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### Phosphane-Pyridine Iron Complexes: Synthesis, Characterization and Application in Reductive Amination through the Hydrosilylation Reaction

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A series of 6 cyclopentadienyl phosphanyl-pyridine pianostool iron complexes was prepared in good yields, characterized, and studied in the catalytic reductive amination of benzaldehyde derivatives through hydrosilylation reactions

#### Introduction

The current interest in the design of mixed donor phosphane-pyridine complexes is considerable because these ligands have a potential importance in catalysis and coordination chemistry. Because of the soft and hard nature of the phosphorus and nitrogen donor atoms, respectively, transition metal complexes bearing the phosphane-pyridine ligand have been extensively studied during the past decades.<sup>[1,2]</sup> One of the less-explored areas of such phosphanylpyridine coordination chemistry is the reactivity of iron complexes.<sup>[3]</sup> Meanwhile, the recent and special significance for homogeneous catalysis for the use of cheap and environmentally benign metals such as iron is becoming a highly attractive and challenging area of research.<sup>[4]</sup> In that regard, the investigation of the synthesis and reactivity of new molecular-defined phosphane-pyridine iron complexes can potentially provide guidelines for the rational design of efficient iron-based catalysts.

On another hand, direct reductive amination of carbonyl compounds with amines is an elegant and efficient method for the preparation of substituted amines. It is usually carried out by using borohydride reducing reagents.<sup>[5]</sup> In this area, the catalytic reductive amination reaction of aldehydes through transition-metal-catalyzed hydrogenation, hydro-

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by using polymethylhydrosiloxane as the hydrosilane source and in dimethylcarbonate as the solvent at 40  $^{\circ}$ C. Single-crystal X-ray structural analyses were performed for all the complexes.

gen transfer,<sup>[6]</sup> or hydrosilylation<sup>[7]</sup> of the in situ formed imines is a simple way in molecular synthesis to obtain amines. Up to now, iron catalysts were used only in scarce examples to perform such a reaction.<sup>[6k,8]</sup>

On the basis of these results and our background in ironcatalyzed reactions,<sup>[9]</sup> and especially in hydrosilylation of  $C=O^{[10]}$  and C=N bonds,<sup>[11]</sup> we pursue our efforts to develop environmentally friendly, molecular defined iron systems. We have recently reported the efficiency of a series of  $[CpFe(CO)_2(PR_3)][X]$  (X = I, BF<sub>4</sub>, PF<sub>6</sub>) complexes to catalyze the hydrosilylation of aldehydes and ketones<sup>[10e]</sup> and esters.<sup>[12]</sup> We report herein the comparative study of pendant and bidentate cyclopentadienyl iron phosphanyl methyl-pyridine complexes **1–6** for reductive amination of aldehydes under hydrosilylation conditions.

#### **Results and Discussion**

According to the established methodology described for the preparation of the monophosphane  $[CpFe(CO)_2(PR_3)]$ -[X],<sup>[10e,13]</sup> the complexes  $[CpFe(CO)_2(Ph_2PCH_2Pyr)][X]$  (1:  $X = PF_6$ ) and (2:  $X = BF_4$ ) were obtained in one step by reaction of 1 equiv. of the (diphenylphosphanyl)methyl-pyridine with 1 equiv. of the precursor  $[CpFe(CO)_2(THF)][X]$ in  $CH_2Cl_2$  at room temperature in the dark for 30 min (Scheme 1).



Scheme 1. Preparation of the Cp-(P-pyr) iron complexes **1**,**2**, **4**, and **5**.

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The corresponding complexes 1 and 2 were obtained in good isolated yields (80 and 68%, respectively) after recrystallization. Single crystals of the new complexes 1 and 2 were obtained, and their molecular structures were confirmed by X-ray crystallography (Figure 1, Table 1, and Supporting Information).



Figure 1. Ortep view of complex 2, drawn at the 50% probability level. Hydrogen atoms and  $BF_4$  are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complexes 1–6.

Complex 1			
Fe–P Fe–Cp Fe–CO Fe–CO	2.2336(6) 1.721 1.784(2) 1.778(2)	P-Fe-CO P-Fe-CO OC-Fe-CO	92.02(7) 94.85(7) 94.80(10)
Complex 2			
Fe–P Fe–Cp Fe–CO Fe–CO	2.2327(6) 1.715 1.781(2) 1.780 (2)	P-Fe-CO P-Fe-CO OC-Fe-CO	89.21(7) 97.91(8) 92.93(10)
Complex 3			
Fe–P Fe–Cp Fe–CO Fe–N	2.2151(7) 1.716 1.769(3) 1.992(2)	P-Fe-CO P-Fe-N N-Fe-CO	94.06(9) 82.52(6) 92.14(11)
Complex 4			
Fe–P Fe–Cp Fe–CO Fe–N	2.2137(5) 1.714 1.7674(19) 1.9987(15)	P–Fe–CO P–Fe–N N–Fe–CO	94.50(6) 82.47(4) 92.57(7)
Complex 5			
Fe–P Fe–Cp Fe–CO Fe–N	2.2192(9) 1.718 1.780(3) 2.004(3)	P–Fe–CO P–Fe–N N–Fe–CO	94.04(11) 82.50(8) 92.98(13)
Complex 6			
Fe–P Fe–Cp Fe–CO Fe–I	2.2100(8) 1.719 1.773(3) 2.6337(4)	P-Fe-CO P-Fe-I P-Fe-CO	94.01(9) 96.08(2) 94.01(9)

The molecular structures of **1** and **2** closely resemble those of the analogous monophosphane Fe complexes  $[CpFe(CO)_2(PR_3)][X]$  reported previously.<sup>[10e]</sup> Typically, four-legged piano-stool geometries were observed, and no significant structural difference was observed between both complexes: for example, the Fe–P distance of 2.23 Å is in the range of those for complexes bearing a monodentate phosphane (2.21-2.26 Å).<sup>[10e]</sup> The IR spectra of both complexes **1** and **2** show the CO stretching bands at 2015, 2056 and 2015, 2058 cm<sup>-1</sup>, respectively.

When complexes 1 and 2 were stirred under visible light irradiation in dry and degassed dichloromethane at room temperature for 7 h, the corresponding P,N-bidentate [CpFe(CO) (Ph<sub>2</sub>PCH<sub>2</sub>Pyr)][X] (4:  $X = PF_6$ ) and (5: X =BF<sub>4</sub>) complexes were obtained quantitatively. When the pyridine arm is coordinated to the metal center, the iron is in a pseudo-tetrahedral geometry, with four different substituents and becomes a stereogenic center:<sup>[14]</sup> characteristic diastereotopic protons of the methylene bridge appear in <sup>1</sup>H NMR spectra as two broad signals, (e.g. for 4 at  $\delta =$ 3.84 and 4.53 ppm). Furthermore, the two phenyl rings on the phosphorus atom are also diastereotopic, which lead to anisochronous <sup>13</sup>C signals.

The iodo analogous compound 3 was prepared by a onepot procedure by reaction of  $[CpFe(CO)_2(I)]$  with 1 equiv. (diphenylphosphanyl)methyl-2-pyridine in toluene of heated overnight at reflux in a 45% isolated yield. Single crystals of the three new P.N-bidentate iron complexes 3-5 were obtained, and their molecular structures were confirmed by X-ray crystallography (Figure 2, Table 1, and Supporting Information). In the molecular structures of 3– 5, typically four-legged piano-stool geometries were observed, and no significant structural difference was observed between the complexes. The bond lengths are fairly constant and have the following mean values [range in bracket] (Å): Fe-P 2.216 [2.2137-2.2192], Fe-CO 1.772 [1.767-1.780], and Fe-N 1.998 [1.992-2.004]. The N-Fe-P bond angles are also constant 82.50° [82.47-82.52]; such small values are the result of the geometric demands imparted by the five-membered chelate rings. The complexes display a CO stretching band at 1980–1982 cm<sup>-1</sup> in their IR spectra. These lower v(CO) frequencies translate the antistretching effect induced by P-Fe-N coordination bonds.



Figure 2. Ortep view of complex 5, drawn at the 50% probability level. Hydrogen atoms and  $BF_4$  are omitted for clarity.

Interestingly, when the same reaction was performed with 1 equiv. of the ligand (diphenylphosphanyl)methyl-2quinoline in toluene heated overnight at reflux, the corresponding P,N-bidentate iron complex was not obtained. Whereas, when the reaction was performed under visible light irradiation in dry and degassed toluene overnight at room temperature, the corresponding [CpFe(CO)<sub>2</sub>-(Ph<sub>2</sub>PCH<sub>2</sub>Quinoline)][I] complex **6** was obtained in an 87%



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isolated yield. After recrystallization by diffusion of pentane into a solution of 6 in dichloromethane, single crystals of the new complex 6 suitable for X-ray diffraction studies were obtained, and their molecular structures were confirmed by X-ray crystallography (Figure 3 and Table 1).



Figure 3. Ortep view of complex 6, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Preliminary studies of the catalytic activity of the novel iron complexes 1-6 and their monodentate analogs 7-9 were performed to explore their potential in the reductive amination of aldehydes under hydrosilylation conditions (Scheme 2).



Scheme 2. Reductive amination of benzaldehyde under hydrosilylation conditions.

The screening of the prepared iron complexes 1-9 was performed on the reaction of benzaldehyde (0.5 mmol) with di(*n*-propyl)amine (0.5 mmol, 1 equiv.) in dichloromethane in the presence of 5 mol-% of the complex and 1 equiv. of phenylsilane as the reducing agent at 30 °C under visible light activation for 1 h.

As illustrated in Table 2, by using the phosphane ligated complexes  $[CpFe(CO)_2(Ph_2P-CH_2-Pyr)][X]$  (1: X = PF<sub>6</sub>) and (2:  $X = BF_4$ ), moderate conversions were obtained, 51 and 68%, respectively (Table 2, Entries 1 and 2). It must be underlined that without light irradiation, a slight decrease in the conversion was observed (56% vs. 68%, Entries 3 vs. 2), which shows that light has a beneficial and notable effect on the catalytic reduction. Notably, when performing the reaction with complexes  $[CpFe(CO)_2(PR_3)][BF_4]$  (7-9) bearing simple phosphanes such as PCy<sub>3</sub>, PPh<sub>3</sub>, or PPhMe<sub>2</sub>, similar level of conversions were observed (35-58%) (Table 2, Entries 9-11), which shows that these cationic bis(carbonyl) iron complexes are modest catalysts for such transformations. When the reaction was performed with diphenylphosphanyl-methyl-pyridine bidentate  $[CpFe(CO)(Ph_2P-CH_2-Pyr)][X]$  (3: X = I) and (4: X =

PF<sub>6</sub>), similar results were obtained and conversions of up to 79% were observed (Table 2, Entries 4 and 5). Interestingly, by varying the nature of the counterion and by using the tetrafluoroborate complex **5**, the conversion was improved to 94% (Table 2, Entry 6). Again, the beneficial effect of light irradiation was observed because in the dark, the conversion decreased to 72% (Table 2, Entry 7). Using the neutral phosphorus-ligated [CpFe(CO)(I)(Ph<sub>2</sub>P–CH<sub>2</sub>–Quin)] complex **6**, a conversion of 83% was obtained (Table 2, Entry 8).

Table 2. Optimization for the reductive amination of benzaldehyde under hydrosilylation conditions with catalysts 1-9.<sup>[a]</sup>

Entry	Catalyst (mol-%)	Silane (equiv.)	Solvent	Time [h]	Conv. [%] <sup>[b]</sup>
1	1 (5)	$PhSiH_{3}(1)$	CH <sub>2</sub> Cl <sub>2</sub>	1	51
2	2 (5)	$PhSiH_3(1)$	$CH_2Cl_2$	1	68
3 <sup>[c]</sup>	2 (5)	$PhSiH_3(1)$	$CH_2Cl_2$	1	56
4	3 (5)	$PhSiH_3(1)$	$CH_2Cl_2$	1	50
5	4 (5)	$PhSiH_3(1)$	$CH_2Cl_2$	1	79
6	5 (5)	$PhSiH_3(1)$	CH <sub>2</sub> Cl <sub>2</sub>	1	94
7 <sup>[c]</sup>	5 (5)	$PhSiH_3(1)$	$CH_2Cl_2$	1	72
8	6 (5)	$PhSiH_3(1)$	CH <sub>2</sub> Cl <sub>2</sub>	1	83
9	7 (5)	$PhSiH_3(1)$	CH <sub>2</sub> Cl <sub>2</sub>	1	35
10	8 (5)	$PhSiH_3(1)$	$CH_2Cl_2$	1	41
11	9 (5)	$PhSiH_3(1)$	CH <sub>2</sub> Cl <sub>2</sub>	1	58
12	5 (5)	PMHS (4)	$CH_2Cl_2$	24	95
13	5 (5)	PMHS (4)	EtOAc	24	68
14	5 (5)	PMHS (4)	CPME	24	50
15	5 (5)	PMHS (4)	2-Me-THF	24	55
16	5 (5)	PMHS (4)	DMC	24	80
17	5 (5)	PMHS (4)	DMC	24 <sup>[d]</sup>	91
18 <sup>[c]</sup>	5 (5)	PMHS (4)	DMC	24 <sup>[d]</sup>	74
19	$\operatorname{FeCl}_2(5)$	PMHS (4)	$CH_2Cl_2$	24	68

[a] Typical conditions: benzaldehyde (0.5 mmol), amine (0.5 mmol), complex **1–9** (0.025 mmol, 5 mol-%), silane (1–4 equiv.), in 1 mL of solvent at 30 °C, under visible light irradiation. [b] Conversion determined by GC. [c] In the absence of light irradiation. [d] 40 °C, 24 h, dimethylcarbonate (DMC), cyclopentylmethylether (CPME).

Encouraged by the good conversion obtained, the amination of benzaldehyde was studied by using cheap PMHS (polymethylhydrosiloxane) as the reducing agent. When performing the reaction at 30 °C in dichloromethane for 24 h, a full conversion was observed (95%) (Table 2, Entry 12). The nature of the solvent was also studied. By replacing dichloromethane by organic solvents such as EtOAc, 2methyltetrahydrofuran (2-Me-THF), or cyclopentylmethylether (CPME), the reaction slowed down and reduced conversions were observed (68, 55, and 50%, respectively) (Table 2, Entries 13–15). Interestingly, the use of a greener solvent such as dimethylcarbonate<sup>[15]</sup> (DMC) permitted an encouraging conversion at 30 °C for 24 h to be obtained (80%, Table 2, Entry 16). By performing the reaction at 40 °C, a conversion of 91 % was reached under light irradiation and 74% in the absence of light (Table 2, Entries 17 and 18). Notably, when iron salts such as FeCl<sub>2</sub> were used, a moderate conversion of 68% was obtained after 24 h at 30 °C, which shows the beneficial effect of the prepared complexes on the reactivity of the reductive amination (Table 2, Entry 19).

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The optimized conditions [aldehyde/amine/PMHS (1:1:4) in the presence of 5 mol-% of complex 5 in 1 mL of dimethylcarbonate at 40 °C for 24-48 h under visible light irradiation] were used to study the scope of this reaction (Scheme 3). Starting from benzaldehyde, several secondary amines, such as di-n-propyl-, allyl-, and benzylamine were tested, and the corresponding tertiary amines were obtained with good isolated yields (73-77%) (Table 3, Entries 1–3). Notably, more hindered secondary amines such as diisopropylamine did not lead to a full reaction, as only 19% conversion was observed (Table 3, Entry 4). Similarly, with a less reactive secondary amine such as diphenylamine, only a low conversion was obtained (Table 3, Entry 5). With these limitations in hand, we decided to investigate the influence of the nature of the aldehydes on the reaction. With classical electron-donating groups such as methyl or methoxy in the *para* position of benzaldehyde, the corresponding amines were obtained in good isolated yields, 85 and 80%,



Scheme 3. Reductive amination of benzaldehydes under hydrosilylation conditions.

Table 3. Scope of iron-catalyzed reductive amination of aldehydes with complex 5.<sup>[a]</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	Product		Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[c]</sup>
1	Н	nPr	Ph N 1	10a	93	75
2	Н	allyl	Ph N 1	lOb	90 <sup>[d]</sup>	73
3	Н	benzyl	Ph N Ph Ph 1	10c	88 <sup>[d]</sup>	77
4	Н	iPr	-		19 <sup>[d]</sup>	-
5	Н	Ph	-		26 <sup>[d]</sup>	-
6	Me	nPr	1	lOd	89	85
7	MeO	nPr	1	l0e	87	80
8	Cl	nPr	1	l0f	71	53
9	Br	nPr	N <sup>-R<sup>2</sup></sup> 1	l0g	73	58
10	CN	nPr	$R^1$ $R^2$ 1	l0h	74	58
11	CO <sub>2</sub> Me	nPr	1	lOi	79	63
12	COMe	nPr	1	lOj	84	72
13	Et <sub>2</sub> N	nPr	1	l0k	70	62
14	OH	nPr			0	-

[a] Typical conditions: aldehyde (0.5 mmol), amine (0.5 mmol), complex **5** (0.025 mmol, 5 mol-%), PMHS (2 mmol, 4 equiv.), in 1 mL of dimethylcarbonate (DMC) at 40 °C, 24 h, under visible light irradiation. [b] Conversion determined by <sup>1</sup>H NMR spectroscopy. [c] Isolated yield after purification by column chromatography. [d] 48 h.

respectively (Table 3, Entries 6 and 7). Interestingly, with electron-withdrawing *para* substituents, slightly lower conversions were observed (71–84%), and the corresponding tertiary amines were produced in moderate yields (53–72%) (Table 3, Entries 8–12).

Of main interest is the chemoselectivity of this reductive amination as no dehalogenation by-product was obtained (Table 3, Entries 8 and 9), and the reaction tolerated functional groups such as cyano, diethylamino, ester, and ketone (Table 3, Entries 10–13). By contrast, when performing the transformation with *p*-hydroxybenzaldehyde, no reaction occurred, which shows the inhibiting effect of the hydroxy group (Table 3, Entry 14).

#### Conclusions

We have developed a range of piano-stool iron complexes imparting heterodifunctional phosphanes such as 2-(2-diphenylphosphanylmethyl)pyridine. From spectral and structural studies, it has been established that the coordinated  $Ph_2P-CH_2-Pyr$  acts as both a unidentate and chelating bidentate ligand. Furthermore, it has been shown that P–N bidentate iron complexes catalyze the reductive amination of aromatic aldehydes through a hydrosilylation process. It must be noted that they are more powerful than the monodentate complexes in such a reaction. It must be pointed out that the reactions were performed (i) under mild conditions (30–40 °C) and (ii) by using dimethylcarbonate as a green solvent and PMHS (polymethoxyhydrosilane) as a cheap silane source.

#### **Experimental Section**

Typical Procedure for Cationic P,N-Bidentate Complex 5 Synthesis: In a Schlenk tube, [CpFe(CO)<sub>2</sub>(THF)]BF<sub>4</sub> (402 mg, 1.2 mmol) and (PPh<sub>2</sub>CH<sub>2</sub>Pyr) (334 mg, 1.2 mmol) were added under argon into dried and degassed CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The Schlenk tube was wrapped with aluminum foil, and the solution was stirred for 30 min at room temperature. After the solution was concentrated, the final complex precipitated in excess diethyl ether, which led to the formation of a beige yellow powder (440 mg, 68% yield). The obtained complex 2 (308 mg, 0.6 mmol) was then added under argon to dried and degassed CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The solution was stirred at room temperature for 7 h under light irradiation. The color of the reaction solution turned to orange. After the solution was concentrated in vacuo, the complex precipitated in diethyl ether. The orange powder was further washed with diethyl ether (3 × 20 mL), dried, and stored under argon (298 mg, 97% yield).

**Typical Procedure for Iron-Catalyzed Reductive Amination of Benzaldehyde Derivatives:** A 10-mL oven-dried Schlenk tube containing a stirring bar was charged with iron complex **5** (0.025 mmol) and dimethyl carbonate (1 mL). After purging with argon (argon-vacuum three cycles), the aldehyde (0.5 mmol) and amine (0.5 mmol) were added followed by PMHS (2.0 mmol). The reaction mixture was stirred in a preheated oil bath at 40 °C for 24 h under light irradiation (24 W compact fluorescent light bulb). MeOH (1 mL) was then added followed by NaOH (1 mL of a 2 M aqueous solution) with vigorous stirring. The reaction mixture was further stirred for 1 h at room temperature and was extracted with diethyl

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ether (2 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL), dried with anhydrous MgSO<sub>4</sub>, filtered, and concentrated under vacuum. The conversion was determined for Table 3 by <sup>1</sup>H NMR spectroscopy. The product was then purified by silica gel column chromatography by using pentane/ethyl acetate mixture (0 to 10%) to achieve the desired product.

CCDC-883398 (for 1), -883399 (for 2), -883400 (for 3), -883401 (for 4), -883402 (for 5), and -883403 (for 6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Supporting Information** (see footnote on the first page of this article): Experimental procedures, descriptions, characterization and crystallographic data, and <sup>1</sup>H and <sup>13</sup>C NMR spectra of complexes **1–6** and the obtained amines are presented.

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# SHORT COMMUNICATION

A series of 6 cyclopentadienyl phosphanylpyridine piano-stool iron complexes was prepared, characterized, and studied in the catalytic reductive amination of benzaldehyde derivatives in dimethylcarbonate through hydrosilylation reactions by using polymethylhydrosiloxane as the hydrosilane source.



**Homogeneous Iron Catalysis** 

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Phosphane-Pyridine Iron Complexes: Synthesis, Characterization and Application in Reductive Amination through the Hydrosilylation Reaction

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