

Iron carbonyl complex containing bis[2-(diphenylphosphino)phenyl]ether enhancing efficiency in the palladium-catalyzed Suzuki–Miyaura reaction

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The reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with bis[2-(diphenylphosphino)phenyl]ether (DPEphos) in refluxing THF afforded a mononuclear complex, $[\text{Fe}(\text{CO})_4(\eta^1\text{-P-DPEphos})]$ (**1**), as major product and a binuclear complex, $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-P,P-DPEphos})]$ (**2**), as minor product respectively. The DPEphos ligand acts as a terminal P-donor in complex **1** and a bridging P,P-donor in complex **2**. Complexes **1** and **2** were characterized by elemental analysis, fast atom bombardment mass spectrometry, FT-IR, ^1H and ^{31}P { ^1H } NMR spectroscopy. The structure of complex **1** has been tentatively assigned by density functional theory calculations and its analogy with reported complexes. Combination of complex **1** and PdCl_2 furnished an active catalyst for the Suzuki–Miyaura cross-coupling reactions of various aryl halides with arylboronic acids. Interestingly, under the same experimental condition, complex **1**/ PdCl_2 as catalyst showed superior activity over the DPEphos/ PdCl_2 system. Copyright © 2012 John Wiley & Sons, Ltd.

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Keywords: iron carbonyl complexes; DPEphos ligand; metal-containing phosphine; density functional theory; Suzuki–Miyaura reaction

Introduction

The coordination chemistry of large-bite-angle diphosphine ligands has received considerable attention in organometallic chemistry because of their potential utility as catalysts in many organic transformation reactions.^[1] For many years, bis[2-(diphenylphosphino)phenyl]ether (DPEphos) has been widely used as a large-bite-angle ligand because of its rich coordination behavior due to the presence of two phosphorus atoms and an oxygen atom as potential donor sites. Several coordination modes of this ligand have been reported, such as *P*-monodentate,^[2] *P*, *P*-chelate,^[2–4] *P,O,P*-chelate,^[4,5] and *P,P*-bridging^[4,6] mode. Literature survey reveals that this ligand formed coordination compounds with a variety of transition metals such as Cu(I),^[2,7–9] Ni(0),^[10] Ni(II),^[8] Rh(I),^[11,12] Ru(II),^[4] Ag(I),^[6,13] Pd(0),^[14] Pd(II),^[3] and Re,^[15–17] and some of the complexes were found to be excellent catalysts for various reactions such as hydrogenation,^[4,15] hydroformylation,^[18] carbonylation,^[11,12] aryl halide amination,^[19,20] and cross-coupling reactions.^[21] Surprisingly, the coordination chemistry of this ligand with iron has not been reported so far. Thus, as a part of our continuing work^[22–24] on the coordination chemistry of iron with phosphine-based ligands, in this work we report our findings on the reactivity of $[\text{Fe}_3(\text{CO})_{12}]$ with DPEphos ligand to synthesize two new iron–carbonyl complexes: $[\text{Fe}(\text{CO})_4(\eta^1\text{-P-DPEphos})]$ (**1**) and $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-P,P-DPEphos})]$ (**2**).

During the last two decades, ligand-promoted palladium-catalyzed Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids have proven to be an attractive strategy for C–C bond formation reactions in organic synthesis.^[25,26] Among various ligands, ferrocenyl phosphines were found to be a very successful class of ligand employed in this reaction.^[27–29]

It is interesting to note that the complex **1**, having an uncoordinated phosphine arm, bears a resemblance to ferrocenyl phosphines, which are considered to be the most versatile classes of metal-containing phosphines used as ligands in organic chemistry to generate bimetallic catalytic systems. It is noteworthy that bimetallic catalysts have been applied to various organic reactions in the recent past and often such catalysts offered superior results in terms of efficiency and selectivity relative to the individual ones.^[30,31] Although, there exist some well-characterized bimetallic Fe–Pd complexes in the literature,^[32–34] such complexes have not been investigated so far as catalysts for the Suzuki–Miyaura reactions. Thus, in order to enlarge this series and to widen the scope of metal-containing phosphines as ligands, herein we have also explored the catalytic efficiency of the complex **1**/ PdCl_2 system for the Suzuki–Miyaura cross-coupling reactions of aryl halides with arylboronic acids.

Results and Discussion

Synthesis, Spectroscopic Characterization and Density Functional Theory (DFT) Study

The reaction of $[\text{Fe}_3(\text{CO})_{12}]$ with different phosphine-based ligands to synthesize mono- and binuclear complexes is well

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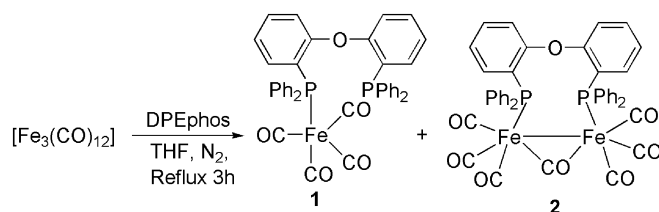
established, but in the majority of cases trimethylamine *N*-oxide was required as a decarbonylating agent.^[35] In this work, we found that the reaction between $[\text{Fe}_3(\text{CO})_{12}]$ and DPEphos in 1:2 molar ratio in THF under refluxing condition proceeded without a decarbonylating agent to produce two new complexes – a mononuclear $[\text{Fe}(\text{CO})_4(\eta^1\text{-P-DPEphos})]$ (**1**) and a binuclear $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-P,P-DPEphos})]$ (**2**) in 46% and 21% yields, respectively (Scheme 1). The elemental analyses and fast atom bombardment (FAB) mass spectra of complexes **1** and **2** are in good agreement with the formulations proposed. The FAB mass spectrum of complex **1** showed a moderate intense molecular ion peak at m/z 707 for $[\text{M}+1]^+$ peak along with four fragment ion peaks corresponding to the sequential loss of four CO ligands. The most intense peak (100%) was observed at m/z 594 for $[\text{M}-4\text{CO}-1]^+$ peak. The ^1H NMR spectra of the complex **1** showed expected resonances for aromatic protons. The ^{31}P NMR spectra displayed two distinct peaks at δ 26.70 and -16.89 ppm. The low field resonance is attributed to the coordinated phosphine, whereas the high field resonance, which is almost same as that of the free ligand δ_{p} value (-16.5 ppm^[17]), is attributed to uncoordinated phosphine. The IR spectra of complex **1** in KBr exhibited three distinct terminal $\nu(\text{CO})$ bands at 2046, 2029 and 1980 cm^{-1} ; this pattern is consistent with other reported tetracarbonyl iron complexes.^[36,37] It may be important to note that theoretically complex **1** could have two possible geometrical isomers depending on whether the phosphorus atom is axially or equatorially located. Literature survey reveals that the number and intensities of CO stretching frequencies are often used to draw conclusions about axial and equatorial arrangement of phosphine ligands in complexes of the type $\text{Fe}(\text{CO})_4(\text{phosphine})$.^[36] Thus, comparing the $\nu(\text{CO})$ values of complex **1** with some reported $\text{Fe}(\text{CO})_4(\text{phosphine})$ -type complexes,^[36,38,39] we propose that the phosphine ligand in complex **1** is axially located. It may be mentioned that the majority of structurally characterized $\text{Fe}(\text{CO})_4(\text{phosphine})$ complexes showed that the phosphine group occupied the axial position.^[24,39–44] To the best of our knowledge, only two structures appeared in the literature in which phosphine occupied the equatorial position.^[44,45] Since we could not develop diffraction-quality crystals for X-ray analysis, we carried out a geometry optimization study for complex **1** using a DFT method. Both the axial and equatorial isomers were considered and optimized at B3LYP/6-31+G(d) level of theory. The optimized structures (Figs S1 and S2) and calculated values (Tables S1 and S2) are shown in the online supporting information. The density functional study showed that the complex **1** adopts slightly distorted trigonal-bipyramidal geometry at the iron center. The calculated values of some of the key parameters of the axial isomer are $[\text{Fe}-\text{P} = 2.33 \text{ \AA}, \text{Fe}-\text{C}(\text{ax}) = 1.79 \text{ \AA}, \text{Fe}-\text{C}(\text{eq}) = 1.80 \text{ \AA}, \angle \text{P}-\text{Fe}-\text{C}(\text{ax}) = 178^\circ; \angle \text{P}-\text{Fe}-\text{C}(\text{eq}) = 90.1^\circ$ (av.); $\angle \text{C}(\text{eq})-\text{Fe}-\text{C}(\text{eq}) = 120^\circ$ (av.)] and the values are comparable to some of the related axial $\text{Fe}(\text{CO})_4(\text{phosphine})$ -type complexes for which X-ray structures are known.^[39–44] For instance, the calculated $\text{Fe}-\text{C}_{\text{ax}}$

and Fe-P bond distances of **1** (1.79 \AA and 2.33 \AA , respectively) are close to those found for analogous complexes, e.g. $[\text{Fe}(\text{CO})_4\text{PPh}_3]$ ^[42] (1.80 \AA and 2.24 \AA), $[\text{Fe}(\text{CO})_4\text{P}(o\text{-tolyl})_3]$ ^[43] (1.78 \AA and 2.31 \AA), $[\text{Fe}(\text{CO})_4\text{PCy}_3]$ ^[39] (1.79 \AA and 2.29 \AA). The calculated average P-Fe-C(ax) bond angle of 178° of complex **1** indicates slight deviation from trigonal-bipyramidal geometry. We have calculated the stability of the isomers in terms of total energy and the axial isomer is 7.34 kcal mol^{-1} more stable than the equatorial one. It is noteworthy that generally the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gap in a complex contributes to its stability. The observed energy gap for the axial isomer is 102.00 kcal mol^{-1} while for equatorial isomer it is 99.55 kcal mol^{-1} . The relatively larger HOMO–LUMO energy gap for the axial isomer compared to that of the equatorial isomer further accounts for higher stability of the axial isomer over its equatorial counterpart.

On the other hand, the FAB mass spectrum of complex **2** showed a very low intense molecular ion peak at m/z 848 along with several fragment ion peaks corresponding to the sequential loss of CO ligands. The most intense peak (100%) was observed at m/z 594 for $[\text{M}-7\text{CO}-\text{Fe}-1]^+$ peak. The IR spectra of complex **2** in KBr exhibited five bands in the range 2047–1928 cm^{-1} for terminal $\nu(\text{CO})$ bands; this pattern is consistent with those reported for other diironheptacarbonyl compounds containing bridging diphosphine.^[46,47] The presence of a $\nu(\text{CO})$ band at 1886 cm^{-1} suggests the presence of a bridging carbonyl group in **2**. The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **2** showed only one signal at 28.71 ppm indicating that the two phosphine moieties are chemically equivalent. Compared to the free ligand, complex **2** showed a downfield shift of about 45 ppm and this value is within the range reported for related complexes, in which the DPEphos ligand bridges the two metal centers.^[4]

Suzuki–Miyaura Cross-Coupling Reaction Using Complexes **1** and **2** as Ligands with PdCl_2 and their Comparison with Ligand-Free and DPEphos/ PdCl_2 Catalytic Systems

It is now almost established that sterically bulky phosphines are one of the best ligands in palladium-catalyzed Suzuki–Miyaura reactions.^[48,49] During the last few years, metal-containing phosphines have gained attention as ligands because of their bulkiness, donor properties and interesting chemistry. Among different metal-containing phosphines, ferrocenyl phosphines are one of the most extensively studied phosphines used as ligands in palladium-catalyzed cross-coupling reactions, including Suzuki–Miyaura reactions.^[27–29,50–53] Besides ferrocenyl phosphines, cobalt-carbonyl-phosphines^[31,54–56] and rhenium-carbonyl-phosphine^[57] are the only other metal-containing phosphines used as ligands in the Suzuki–Miyaura. Since, complex **1** is sufficiently bulky and has an uncoordinated phosphine arm, we were intrigued to see whether this free arm of complex **1** could be exploited as a ligand in the palladium-catalyzed



Scheme 1. Synthesis of iron–carbonyl complexes.

Suzuki–Miyaura reaction. For the initial study, the reaction between 4-bromonitrobenzene and phenylboronic acid was chosen as a model reaction using DMF as solvent and K_2CO_3 as base, and the reaction was performed at 60°C in the presence of a catalyst generated *in situ* from $PdCl_2$ (0.5 mol%) and the iron-containing phosphine **1** (1 mol%). Interestingly, the $PdCl_2$ /complex **1** system afforded a highly active catalyst producing almost quantitative product in 2 h of reaction time. Noteworthy is that the same reaction could also be performed at room temperature but slightly less yield (86%) was obtained and a longer reaction time was required (24 h) (Table 1, entry 2). For the sake of comparison, the catalytic experiments were also performed using free $PdCl_2$ (without any ligand), $PdCl_2$ /DPEphos (1:2) and $PdCl_2$ /complex **2** (1:2) as catalysts and the results are shown in Table 1. Our results showed that, even in the absence of any ligand, $PdCl_2$ could perform the coupling reaction, producing the cross-coupling product in good yield (66%). However, the use of complex **1** as ligand significantly improved the product formation (98%). Interestingly, our catalytic system was found to be more effective than $PdCl_2$ /DPEphos (entry 2) and the $PdCl_2$ /complex **2** (entry 4) system under identical conditions. We know that, usually in the Suzuki–Miyaura reaction, *in situ* generated catalyst and well-defined catalyst prepared from the same set of reagents often give different results.^[58,59] However, to check this effect, we tried to prepare a compound by reacting two equivalent of complex **1** with one equivalent of $PdCl_2$ in refluxing THF. A light-green colored compound was isolated, but unfortunately we could not completely reveal its identity. It may be important to mention that about two decades ago Shaw and co-workers had synthesized a green-colored bimetallic Fe–Pd complex by reacting $[Fe(CO)_4(dppm-P)]$ (analogous to complex **1**) with $[PdCl_2(\eta^3-C_3H_5)_2]$ and suggested that the green color was due to strong metal–metal interaction.^[33] However, in our case, we were anticipating to get a different complex, $[Fe_2(CO)_8(\mu-P,P-DPEphos)PdCl_2]$, in which there was a remote possibility of forming such an Fe–Pd bond. Although the FAB mass spectrum of the green compound supports our expected composition, $[Fe_2(CO)_8(\mu-P,P-DPEphos)$

$PdCl_2]$, by showing a very low intense (10%) molecular ion peak at m/z 1552 $[M-Cl-2]^+$, the fragment ion peaks could not be assigned properly. The elemental analyses data are also not very conclusive. The ^{31}P NMR spectra at room temperature gave a broad signal at δ 18.2 ppm might indicate that a fluxional process took place between the two phosphorus atoms. 1H NMR also showed broad resonances in the aromatic region. The FTIR spectrum showed multiple $\nu(CO)$ bands in the range 2046–1887 cm^{-1} . Nevertheless, we have performed a catalytic test of this green compound in the model reaction and slightly less yield (88%) was obtained compared to the *in situ* catalytic system (Table 1, entry 5). The effect of complex **1** as ligand with palladium becomes much more prominent when we used less reactive 4-chloronitrobenzene as substrate at 90°C with 1.5 mol% catalyst. For instance, when we carried out the reaction under ligand-free conditions, only 12% product was isolated, while when the same reaction was performed with complex **1**/ $PdCl_2$ -based *in situ* catalyst a dramatic improvement in the product yield (68%) was obtained (Table 1, entry 6 vs. 8). In fact, the Fe–Pd-based pre-formed catalyst (green compound) also showed significant improvement over ligand-free catalyst.

Having established the fact that complex **1**/ $PdCl_2$ -based *in situ* catalyst gave the best result with our model system, we wanted to investigate the system further for other substrates. A wide range of electronically diverse aryl halides (bromides and chlorides) and arylboronic acids were examined using complex **1**/ $PdCl_2$ *in situ* catalyst and the results are summarized in Table 2. Irrespective of activating (entries 1–5) or deactivating groups (entries 6–8) present on the aryl bromides, good to excellent yields were observed. However, deactivating substrates including *ortho*-substituted aryl bromide required slightly longer reaction time as compared to activated substrates. Besides phenylboronic acid, other boronic acids such as *p*-tolylboronic acid (entry 4) or *p*-chloroboronic acid (entry 3) also gave good results. It may be important to mention that generally aryl chlorides are less reactive than aryl bromides in the Suzuki–Miyaura reactions and often require more drastic conditions and/or higher catalyst

Table 1. Effects of various catalysts in the Suzuki–Miyaura cross-coupling reactions^a

X = Cl, Br

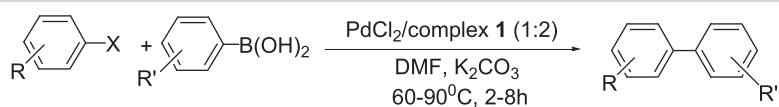
Entry	Substrate (X)	Catalyst	Temp. (°C)	Pd (mol%)	Time (h)	Yield (%) ^b
1	Br	$PdCl_2$	60	0.5	2	66
2	Br	$PdCl_2$ /DPEphos	60	0.5	2	78
3	Br	$PdCl_2$ / 1	60	0.5	2	98 (91) ^d
4	Br	$PdCl_2$ / 2	60	0.5	2	82
5	Br	Pd–Fe compound	60	0.5	2	88
6	Cl	$PdCl_2$	90	1.5	8	12
7	Cl	$PdCl_2$ /DPEphos	90	1.5	8	22
8	Cl	$PdCl_2$ / 1	90	1.5	8	68
9	Cl	$PdCl_2$ / 2	90	1.5	8	28
10	Cl	Pd–Fe compound	90	1.5	8	42

^aReaction conditions: aryl halide (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (3 mmol), DMF (6 ml), Pd:L = 1:2.

^bIsolated yield.

^cYields are the average of two runs.

^dAmount in parentheses is for Pd:L = 1:1.

Table 2. Suzuki–Miyaura cross-coupling reactions of various aryl bromides (at 60°C with 0.5 mol% catalyst loading) and chlorides (at 90°C catalyst loading 1.5 mol%) with arylboronic acids using PdCl₂/1 catalytic system


Entry	R	X	R'	Reaction condition ^a	Yield (%) ^b
1	NO ₂	Br	H	60°C, 2 h, 0.5 mol% Pd	98
2	NO ₂	Br	H	rt, 24 h, 0.5 mol% Pd	86
3	NO ₂	Br	Cl	60°C, 3 h, 0.5 mol% Pd	89
4	NO ₂	Br	CH ₃	60°C, 4 h, 0.5 mol% Pd	84
5	COCH ₃	Br	H	60°C, 2 h, 0.5 mol% Pd	92
6	H	Br	H	60°C, 2 h, 0.5 mol% Pd	95
7	OCH ₃	Br	H	60°C, 4 h, 0.5 mol% Pd	94
8	<i>o</i> -OCH ₃	Br	H	60°C, 4 h, 0.5 mol% Pd	86
9	NO ₂	Cl	H	60°C, 4 h, 0.5 mol% Pd	18
10	NO ₂	Cl	H	90°C, 8 h, 1.5 mol% Pd	68
11	CHO	Cl	H	90°C, 8 h, 1.5 mol% Pd	62
12	H	Cl	H	90°C, 8 h, 1.5 mol% Pd	52
13	CH ₃	Cl	H	90°C, 8 h, 1.5 mol% Pd	42

^aGeneral conditions: aryl halide (1 mmol), arylboronic acid (1.1 mmol), K₂CO₃ (3 mmol), DMF (6 ml).
^bIsolated yield.
^cYields are the average of two runs.

loadings. Since using 0.5 mol% of the catalyst (PdCl₂/1) very little product was isolated (entry 9), we increased the reaction temperature to 90°C and the catalyst quantity up to three times (entry 10), and a much improved yield was obtained. As expected, activated aryl chlorides gave slightly better yields than the non-activated aryl chlorides (entries 10 and 11 vs. entries 12 and 13).

Experimental

General Information

The starting complex [Fe₃(CO)₁₂] and the ligand DPEphos were purchased from Across Chemicals. PdCl₂ and other necessary chemicals were purchased from RENKEM, India. The solvents used were of analytical grade and distilled prior to utilization. Elemental analyses were recorded using Elementar Vario EL III Carlo Erba 1108. IR spectra (4000–250 cm⁻¹) were recorded in KBr using a Shimadzu (Prestige-21) spectrophotometer. The ¹H and ³¹P{¹H} NMR spectra were recorded in CDCl₃ operating at 300.13 MHz and 121.50 MHz, respectively, on a Bruker 300 MHz spectrometer. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature.

Synthesis of [Fe(CO)₄(η¹-P-DPEphos)] (1) and [Fe₂(CO)₆(μ-CO)(μ-P,P-DPEphos)] (2)

To a THF solution of [Fe₃(CO)₁₂] (302 mg, 0.60 mmol), bis(2-diphenylphosphinophenyl)ether (366 mg, 1.2 mmol) was added. The reaction mixture was refluxed under nitrogen for 3 h, during which the color of the solution changed from green to orange-brown. After cooling, the reaction mixture was filtered and the solvent was removed under reduced pressure to afford an orange-brown solid. The residue was dissolved in a minimal amount of CH₂Cl₂ and then chromatographed on a silica gel

column. Elution of hexane–CH₂Cl₂ (80:20) gave complex **1** as a dark-brown solid and **2** as a yellow solid.

Complex 1: Yield: 46%; Anal. Calc. for C₄₀H₂₈O₅P₂Fe; C: 67.99%, H: 3.97%. Found: C: 68.12%, H: 3.99%; FAB mass, *m/z* (%) = 707 (40) [M+1]⁺, 678 (25) [M–CO]⁺; 650 (60) [M–2CO]⁺; 622 (50) [M–3CO]⁺; 594 (100) [M–4CO]⁺; IR (KBr): 2046, 2029, 1980 cm⁻¹, ν_{CO}; ¹H NMR (δ ppm): 7.8–6.8 (m, Ph); ³¹P{¹H} NMR (δ ppm): 26.7 (Fe–PPh₂), –16.89 (free PPh₂).

Complex 2: Yield: 21%; Anal. Calc. C₄₃H₂₈O₈P₂Fe₂; C: 60.99%, H: 3.31%. Found: C: 61.23%, H: 3.33%; FAB mass, *m/z* (%) = 848 (10) [M+2]⁺, 818 (10) [M–CO+2]⁺; 735 (20) [M–4CO+1]⁺; 707 (30) [M–5CO+1]⁺; 678 (25) [M–6CO+1]⁺; 650 (50) [M–7CO]⁺; 594 (100) [M–7CO–Fe]⁺; IR (KBr, cm⁻¹): 2047, 2031, 1969, 1942, 1928, 1886 (ν_{CO} bridging); ¹H NMR (δ ppm): 7.8–6.6 (m, Ph); ³¹P{¹H} NMR (δ ppm, 300 K): 28.71.

General Information about Catalytic Experiments

The Suzuki–Miyaura cross-coupling reactions were carried out under aerobic conditions. The progress of the reactions was monitored by thin-layer chromatography (TLC) using aluminum-coated TLC plates (Merck) under UV light. The products were purified by column chromatographic technique using silica gel (60–120 mesh). The various products separated were characterized by melting point, mass spectroscopy and ¹H NMR spectroscopy, and compared with the authentic samples. Mass spectra of the compounds were recorded in a GEOL GCmate instrument in EI⁺ mode.

General Procedure for the Suzuki–Miyaura Reactions of Aryl Halides

A 50 ml round-bottomed flask was charged with a mixture of aryl halide (1 mmol), arylboronic acid (1.1 mmol), K₂CO₃ (3 mmol), complex **1** (appropriate quantity), and DMF (6 ml). The mixture was stirred at 60°C (for aryl bromides) or 90°C (for aryl chlorides) for the required time. After completion, the mixture was diluted

with water (20 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with brine (3 × 20 ml) and dried over Na₂SO₄. After evaporation of the solvent under reduced pressure, the residue was chromatographed (silica gel, ethyl acetate/hexane, 1:9) to obtain the desired products.

Computational Details

The geometrical minima of the species were optimized with 6-31+G(d) basis set using Becke three-parameter exchange and Lee, Yang and Parr correlation functional B3LYP,^[60,61] and was confirmed by frequency calculations. All calculations were performed using a Gaussian 09.^[62]

Conclusion

In summary, we have synthesized two new iron–carbonyl complexes – [Fe(CO)₄(η¹-P-DPEphos)] (**1**) and [Fe₂(CO)₆(μ-CO)(μ-P,P-DPEphos)] (**2**) – and characterized them by different spectroscopic techniques. In the absence of crystal structure, DFT calculations were performed on complex **1** to gain structural information. The potentiality of complex **1** as ligand was explored for the palladium-catalyzed Suzuki–Miyaura reaction and it was found that combination of PdCl₂/complex **1** system furnished an effective catalyst for the cross-coupling reaction. A range of electronically diverse aryl bromides and chlorides underwent the coupling reactions in moderate to excellent yields. Although our PdCl₂/complex **1**-based catalyst is relatively less effective than some of the reported ferrocenyl phosphine-based catalysts,^[50,51] the present catalytic system is significant in that for the first time we are introducing a non-ferrocene-based iron-containing phosphine that can be used as a ligand for the palladium-catalyzed Suzuki–Miyaura reaction.

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