2 method with SHELXL-97.

2.3. Synthesis of ^RPONOPFeCl₂ complexes

2.3.1. ⁱPrPONOPFeCl₂ (1**)**—2,6-bis(diisopropylphosphinito)pyridine (4.01 g; 11.68 mmol) was dissolved in THF (35 mL). Iron dichloride (1.48 g; 11.68 mmol) was added and the reaction mixture was stirred for sixteen hours at room temperature producing a clear brown solution. The solvent was removed under vacuum to isolate a yellow solid. The crude product was recrystallized in toluene and washed in pentane to yield a shiny golden solid (4.30 g; 78.3% yield). Crystals suitable for x-ray analysis were grown by slow evaporation of toluene from a saturated solution. ¹H NMR (CD₂Cl₂): $\delta = -20.86$ (bs, 1H, Py-*H_p*), 9.18 (bs, 12H, CH(CH₃)₂), 10.37 (bs, 12H, CH(CH₃)₂), 50.53 (bs, 2H, Py-*H_m*), 121.28 (bs, 4H, CH(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂): $\delta = -234.73$ (s), 97.65 (s), 114.96 (s), 272.21 (s), 273.85 (s), 420.48 (s), 829.75 (s). Analysis for C₁₇H₃₁Cl₂FeNO₂P₂: Calcd C, 43.43; H, 6.65; N, 2.98. Found C, 43.84; H, 6.60; N, 2.73.

2.3.2. ^tBuPONOPFeCl₂ (2**)**—2,6-bis(ditertbutylphosphinito)pyridine (2.53 g; 6.33 mmol) was dissolved in THF (22 mL). Iron dichloride (0.72 g; 5.68 mmol) was added and the reaction mixture was stirred for seventeen hours at room temperature producing a light orange solution. The solvent was removed under vacuum and the crude product recrystallized in a 10:1 mixture of ether and dichloromethane at -35°C to afford a shiny gold solid (2.30 g; 76.6% yield). Crystals suitable for x-ray analysis were grown at -35°C in a saturated diethyl ether solution. ¹H NMR (CDCl₃): $\delta = -18.59$ (bs, 1H, Py-*H_p*), 15.67 (s, 36H, C(CH₃)₃), 51.54 (bs, 2H, Py-*H_m*). ³¹P{¹H} NMR (CDCl₃): $\delta = 138$ (s), 148 (s). Analysis for C₂₁H₃₉Cl₂FeNO₂P₂: Calculated C, 47.93; H, 7.47; N, 2.66. Found C, 48.24; H, 7.68; N, 2.40.

2.4. Synthesis of iron carbonyl complexes supported by ⁱPrPONOP

2.4.1. ⁱPrPONOPFe(CO)Cl₂ (3**)**—A round bottom flask filled with argon was evacuated and refilled with carbon monoxide and a carbon monoxide balloon was attached. ⁱPrPONOPFeCl₂ (0.64 g; 1.36 mmol) dissolved in THF (6 mL) was injected into the flask. Upon exposure to the CO atmosphere, the yellow solution immediately turned purple. The reaction was stirred for 24 hours and then the solvent was removed under vacuum. The crude product was dissolved in toluene, filtered through Celite and the filtrate dried *in vacuo* to afford a purple solid (0.49 g; 72.2% yield). Crystals suitable for x-ray analysis were grown by slow evaporation of toluene from a saturated solution. ¹H NMR (C₆D₆): $\delta = 1.42$ (d, 24H, *J_{H,H}* = 7.2 Hz, CH(CH₃)₂), 3.38 (sept, 4H, *J_{H,H}* = 7.2 Hz, CH(CH₃)₂), 6.31 (d, 2H, Py-*H_m*), 6.74 (t, 1H, Py-*H_p*). ¹³C NMR (C₆D₆): $\delta = 17.13$ (s, CH(CH₃)₂), 18.12 (s, CH(CH₃)₂), 27.54 (vt, *J_{P,C}* = 8.64 Hz, CH(CH₃)₂), 103.81 (s, Py-*C_m*),

143.20 (s, Py- C_p), 165.46 (t, $J_{P,C} = 5.58$ Hz, Py- C_o), 222.52 (t, $J_{P,C} = 20.66$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 216.09$. IR (neat, cm^{-1}) 1969 ($\nu_{\text{C}\equiv\text{O}}$). Analysis for $\text{C}_{18}\text{H}_{31}\text{Cl}_2\text{FeNO}_3\text{P}_2$: Calculated C, 43.40; H, 6.27; N, 2.81. Found C, 43.56; H, 6.35; N, 2.59.

2.4.2. $i\text{PrPONOPFe}(\text{CO})_2$ (4)—A reaction flask was charged with a 0.5% sodium amalgam prepared from 0.058 g (2.52 mmol) and 10.04 g (50.05 mmol) of mercury in pentane (30 mL) under argon. $i\text{PrPONOPFeCl}_2$ (0.20 g, 0.42 mmol) was added and the flask was transferred to a liquid nitrogen bath to freeze the slurry. The flask was evacuated and refilled with one atmosphere of carbon monoxide. The reaction mixture was stirred at 0 °C for three hours at which point it was warmed to room temperature. The reaction mixture was stirred for an additional 45 hours during which time it turned red and a fine grey precipitate formed. The carbon monoxide was removed and the reaction mixture filtered through Celite to isolate a clear red filtrate. The filtrate was dried *in vacuo* and the crude product was washed repeatedly with pentane to yield an orange solid (0.040 g, 20.7% yield). ^1H NMR (C_6D_6): $\delta = 1.25$ (dd, 12H, $J_{H,H} = 6.8$ Hz, $J_{P,H} = 8.0$ Hz $\text{CH}(\text{CH}_3)_2$), 1.29 (dd, 12H, $J_{H,H} = 7.2$ Hz, $J_{P,H} = 10.2$ Hz $\text{CH}(\text{CH}_3)_2$), 2.38–2.52 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 6.10 (d, 2H, $J_{H,H} = 8.0$ Hz, Py- H_m), 6.52 (t, 1H, $J_{H,H} = 8.0$ Hz, Py- H_p). ^{13}C NMR (C_6D_6): $\delta = 16.70$ (t, $J_{P,C} = 2.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 17.22 (s, $\text{CH}(\text{CH}_3)_2$), 32.81 (t, $J_{P,C} = 10.2$ Hz, $\text{CH}(\text{CH}_3)_2$), 100.18 (s, Py- C_m), 134.90 (s, Py- C_p), 164.64 (t, $J_{P,C} = 5.9$ Hz, Py- C_o), 219.55 (t, $J_{P,C} = 27.0$ Hz, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 255.72$. IR (neat, cm^{-1}) 1824, 1876 ($\nu_{\text{C}\equiv\text{O}}$).

2.5. Synthesis of $^{\text{OEt}}$ PONOP and $^{\text{Cat}}$ PONOP ligands

2.5.1. 2,6-bis(diethylphosphito)pyridine [$^{\text{OEt}}$ PONOP] (5)—A Schlenk tube under argon was charged with 2,6 dihydroxypyridine hydrochloride (0.89 g; 6.03 mmol) and THF (40 mL). TMEDA (1.41 g; 12.13 mmol) and triethylamine (3.66 g; 36.17 mmol) were added and the mixture was chilled. A cold solution of diethylchlorophosphite (2.08 g; 13.29 mmol) in THF (5 mL) was added portionwise and the reaction mixture was stirred for 20 hours at 65°C. The reaction mixture was filtered through Celite under inert atmosphere, the filtrate collected and the solvent removed under vacuum resulting in isolation of an orange oil. The crude product was dissolved in pentane (5 mL) and filtered through Celite to remove an insoluble orange impurity, affording a yellow oil after the filtrate was dried *in vacuo* (1.94 g, 91.7% yield). ^1H NMR (CD_2Cl_2): $\delta = 1.27$ (t, $J_{H,H} = 13.0$ Hz, 12H, CH_2CH_3), 4.04 (q, $J_{H,H} = 13.0$ Hz, 4H, CH_2CH_3), 4.06 (q, $J_{H,H} = 13.0$ Hz, 4H, CH_2CH_3), 6.47 (d, $J_{H,H} = 7.6$ Hz, 2H, Py- H_m), 7.59 (t, $J_{H,H} = 7.6$ Hz, 1H, Py- H_p). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 133.86$ (s).

2.5.2. 2,6-bis(o-phenylenephosphito)pyridine [$^{\text{Cat}}$ PONOP] (6)—A Schlenk tube under argon was charged with 2,6 dihydroxypyridine hydrochloride (0.57 g; 3.86 mmol) and THF (60 mL). TMEDA (0.88 g; 7.57 mmol) and triethylamine (2.48 g; 24.51 mmol) were added and the mixture was chilled. A cold solution of o-phenylene phosphorochloridate (1.43 g; 8.19 mmol) in THF (20 mL) was added portionwise and the reaction mixture stirred for 23 hours at 65°C. The reaction mixture was filtered through Celite under inert atmosphere, the filtrate collected and the solvent removed under vacuum to afford a light red-brown solid. The crude product was dissolved in toluene and filtered through Celite three times. The filtrate was then dried *in vacuo* to afford a tan solid (1.39 g, 92.4%

yield). ^1H NMR (CDCl_3): δ = 6.42 (d, $J_{\text{H,H}}$ = 8.0 Hz, 2H, Py- H_m), 7.00–7.28 (m, 8H, Ar- H), 7.54 (t, $J_{\text{H,H}}$ = 8.0 Hz, 1H, Py- H_p). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 131.43 (s). Analysis for $\text{C}_{17}\text{H}_{11}\text{NO}_6\text{P}_2$: Calculated C, 52.73; H, 2.86; N, 3.62. Found C, 52.61; H, 2.92; N, 3.57. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calculated for $\text{C}_{17}\text{H}_{12}\text{NO}_6\text{P}_2$ 388.0140; Found 388.0180.

2.6. Synthesis of iron trimethylphosphine complexes supported by bis-phosphite PONOP ligands

2.6.1. $^{\text{OEt}}\text{PONOPFe}(\text{PMe}_3)_2$ (7)—Tetrakis(trimethylphosphine) iron (0.059 g, 0.16 mmol) was added to a solution of $^{\text{OEt}}\text{PONOP}$ (0.061 g, 0.17 mmol) in toluene to produce a red solution. The reaction mixture was stirred for two hours and then dried in vacuo to afford a dark red solid (0.094 g, 90% yield). ^1H NMR (C_6D_6): δ = 1.22–1.27 (m, 30H, OCH_2CH_3 and $\text{P}(\text{CH}_3)_3$), 4.08–4.22 (m, 4H, OCH_2CH_3), 4.26–4.38 (m, 4H, OCH_2CH_3), 6.29 (d, 2H, $J_{\text{H,H}}$ = 8.0 Hz, Py- H_m), 6.65 (t, 1H, $J_{\text{H,H}}$ = 8.0 Hz, Py- H_p). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ = 200.26 (t, $J_{\text{P,P}}$ = 46.7 Hz), 21.61 (bs).

2.6.2. $^{\text{Cat}}\text{PONOPFe}(\text{PMe}_3)_2$ (8)— $^{\text{Cat}}\text{PONOP}$ (0.25 g, 0.65 mmol) was added to a solution of tetrakis(trimethylphosphine) iron (0.23 g, 0.64 mmol) in toluene (6 mL). The orange-brown reaction mixture was stirred for 9 hours and then filtered through a glass frit. The filtrate was dried in vacuo to produce an orange-brown residue. The crude product was recrystallized in pentane to afford a bright orange solid (0.015 g, 4% yield). ^1H NMR (C_6D_6): δ = 1.10 (vt, 18H, $J_{\text{H,H}}$ = 3.6 Hz, $\text{P}(\text{CH}_3)_3$), 5.94 (d, 2H, $J_{\text{H,H}}$ = 8.0 Hz, Py- H_m), 6.36 (t, 1H, $J_{\text{H,H}}$ = 8.0 Hz, Py- H_p), 6.71 (dd, 4H, $J_{\text{H,H}}$ = 3.6 Hz, $J_{\text{H,H}}$ = 5.2 Hz, Ar- H), 7.01 (dd, 4H, $J_{\text{H,H}}$ = 3.6 Hz, $J_{\text{H,H}}$ = 5.2 Hz, Ar- H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 191.35 (t, $J_{\text{P,P}}$ = 46.2 Hz), 22.18 (t, $J_{\text{P,P}}$ = 46.2 Hz).

2.7. Synthesis of an iron carbonyl complex supported by $^{\text{OEt}}\text{PONOP}$

2.7.1. $^{\text{OEt}}\text{PONOPFe}(\text{CO})_2$ (9)—A solution of $^{\text{OEt}}\text{PONOP}$ ligand (0.28 g, 0.80 mmol) dissolved in THF (3 mL) was added dropwise to a THF slurry of iron dichloride (0.10 g, 0.79 mmol). Over the course of five minutes, the reaction mixture became deep red. After 24 hours, the red reaction mixture was dried in vacuo to afford a viscous magenta oil (0.38 g). A portion of this oil (0.28 g) was added to a reaction flask containing a 0.5% sodium amalgam prepared from 0.029 g (1.25 mmol) and 4.98 g (24.83 mmol) of mercury in pentane (10 mL) under argon. The flask was partially immersed in a liquid nitrogen bath to freeze the slurry. The flask was then evacuated and refilled with one atmosphere of carbon monoxide. The reaction mixture was stirred at 0 °C for five hours and then warmed to room temperature. The reaction mixture was stirred for an additional 20 hours during which time it turned orange red and a fine grey precipitate formed. The carbon monoxide was removed and the reaction mixture filtered through Celite to isolate an orange brown filtrate. The filtrate was dried under vacuum. The crude product was dissolved in benzene and then passed through silica gel to isolate a yellow solution that was dried under vacuum to afford a yellow oil (0.011 g, 5.4% yield). ^1H NMR (C_6D_6): δ = 1.31 (t, 12H, $J_{\text{H,H}}$ = 7.2 Hz, CH_2CH_3), 3.96–4.07 (m, 4H, CH_2CH_3), 4.16–4.27 (m, 4H, CH_2CH_3), 6.22 (d, 2H, $J_{\text{H,H}}$ = 8.0 Hz, Py- H_m), 6.60 (t, 1H, $J_{\text{H,H}}$ = 8.0 Hz, Py- H_p). ^{13}C NMR (C_6D_6): δ = 16.59 (t, $J_{\text{P,C}}$ = 3.1 Hz, CH_2CH_3), 30.55 (s, CH_2CH_3), 62.90 (t, $J_{\text{P,C}}$ = 2.16 Hz, CH_2CH_3) 100.68 (t, $J_{\text{P,C}}$ =

3.1 Hz, Py-C_m), 134.29 (s, Py-C_p), 160.59 (t, J_{P,C} = 9.25 Hz, Py-C_o), 215.95 (t, J_{P,C} = 37.2 Hz, CO). ³¹P{¹H} NMR (C₆D₆): δ = 221.52. IR (neat, cm⁻¹) 1871, 1927 (ν_{C=O}).

3. Results and Discussion

3.1. Synthesis and characterization of ^RPONOPFeCl₂ complexes

Addition of ferrous dichloride to a THF solution of free ^RPONOP ligand resulted in the formation of the corresponding yellow iron species in good yields at room temperature (Scheme 1).

Single crystals of the isopropyl substituted PONOPFeCl₂ complex were grown by slow evaporation of toluene from a saturated solution at room temperature and analyzed by X-ray crystallography. The solid-state structure of ^{iPr}PONOPFeCl₂ is presented in Figure 1.

The geometry around the iron can be described as distorted square pyramidal with one chloride ligand in the apical position and the nitrogen of the pyridine ring, the two phosphorus atoms and the remaining chlorine forming the basal plane. The geometry is consistent with the previously reported crystal structure for the analogous structure, ^{tBu}PNPFeCl₂.²⁶ The iron is raised above the basal plane by a distance of 0.668 Å. Selected bond distances and bond angles are provided in Table 1.

X-ray quality crystals of the tert-butyl substituted PONOPFeCl₂ were grown at -35°C from diethyl ether. X-ray diffraction analysis found that the unit cell comprised two very similar yet distinct molecules. This observation was reported also for the ^{tBu}PNPFeCl₂ complex by Zhang and coworkers, who determined that the two structures were not significantly different.²⁶ The solid-state structure for one of the ^{tBu}PONOPFeCl₂ complexes is provided in Figure 2.

Both structures possess a distorted square pyramidal geometry around the iron. A primary difference between the two molecules is the position of the metal center. The iron is raised above the basal plane by a distance of 0.646 Å for the Fe1 structure and 0.657 Å for the Fe2 structure. The orientation of the plane containing the pyridine with respect to the line connecting the two phosphorus atoms is also different. The PONOPFeCl₂ complexes exhibit the long iron-ligand bond lengths reported for the PNP iron complexes, with an Fe-N bond length ranging from 2.264 Å to 2.310 Å for the PONOPFeCl₂ complexes. By comparison, the Fe-N bond length for ^{tBu}PNPFeCl₂ is 2.303 Å and the iron-pyridine nitrogen bond distance for ^{iPr}PDIFeCl₂ is 2.091 Å. Selected bond distances and bond angles for each structure are provided in Table 1. Analogous bond distances for ^{tBu}PNPFeCl₂ have been provided as well.²⁶

NMR spectra for both of these sixteen-electron complexes exhibit features associated with paramagnetism. For the CD₂Cl₂ ¹H NMR spectrum of ^{iPr}PONOPFeCl₂, the peaks are broadened and span a range of over 140 ppm, while the CDCl₃ ¹H NMR spectrum of ^{tBu}PONOPFeCl₂ spans over 70 ppm. Peak broadening in the ¹H NMR spectra precludes the determination of multiplicity. However, the ¹H NMR peaks are sufficiently distinct that assignment can be made using the integration values. For both structures, the resulting

assignments are consistent with molecules possessing C_{2v} symmetry in solution. The observed proton chemical shifts for $iPrPONOPFeCl_2$ fall in ranges similar to those observed for the related paramagnetic complex, $iPrPNNNPFeCl_2$ reported by Benito-Garagorri and coworkers.²⁷

The ^{13}C NMR spectrum of $iPrPONOPFeCl_2$ is also consistent with a paramagnetic compound. The peaks span over 1000 ppm and range from -234 ppm to 829 ppm. Benito-Garagorri and coworkers have reported a ^{13}C NMR spectrum for $iPrPNNNPFeCl_2$ which contains peaks in similar ranges.²⁷ Attempts to assign the carbon signals using two-dimensional NMR experiments have been unsuccessful to date, likely due to low carbon peak intensities and the effects of the paramagnetic iron center.

A notable feature of the 1H NMR spectrum for $tBuPONOPFeCl_2$ is the presence of minor peaks that cannot be assigned to the main compound. One minor peak appears upfield of the pyridine *para* proton resonance at -24 ppm while minor peaks appear both upfield and downfield of the pyridine *meta* proton peak at 49 ppm and 55 ppm respectively (Figure 3). In addition, a distinct shoulder can be observed on the tert-butyl methyl proton signal at 14 ppm and a broad peak of approximately the same height as this shoulder can be seen further upfield at -1 ppm (Figure 3).

These features appear consistently, regardless of the solvent used for data collection, and persisted even when the NMR sample was prepared from a single crystal. Given the location and number of these small peaks, a possible explanation is the existence of a minor species in which the ligand is coordinated in a bidentate fashion to the iron center whereby one of the phosphinite groups remains dissociated. Such a configuration would lack the symmetry present in the major species, rendering both of the pyridine *meta* protons inequivalent as well as leading to two signals for the methyl protons of the tert-butyl groups. The relative integration values for the peaks are consistent with the presence of this proposed minor species.

The ^{31}P NMR spectrum obtained for $tBuPONOPFeCl_2$ in C_6D_6 contains two small peaks at 138 ppm and 148 ppm. These resonances are extremely faint and were detectable only after using a four hour acquisition time. By contrast, no ^{31}P NMR signal could be located for the $iPrPONOPFeCl_2$ complex despite prolonged acquisition times and careful scrutiny of expanded acquisition windows. The absence of a ^{31}P NMR signal has been reported for the $tBuPNPFeCl_2$ complex.³⁵ A possible explanation is that the proximity of the coordinated phosphorus atoms in the $RPNP$ and $RPONOP$ ligands to the paramagnetic iron center leads to broadening of their resonances, hindering detection. In the case of $tBuPONOPFeCl_2$, at least one of the observed ^{31}P NMR resonances could be attributed to the proposed minor species, as the uncoordinated phosphorus atom would not be as affected by the metal.

It is significant that this phenomenon is observed only for $tBuPONOPFeCl_2$. This distinction may be a consequence of two concurrent factors: (1) the greater steric bulk of the tert-butyl groups in $tBuPONOPFeCl_2$ compared to the isopropyl groups of $iPrPONOPFeCl_2$; and (2) the increased length of the PONOP backbone due to the larger oxygen atoms replacing the methylene linkers of the PNP ligand. Each factor contributes to a mismatch between the size

of the pincer in ^tBuPONOP and iron. Further support for the size mismatch between the PONOP ligand and iron may be found in an examination of the ^RPOCOPFe(H)(PMe₃)₂ complexes. Bhattacharya and coworkers reported the successful synthesis of ⁱPrPOCOPFe(H)(PMe₃)₂ and ^{Ph}POCOPFe(H)(PMe₃)₂.²⁸ However, the synthesis of the ^tBuPOCOP analogue was unsuccessful and a majority of the starting material remained unreacted. They noted that only a minor amount of an iron hydride species with one PMe₃ was formed due to the steric crowding from the bulkier ligand.

Several methods were employed to attempt the reduction of the PONOP iron complexes. Stirring the dichloride complexes with 0.5% sodium amalgam in pentane under one atmosphere of nitrogen produced a mixture of free ligand and a dark, insoluble iron-containing solid. Both the tert-butyl and isopropyl substituted PONOP iron dichloride complexes were also reacted with magnesium and zinc. However, stirring a THF solution of the complexes with one or two equivalents of magnesium or zinc under nitrogen led to similar results. Running the reduction reactions at low temperature was unsuccessful as well. These observations are consistent with previous reports for the ⁱPrPNPFeCl₂ complex which also was reported to undergo degradation during reduction reactions.²⁵

3.2. Synthesis and characterization of iron carbonyl complexes supported by ⁱPrPONOP

Carbonyl complexes of PONOP iron were targeted to elucidate the electronic properties of the PONOP ligands. When ⁱPrPONOPFeCl₂ dissolved in toluene was exposed to one atmosphere of CO at room temperature, the yellow solution immediately turned purple, forming ⁱPrPONOPFe(CO)Cl₂. The ¹H NMR spectrum is characteristic of a diamagnetic species and features only one resonance for the methyl groups and only one resonance for the methine protons, consistent with retention of C_{2v} symmetry. The ¹³C NMR spectrum shows a triplet at 222.52 ppm (*J_{P,C}* = 20.66 Hz) for the CO ligand, which is also consistent with C_{2v} symmetry and with one carbonyl positioned trans to the PONOP's pyridine ring.

X-ray quality crystals of the purple carbonyl complex were grown by slow evaporation from toluene. The solid-state structure (Figure 4) exhibits a distorted octahedral geometry around the iron with both the P1-Fe1-P2 and the Cl2-Fe1-Cl1 bond angles bent toward the pyridine ring. The most significant distortion lies in the phosphorus-iron-phosphorus bond angle of 163°. Selected bond distances and bond angles are provided in Table 1.

The infrared spectrum of ⁱPrPONOPFe(CO)Cl₂ was obtained in ATR mode and the carbonyl stretching frequency found to be 1969 cm⁻¹. Benito-Garagorri and coworkers reported preparation of ⁱPrPNNPFe(CO)Cl₂, which was found to exist in the cis and trans configurations with a red cis-dichloro complex resulting from solid state synthesis and a blue trans-dichloro complex resulting from synthesis in solution.²⁷ The CO absorption bands reported were found by ATR to be 1947 cm⁻¹ for the cis-dichloro complex and 1956 cm⁻¹ for the trans-dichloro complex. Langer and coworkers reported a solid state structure for ⁱPrPNPFe(CO)Br₂.¹² The frequency of the carbonyl absorption band for this blue structure was determined to be 1944 cm⁻¹. Benito-Garagorri and coworkers prepared the dichloro analog of this complex ⁱPrPNPFe(CO)Cl₂ which they found to exist only in the cis-dichloro configuration.²⁷ The frequency of the carbonyl absorption band for this structure was found to be 1943 cm⁻¹, slightly lower than that obtained for the cis-

dichloro $i\text{PrPNNNPF}(\text{CO})\text{Cl}_2$. The CO stretching frequencies for all of these structures are summarized in Figure 5. Comparison of these CO stretching frequencies to that obtained for $i\text{PrPONOPFe}(\text{CO})\text{Cl}_2$ suggests a less electron rich metal center for the PONOP complex and reduced back-donation to the carbonyl when compared to both the PNNNP and the PNP iron complexes (Figure 5).

The dicarbonyl complex $i\text{PrPONOPFe}(\text{CO})_2$ was accessed by reducing $i\text{PrPONOPFeCl}_2$ with 0.5% sodium amalgam in pentane under carbon monoxide to afford a diamagnetic orange solid. The ^{13}C NMR spectrum has been assigned on the basis of its similarity to the previously reported spectrum for $i\text{PrPNPFe}(\text{CO})_2$.²⁵ The carbonyl carbon appears at 219.55 ppm as a triplet with a coupling constant of $J_{\text{P,C}} = 27.0$ Hz. This value is identical to the coupling constant reported for the analogous PNP structure. The chemical shifts and coupling constants of the remaining peaks are extremely similar to those reported for the PNP complex.

Carbonyl stretching frequencies for $i\text{PrPNPFe}(\text{CO})_2$ were observed at 1879 and 1827 cm^{-1} when analyzed neat. For comparison, Trovitch and coworkers have reported infrared spectra using KBr pellet for the dicarbonyl $i\text{PrPNPFe}(\text{CO})_2$ (Figure 6, left) with carbonyl bands at 1842 and 1794 cm^{-1} and their diisopropyl PDI iron dicarbonyl (Figure 6, right) with carbonyl bands at 1950 and 1894 cm^{-1} .^{19,25} The structures in Figure 6 are arranged in order of increasing π -acidity of the ligand. In a similar trend to that observed for the monocarbonyl complexes, the PONOP complex again appears to contain a less electron rich iron center when compared to the PNP iron structure.

3.3. Synthesis and characterization of iron trimethylphosphine complexes supported by bis-phosphite PONOP ligands

The synthesis of bis-phosphite PONOP ligands [$^{\text{OR}}\text{PONOP} = 2,6-((\text{OR})_2\text{PO})_2(\text{C}_5\text{H}_3\text{N})$] was targeted with the goal of better stabilizing a reduced iron center by increasing the π -acidity of the ligand. Two bis-phosphite PONOP ligands were synthesized in an analogous manner to bis-phosphinite PONOP: the ethoxy-containing $^{\text{OEt}}\text{PONOP}$ and the catechol-derived $^{\text{Cat}}\text{PONOP}$ (Figure 7).

Both ligands were reacted with iron dichloride in an attempt to form the chelates. However, no reaction was observed between iron dichloride and $^{\text{Cat}}\text{PONOP}$ despite extended reaction times and use of elevated temperature. The reaction of $^{\text{OEt}}\text{PONOP}$ with iron dichloride in THF afforded a magenta product. The ^1H NMR spectrum of the product is too complicated to assign and attempts to purify the product were unsuccessful. The ^{31}P NMR spectrum in CD_2Cl_2 for the resulting compound contains a triplet at 184 ppm coupled to a doublet at 172 ppm. One possible explanation for this splitting pattern is a complex containing a monodentate or bidentate PONOP in addition to the tridentate PONOP ligand. Attempts to isolate these species have been unsuccessful thus far.

Following a report of Bhattacharya and coworkers on the metallation of $^{\text{R}}\text{POCOP}$ using $\text{Fe}(\text{PMe}_3)_4$,²⁸ bis-phosphite ligands $^{\text{OEt}}\text{PONOP}$ and $^{\text{Cat}}\text{PONOP}$ were reacted with $\text{Fe}(\text{PMe}_3)_4$ in toluene and NMR analysis of the reaction mixtures is consistent with successful formation of the chelates. The ^1H NMR spectra are consistent with formation of

diamagnetic products with C_{2v} symmetry. The ^{31}P NMR of each structure contains two distinct resonances that can be assigned to the PONOP ligand and the PMe_3 ligands. The PONOP resonances appear as triplets, which is consistent with the presence of two chemically equivalent trimethylphosphines in the products. The PMe_3 resonance for the $^{\text{OEt}}\text{PONOP}$ structure appears as a broad singlet at 21.5 ppm, while the PMe_3 signal for the $^{\text{Cat}}\text{PONOP}$ iron complex appears as a distinct triplet, allowing for the determination of the coupling constant ($J_{\text{P,P}} = 46.2$ Hz).

Attempts to grow crystals of the trimethylphosphine complexes for structure determination have been unsuccessful. The $^{\text{OEt}}\text{PONOP}$ complex exhibits high solubility in most common solvents. The $^{\text{Cat}}\text{PONOP}$ complex also exhibits high solubility. Small crystals of the $^{\text{Cat}}\text{PONOP}$ complex were grown in pentane at -35°C . Unfortunately, the crystals rapidly lost solvent upon separation from the mother liquor rendering them unsuitable for X-ray analysis.

The preparation of bis-phosphinite PONOP complexes from $\text{Fe}(\text{PMe}_3)_4$ was attempted also. Stirring toluene solutions of either $^{\text{iPr}}\text{PONOP}$ or $^{\text{tBu}}\text{PONOP}$ in the presence of $\text{Fe}(\text{PMe}_3)_4$ led to no reaction. This notable difference in reactivity between the bis-phosphinite and bis-phosphite PONOP ligands may underscore the difference in their electronic properties. The more π -acidic bis-phosphite PONOP ligands may be able to stabilize an $\text{Fe}(0)$ center, but unable to effectively stabilize an $\text{Fe}(\text{II})$ ion, while the bis-phosphinite PONOP ligands can easily stabilize an $\text{Fe}(\text{II})$ ion but not the $\text{Fe}(0)$ center.

3.4. Synthesis and characterization of an iron carbonyl complex supported by $^{\text{OEt}}\text{PONOP}$

In order to access the dicarbonyl iron complex of $^{\text{OEt}}\text{PONOP}$, the product resulting from the complexation of the bis-phosphite PONOP ligand with FeCl_2 was reduced with 0.5% sodium amalgam under an atmosphere of CO . The crude product was dissolved in benzene and passed through a small silica gel pipet to isolate a pale yellow oil. The ^1H NMR spectrum is consistent with formation of a diamagnetic complex with C_{2v} symmetry. The ^{13}C NMR spectrum contains a triplet at 216 ppm assigned to the carbonyl carbons with a coupling constant of $J_{\text{P,C}} = 37.2$ Hz, which is significantly higher than the coupling constant observed for $^{\text{iPr}}\text{PONOPFe}(\text{CO})_2$ and the analogous $^{\text{iPr}}\text{PNPFe}(\text{CO})_2$.²⁵ The remaining carbon peaks are extremely similar to those observed for the previously reported dicarbonyl PNP iron complex in terms of chemical shift and multiplicity and have been assigned on this basis.

Carbonyl bands were observed at 1926 and 1870 cm^{-1} for the bis-phosphite PONOP complex. As mentioned previously, Trovitch et al. have reported infrared spectra using KBr pellet for the dicarbonyl $^{\text{iPr}}\text{PNPFe}(\text{CO})_2$ (Figure 8, far left) with carbonyl bands at 1842 and 1794 cm^{-1} and the diisopropyl PDI iron dicarbonyl (Figure 8, far right) with carbonyl bands at 1950 and 1894 cm^{-1} .^{19,25} Comparing the carbonyl stretching frequencies, it can be seen that the bis-phosphite PONOP iron complex contains a more electron rich metal center than observed for the PDI iron complex. However, the metal center for the bis-phosphite PONOP complex is less electron rich than the metal center in the bis-phosphinite PONOP iron complex. The bis-phosphite PONOP complexes exhibit electronic properties that fall between the iron PDI complexes and the bis-phosphinite PONOP complexes.

The structures in Figure 8 are arranged in order of increasing π -acidity of the ligand with the complex containing the most reduced metal center on the left and the complex with the most oxidized metal center on the right.

4. Conclusions

Based upon the spectroscopic data above, it may be stated that the bis-phosphite PONOP ligands are stronger π -acids than the bis-phosphinite PONOP ligands, as would be expected for the stronger π -acceptor character of the phosphite ligands. The electronic properties of the bis-phosphinite PONOP and bis-phosphite PONOP iron complexes are intermediate between PNP iron and PDI iron complexes, with PONOP ligands exhibiting stronger electron donating ability than observed for PDI ligands, but promoting a less electron rich metal center than observed for PNP iron complexes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- (^RPONOP)FeCl₂ complexes (^RPONOP = 2,6-(R₂PO)₂(C₅H₃N); R = ⁱPr, ^tBu) were prepared.
- X-ray structures of (ⁱPrPONOP)FeCl₂ and (^tBuPONOP)FeCl₂ were determined.
- X-ray structure of (ⁱPrPONOP)Fe(CO)Cl₂ was also determined.
- Two new ligands 2,6-(R₂PO)₂(C₅H₃N) (R = OEt; R₂ = catechol) were prepared.
- ν(CO) of (ⁱPrPONOP)Fe(CO)₂, (^{OEt}PONOP)Fe(CO)₂, (ⁱPrPONOP)Fe(CO)Cl₂ are reported.

Figure 1. Solid-state structure of $i\text{PrPONOPFeCl}_2$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability.

Figure 2.
Solid-state structure of $t\text{BuPONOPFeCl}_2$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability.

Figure 3.
Close up of ^1H NMR spectrum for tBuPONOPFeCl_2 .

Figure 4. Solid-state structure of $i\text{PrPONOPFe(CO)Cl}_2$. Hydrogen atoms omitted for clarity. Thermal ellipsoids at 50% probability.

Figure 5.
CO stretching frequencies for PONOP, PNP and PNNP iron complexes.

Figure 6.
CO stretching frequencies for $ArPDIFe(CO)_2$, $iPrPONOPFe(CO)_2$ and $iPrPNPFe(CO)_2$.

Figure 7.
Drawings of the ^{OEt}PONOP and ^{Cat}PONOP ligands.

Figure 8.
CO stretching frequencies for PDI, PNP and PONOP dicarbonyl complexes.

Scheme 1.
Synthesis of $R_2PONOPFeCl_2$

Table 1

Selected measurements for $iPr_2PONOPFeCl_2$, $tBuPONOPFeCl_2$, $tBuPNPFeCl_2$, $iPr_2PONOPFe(CO)Cl_2$

Measurement	$iPr_2PONOPFeCl_2$	$tBuPONOPFeCl_2$	$tBuPNPFeCl_2$	$iPr_2PONOPFe(CO)Cl_2$
Bond lengths (Å)				
Fe1-N1	2.264(3)	2.2720(15)	2.303(2)	1.9829(9)
Fe1-Cl1	2.3458(13)	2.2706(6)	2.317(1)	2.3081(4)
Fe1-Cl2	2.2734(15)	2.3561(6)	2.375(1)	2.3046(3)
Fe1-P1	2.4734(13)	2.5317(6)	2.507(1)	2.2392(3)
Fe1-P2	2.4922(14)	2.5413(6)	2.540(1)	2.2415(4)
Fe1-Cl8	NA	NA	NA	1.7661(12)
Bond angles (°)				
N1-Fe1-Cl1	141.65(10)	108.74(4)	95.75(7)	87.72(3)
N1-Fe1-Cl2	98.35(9)	142.08(4)	160.14(6)	87.64(3)
Cl1-Fe1-Cl2	119.89(6)	109.13(2)	103.74(4)	175.102(14)
P1-Fe1-P2	144.57(5)	145.140(19)	139.70(3)	163.517(14)
N1-Fe1-Cl8	NA	NA	NA	179.31(6)