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Infrared irradiation or microwave assisted cross-coupling reactions using sulfur-containing ferrocenyl-palladacycles

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ABSTRACT

The synthesis of four new sulfur-containing palladacycles **3a-d** [FcC(S)OEtPdClZR$_3$, where: **3a**, ZR$_3$: PPh$_3$; **3b**, ZR$_3$: P(*o*-Tol)$_3$; **3c**, ZR$_3$: PMe$_3$; **3d**, ZR$_3$: SbPh$_3$] from ferrocenyl thionoester **1** [FcC(S)OEt] in good yields is reported. The catalytic applications of these cyclopalladated complexes in Heck and Suzuki cross-coupling reactions were also evaluated, in combination with infrared or microwave as energy sources. The coupled products of these reactions were obtained in good to excellent yields, short reaction times and low catalyst loading.

1. Introduction

Since the first report in 1995, on the synthesis and applications of Herrmann-Beller's palladacycle in catalytic C–C coupling reactions [1], palladacycles with a widespread range of structural arrangements and synthetic accessibility have attracted great interest as catalytic precursors [2,3]. Currently, diverse examples of palladacycles synthesized from ferrocenyl compounds like ferrocenyl imines [4], ferrocenyl oximes [5], (dimethylaminomethyl) ferrocene [6], and 2-pyridylferrocene and their analogues [7], ferrocenyl imidazoline [8], and ferrocenyl oxazoline [9] have been reported.

Likewise, organosulfur ligands are very common precursors used in the synthesis of very stable palladacycles [2], and include different frameworks such as pincer type ligands, thioethers, thiourea based ligands, sulfur substituted NHCs, thiosemicarbazones and sulfated Schiff bases [10]. However, only some palladacycles using ferrocenyl thiocarbonyl compounds are known [11], maybe due to the difficulty of extending routine synthetic methodologies to ferrocenyl compounds. An approach for obtaining these kinds of palladacycles is using ferrocenyl thioamides as ligands [12]. Thiocarbonyl precursors can be prepared via a Willgerodt-Kindler reaction [13] or using a sulfurative demetalation reaction of Fischer ferrocenyl carbene complexes [14].

On the other hand, infrared irradiation is an energy source scarcely used as non-conventional heating in comparison to microwaves [15]. Some applications in organic synthesis show that infrared irradiation efficiently promotes condensation reactions [16], oxidation reactions [17], heterocyclic compound syntheses [18], and Diels-Alder reactions [19], among others [20]. As a research program focused on the use of infrared irradiation in C–C coupling reactions, we have started to explore the use of IR to assist the Heck coupling reaction with very good results [21]. In this context and, with regards to further applications of ferrocenyl thiocarbonyls, we hereby report the synthesis of four new monomeric cyclopalladated complexes, using as a precursor a *O*-ethyl ferrocenyl thionoester and three different trialkylphosphines and triphenylstibine. We also describe the catalytic applications of these new cyclopalladated complexes in Mizoroki-Heck and

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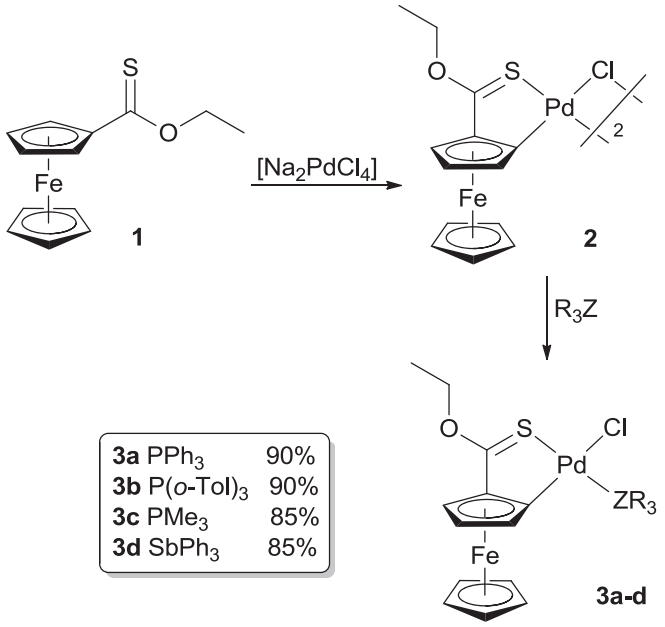
Suzuki-Miyaura cross-coupling reactions promoted by different heating sources, such as microwave and infrared.

2. Results and discussion

2.1. Synthesis and characterization of palladacycles *3a-d*

At first, *O*-ethyl ferrocenyl thionoester **1** was prepared by a sulfurative demetalation reaction in good yields, from a ferrocenyl ethoxycarbene chromium complex [22], in accordance with a protocol developed earlier by our group [14]. Palladacycles **3a-d** were prepared by direct cyclopalladation of **1** with [Na_2PdCl_4] generated *in situ* in methanol at room temperature, obtaining a deep purple solid, insoluble in chlorinated solvents. FAB^+ mass spectrometry showed a molecular ion at 830 *m/z* assigned to the dimeric species [$Pd_2L_2Cl_2$], suggesting a chlorine-bridged dimeric complex **2**. This complex immediately reacted with three different phosphines: PPh_3, P(*o*-Tol)$_3$, and PMe_3. In the case of **3d**, this complex was obtained by the reaction between complex **2** and $SbPh_3$ (Scheme 1). In all cases, the new complexes **3a-d** were obtained in good yields, showing remarkably stability to air and moisture.



Scheme 1. Synthesis of palladacycles **3a-d**.

The complexes **3a-d** were fully characterized by conventional spectroscopic methods and elemental analysis. The mass spectra of these complexes revealed molecular ions in all cases. The infrared spectra of these complexes showed a medium band assigned to the C=S group around 1256 cm^{-1} slightly shifted at high wavenumbers in comparison to *O*-ethyl ferrocenyl thionoester **1** (1232 cm^{-1}) [14], which reveals the singular coordination of the thiocarbonyl sulfur to palladium atom [23].

As expected, their ^{31}P NMR spectra showed that the coordinated phosphine signals are shifted to higher frequencies compared to the corresponding free phosphine, due to coordination with the Pd atom, and evidencing the cleavage of dimer **2**. The ^1H NMR spectrum of **3a** shows two multiple signals at 7.76 and 7.42 ppm assigned to hydrogens of the tri-Phenylphosphine ligand. Three multiple signals are also observed at 4.65 (3H), 4.37 (1H) and 3.88 (6H) ppm. Each signal includes the *CH* of the disubstituted Cp ring, being the first and the last overlapped with the hydrogens of the methylene group and non-substituted Cp ring. Finally, a triplet at 1.54 ppm is assigned to the methyl group of this compound.

Similar spectroscopic data are observed for compounds **3b** and **3d**. In the case of **3c**, a double signal at 1.76 ppm with a $J_{HP} = 9.6$ Hz is observed for methyl groups of the PMe_3 ligand. The ^{13}C NMR spectrum of **3a** displays representative signals at 89.5, 95.5 and 224.2 ppm from the quaternary carbons of the disubstituted Cp ring and *C*(S)OEt moiety, the last shifted down-field related to **1** ($\delta = 216.5$) [14], which confirms the coordination of a thionoester group to the palladium atom. Similar spectroscopic data were observed throughout the series **3b-d**.

The structure of palladacycle **3b** was further confirmed by single-crystal X-ray analysis (Fig. 1). The structure indicates that the substituted Cp ring was palladated in 2-position to thiocarbonyl group, forming a five member metallacycle, as expected. The Pd^{II} atom is square planar coordinated, with a small deviation from the least-squares being 0.020(1) Å at the Pd atom. The phosphine molecule and the sulfur atom adopt a *trans* arrangement with P(1) Pd(1)S(1) angle of 173.03°. This behavior agrees with the *trans-phobia effect* of a phosphine group placed in *trans* position to a carbon group observed in others palladacycle complexes [24].

2.2. Mizoroki-Heck cross-coupling reaction

Having synthesized palladacycles **3a-d**, we started to explore their catalytic properties as catalytic precursors in the Mizoroki-Heck cross-coupling reaction (Table 1). Initially, we evaluated the effect of the concentration of the Pd-complex on the Heck reaction between methyl acrylate and 4-iodotoluene, under thermal heating conditions. We chose complex **3a** as a model precatalyst. The coupling reaction was conducted in reflux of DMF (5 mL), for 1 h using different concentrations of precatalyst **3a**, and in all cases molar ratios of 4-iodotoluene/methyl acrylate/K_3PO_4: 1/1.2/1.2. Good yields were obtained within 1 h, when 0.1 and 0.5% mol of **3a** were used (Table 1, entries 1–3). The influence of a base was also evaluated and three experiments were conducted using Na_2CO_3, Na_3PO_4, K_3PO_4, being the last, which gave the best result (entry 3). It is important to notice that all reactions were conducted in open atmosphere. To improve reaction conditions, we carried out the coupling reaction decreasing catalyst load to 0.05% mol, obtaining good results when the reaction time was extended until 2 h (entry 7). After that, we carried out two additional experiments for finding the best reaction temperature (Table 1, entries 7–9). The coupled product was obtained in good yield, when the reaction is conducted at 140° C. After analyzing the results obtained, we concluded that the best conditions are 0.05% mol of complex **3a**, 2 h of reaction time at 140 °C and K_3PO_4 as base, with turnovers of (TON) around 2×10^3.

We have also studied the influence of phosphine and stibine ligands on catalytic activity. We tested palladacycles **3b**, **3c** and **3d** under the same reaction conditions as **3a**. The results are shown in Table 1 (entries 10–12). As can be seen, complex **3b** compared to **3a** shows similar catalytic activity (entries 7 and 10). These results can be rationalized in terms of bulk and electronic effects [25] given by the spectator ligand. Thus, phosphines such as PPh_3 ($\theta = 145°$) [26] or P-(*o*-Tol)$_3$ ($\theta = 194°$) with higher cone angles increase the reaction rate, because they can easily dissociate and generate vacant sites more efficiently. Although, bulk effect is important, the σ-donor or π-acceptor character in the spectator ligand also plays an important role. If we look at the extremes, the **3c** complex (PMe_3, $\theta = 118°$) contains a purely σ-donor ligand or **3d** ($SbPh_3$, $\theta = 138°$) [27] includes a good π-acceptor ligand. In both cases, we observe a decrease of catalytic activity (entries 11 and 12). These results show that **3a** or even **3b** possess the appropriate tuning features for good catalytic activity. Likewise, we also decided to explore the reactivity

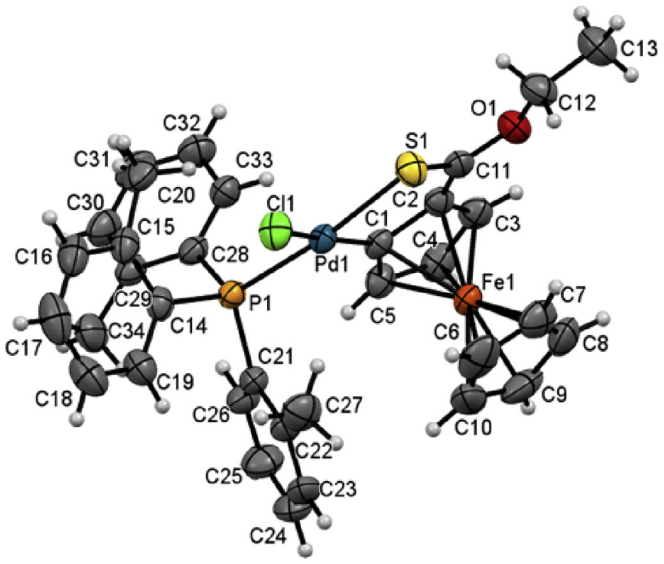


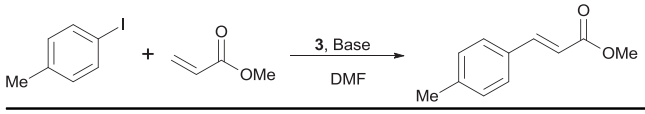
Fig. 1. ORTEP drawing of **3b**. Thermal ellipsoids at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pd1–C1 1.997(3), Pd1–P1 2.2977(8), Pd1–S1 2.3648(9), Pd1–Cl1 2.3730(8), S1–C11 1.675(3), P1–C21 1.832(3), P1–C28 1.841(3), P1–C14 1.842(3), O1–C-11 1.319(4), Fe1-Cg1 1.641(1), Fe1-Cg2 1.659(2), Cg(1)–Fe(1)–Cg(2) 178.8(1). Cg(1) and Cg(2) are the centroids of the (C1,C2,C3,C4,C5) Cp ring and the (C6,C7,C8,C9,C10) Cp ring, respectively. C1–Pd1–P1 94.06(9), C1–Pd1–S1 85.40(9), P1–Pd1–Cl1 95.48(3), S1–Pd1–Cl1 85.61(3), P1–Pd1–S1 173.03(3), C1–Pd1–Cl1 85.61(3).

detected.

To evaluate the scope of **3a** as catalytic precursor in Heck coupling reaction, a variety of activated and deactivated aryl iodides with methyl acrylate were examined using the palladacycle **3a**, in the best reaction conditions (Table 2). Thus, when aryl iodides containing electron donating groups are used (entries 1–5), good yields of coupling product are obtained. When, electron withdrawing groups are in *p*-position of aryl iodide (entries 7–10), in some cases, long reaction times (12 h) are needed to get moderate yields, with the formation of some by-products [29]. In order to study the steric hindrance of this reaction, we have incorporated a methyl group in different relative positions to iodine (entries 3–5), obtaining in all cases the coupling product in good yields. These results indicated that the steric effect does not play an important role in this coupling reaction. We also looked the viability of promoting this reaction using microwave irradiation, but surprisingly no-coupling product was obtained.

Recently, we reported the use of IR to assist the Heck coupling reaction with very good results [21]. With this in mind, we decided to study the effect of infrared irradiation as alternative energy source. We have thus tested the catalytic performance of complex **3a** in this conditions, and the results are also listed in Table 2. As we can see, the Heck coupling reactions yields almost the same results in comparison with the reactions conducted under conventional heating, however the reaction time decreases in all cases, showing that infrared irradiation as heating source positively affects the efficiency of this reaction.

Table 1
Evaluation of catalytic conditions for Mizoroki-Heck cross-coupling of 4-iodotoluene with methyl acrylate using complex **3a**-**d**.[a]



Entry	% Mol [Pd]	Complex	Time (h)[b]	Base	Temp (°C)	Yield (%)[c]	TON[f]	TOF (h^{-1})[g]
1	1	**3a**	1	K_3PO_4	140	94	94	94
2	0.5	**3a**	1	K_3PO_4	140	95	190	190
3	0.1	**3a**	1	K_3PO_4	140	95	950	950
4	0.1	**3a**	1	Na_2CO_3	140	64	640	640
5	0.1	**3a**	1	Na_3PO_4	140	80	800	800
6	0.05	**3a**	1	K_3PO_4	140	71	1420	1420
7	**0.05**	**3a**	**2**	**K_3PO_4**	**140**	**95**	**1900**	**950**
8	0.05	**3a**	2	K_3PO_4	120	80	1600	800
9	0.05	**3a**	2	K_3PO_4	100	22	440	220
10	0.05	**3b**	2	K_3PO_4	140	95	1900	950
11	0.05	**3c**	2	K_3PO_4	140	88	1760	880
12	0.05	**3d**	2	K_3PO_4	140	88	1760	880
13[d]	0.05	**3a**	24	K_3PO_4	140	28	560	23
14[e]	0.05	**3a**	24	K_3PO_4	140	80	1600	66

Bold signifies the best results obtained after screening different reaction conditions.
[a] All reactions were performed with 1 mmol of the 4-iodotoulene, 1.2 mmol of the alkene, DMF (5 mL) and 1.2 mmol of base.
[b] Time reaction based on total consumption of aryl iodide determined by TLC.
[c] Isolated yields after SiO_2 column chromatography.
[d] 4-Bromotoluene was used as substrate and 10% mol of n-Bu_4NBr.
[e] 4-Bromotoluene was used as substrate and 20% mol of n-Bu_4NBr.
[f] TON = ratio of moles of product formed to moles of catalyst used.
[g] TOF = TON/t (h).

of aryl bromides, we chose 4-bromotoluene as substrate in the presence of TBAB as additive in different percentages [28]. When this coupling reaction was conducted in the presence of 10% of TBAB, the coupling product was obtained in low yield (Table 1, entry 13). However, when the TBAB percentage was duplicated, a good result was obtained (entry 14). Finally, if the same reaction was carried out in absence of the additive, no coupling product was

2.3. Suzuki-Miyaura cross-coupling reaction

In order to extend the study of the catalytic properties of complex **3a**, we performed a series of experiments using the Suzuki cross-coupling reaction (Table 3). The coupling reaction between 4-iodotoluene and phenylboronic acid was selected as a model reaction. In a first attempt, we used a load of 0.1% mol of **3a**, methanol,

K_2CO_3 as base, at reflux conditions under conventional heating, obtaining a nearly quantitative yield of the coupling product (Table 3, entry 1). The same reaction conducted at room temperature produces only 74% yield, in 390 min (Table 3, entry 2). Interested for exploring other alternative methodologies to promote this reaction, we decided to use ultrasound, at room temperature. Under this conditions, the reaction was not complete, but when we slightly increased the temperature to 40 °C, the substrates where totally consumed, leading 99% of yield of the coupling product in 2 h (Table 3, entries 3 and 4). Encouraged for this result, we conducted the same reaction using IR (Table 3, entry 5) obtaining a good yield of the coupling product in 25 min. Finally, we compared the effectiveness of microwave irradiation, obtaining an excellent yield of the coupling product in only 6 min (Table 3, entry 6). In order to improve this result, we also carried out different catalytic tests modifying catalytic loading (Table 3, entries 6–8), we found that the best yield of the coupling product is obtained when **3a** is used in 0.1% mol (entry 6).

Finally, different bases were tested (Table 3, entries 6, 9 and 10), the results obtained indicate that K_2CO_3 is the best base. Analyzing these results, we consider that a suddenly heating promoted by an efficient energy source such as microwave or infrared irradiation favors this coupling reaction. Thus, optimized conditions for this cross-coupling reaction involves the use of 0.1% mol of **3a**, 90 °C and K_2CO_3 as base, under microwave heating.

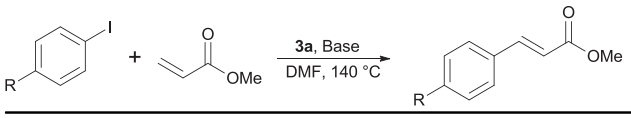
Subsequently, we evaluated the scope of this reaction studying both different aryl iodides and boronic acids (Table 4). In every case, the substrates were cleanly converted to the corresponding biphenyl with isolated yields, after purification ranging from 75 to 99%. The results show that the yield and time of the coupling reaction slightly depend on the nature of the substituent on aryl iodide. Electron-rich aryl iodides, considered more difficult than the electron deficient analogues for Suzuki cross-coupling have been coupled in less time, showing that the complex **3a** is active and tolerates a wide range of substituents. Entry 3 is an interesting result, when we used 1-bromo-4-iodobenzene as substrate, this palladacycle activates not only C–I bond, but also C–Br bond, affording a mixture of the corresponding biphenyl plus the *p*-terphenyl. This result led us to assess the effectiveness of this catalytic system with other aryl bromides, such as 4-bromotoluene and 1-bromonaphtalene as starting material (Table 4, entries 5–6 and 9). We obtained good yields of the coupling product, demonstrating the catalytic performance of **3a**. Then, we decided to test the reactivity of 4-chlorotoluene in the same reaction conditions (Table, 4, entry 7). The result obtained shows that this catalytic system promotes the C–Cl bond activation, but is less efficient compared to other aryl halides.

Likewise, we also evaluated the nature of boronic-acid in this coupling reaction (Table 4, entries 14–18). Thus, electron deficient boronic acids react slowly than electron rich analogues (Table 4, entry 17). Finally, we test the reach of this catalytic system by synthesizing a push-pull biphenyl, where $R_1 = NH_2$ and $R_2 = NO_2$, which can display interesting optical applications. Although, the synthesis of this biphenyl compound has been reported in the literature [30], the current methodologies involve drastic reaction conditions or multi-step protocols, with poor global yields. Using a Suzuki reaction promoted by complex **3a**, we obtain the target biphenyl compound in high yield, mild conditions and one reaction step (Table 4, entry 18).

3. Conclusions

We have developed the synthesis of four new palladacycles complexes **3**(**a**–**d**) in good yields via C–H bond activation on a ferrocenyl thionoester precursor. As we have shown, these new palladium (II) complexes are promising as catalytic precursors for Heck and Suzuki coupling reactions. Their stability to air and moisture, avoids the use of inert conditions and facilitates all the manipulation in open atmosphere. The coupled products of these reactions were obtained in good to excellent yields, short reaction times and low catalyst loading. The use of different source of heating such as microwave or infrared to promote these reactions was compared. Therefore, we found that infrared irradiation (IR) is an efficient, economical and accessible alternative source of energy to assist both coupling reactions.

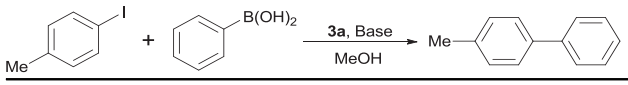
Table 2
Scope of Mizoroki-Heck cross-coupling of aryl iodides under conventional heating and infrared irradiation.



Entry	R	Reactions conducted under conventional heating[a]				Reactions conducted under infrared irradiation [a,b]			
		Time (min)[c]	Yield %[d]	TON[e]	TOF (h^{-1})[f]	Time (min)[c]	Yield %[d]	TON[e]	TOF (h^{-1})[f]
1	4-MeO	120	87	1740	870	45	92	1840	2453
2	4-NH_2	120	85	1700	850	45	90	1800	2400
3	4-Me	120	95	1900	950	45	89	1780	2373
4	2-Me	90	88	1780	1186	40	90	1800	2727
5	3-Me	120	86	1720	860	45	88	1760	2346
6	H	120	97	1940	970	45	91	1820	2427
7	4-Br	120	70	1400	700	60	77	1540	1540
8	4-CF_3	120	80	1600	1600	30	87	1740	3480
9	4-COMe	720	45	900	75	360	53	1060	177
10	4-NO_2	720	50	1000	83	360	50	1000	177

[a] All reactions were performed with 1 mmol of the corresponding aryl iodide, 1.2 mmol of the alkene, DMF (5 mL), 0.05% mol of **3a** and 1.2 mmol of K_3PO_4 at 140 °C.
[b] Reaction conducted under infrared irradiation using an Osram lamp (bulb model Thera-Therm, 250 W, 125 V). For controlling the temperature, a Digi-Sense variable-time power controller was used.
[c] Time reaction based on total consumption of aryl halide determined by TLC.
[d] Isolated yield after SiO_2 column chromatography.
[e] TON = ratio of moles of product formed to moles of catalyst used.
[f] TOF = TON/t (h).

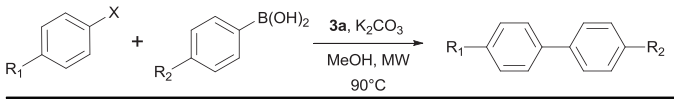
Table 3
Suzuki cross-coupling of 4-iodotoluene with phenyl boronic acid using complex **3a** and different energy sources.[a]



Entry	% Mol [Pd]	Temperature (°C)	Heating conditions	Time (min)[f]	Base	Yield (%)[g]	TON[h]	TOF (h^{-1})[i]
1	0.1	65	Conventional[b]	240	K_2CO_3	99	990	248
2	0.1	20	–	390	K_2CO_3	74	740	114
3	0.1	20	US[c]	110	K_2CO_3	48	480	262
4	0.1	40	US[c]	120	K_2CO_3	99	990	495
5	0.1	65	IR[d]	25	K_2CO_3	92	920	2208
6	**0.1**	**90**	**MW[e]**	**6**	**K_2CO_3**	**98**	**980**	**9800**
7	0.5	90	MW[e]	5	K_2CO_3	94	188	2256
8	0.05	90	MW[e]	10	K_2CO_3	59	1180	7080
9	0.1	90	MW[e]	17	K_3PO_4	88	880	3106
10	0.1	90	MW[e]	6	$Ba(OH)_2$	88	880	8800

Bold signifies the best results obtained after screening different reaction conditions.
[a] All reactions were performed with 1 mmol of the aryl iodide, 1.2 mmol of the phenyl boronic acid, MeOH (5 mL) and 1.2 mmol of K_2CO_3, 0.1% mol of **4a** at 90 °C.
[b] Conventional heating.
[c] Reaction conducted on ultrasound.
[d] Reaction conducted under infrared irradiation using an Osram lamp (bulb model Thera-Therm, 250 W, 125 V). For controlling the temperature, a Digi-Sense variable-time power controller was used.
[e] Reaction conducted under microwave.
[f] Time reaction based on total consumption of aryl halide determined by TLC.
[g] Isolated yield after SiO_2 column chromatography.
[h] TON = ratio of moles of product formed to moles of catalyst used.
[i] TOF = TON/t (h).

Table 4
Scope of Suzuki cross-coupling of aryl halides and phenyl boronic acid under microwave irradiation.[a]



Entry	R_1	X	R_2	Time (min)	Yield (%)[b]	TON[g]	TOF (h^{-1})[h]
1	MeO	I	H	8	94	940	7050
2	NH_2	I	H	10	95	950	5700
3	Br	I	H	13	37[c]	370	1708
4	Me	I	H	6	98	980	9800
5	Me[d]	Br	H	20	73	730	2190
6	Me[d, e]	Br	H	4320	84	840	12
7	Me[d]	Cl	H	35	23	230	394
8	H	I	H	7	94	940	8057
9	H[d,f]	Br	H	20	92	920	2760
10	COMe	I	H	11	93	930	5072
11	COOMe	I	H	21	94	940	2685
12	NO_2	I	H	10	99.9	999	5994
13	CF_3	I	H	10	94	940	5640
14	Me	I	NO_2	30	91	910	1820
15	Me	I	CF_3	10	95	950	5700
16	Me	I	SO_2Me	10	75	750	4500
17	Me	I	NMe_2	6	88	880	8800
18	NH_2	I	NO_2	35	90	900	1543

[a] All reactions were performed with 1 mmol of the aryl halide, 1.2 mmol of the phenyl boronic acid, MeOH (5 mL) and 1.2 mmol of K_2CO_3, 0.1% mol of **4a** at 90 °C.
[b] Isolated yield after SiO_2 column chromatography.
[c] 37% yield corresponding to biphenyl plus 32% corresponding to *p*-terphenyl due to the double activation (C–I and C–Br).
[d] 20% TBAB was used as additive.
[e] Conventional heating.
[f] 1-Bromonaphtalene was used as starting material.
[g] TON = ratio of moles of product formed to moles of catalyst used.
[h] TOF = TON/t (h).

4. Experimental

4.1. General considerations

The synthesis of precursor **1** was carried out in an inert atmosphere of nitrogen gas using standard Schlenk techniques. Anhydrous THF was obtained by distillation under an inert atmosphere over sodium benzophenone. Column chromatography was performed using 70–230 mesh silica gel. All reagents and solvents were obtained from commercial suppliers and used without further purification. All compounds were characterized by IR spectra, recorded on a Perkin-Elmer 283B or 1420 spectrophotometer, by means of film and KBr techniques, and all data are expressed in wave numbers (cm^{-1}). Melting points were obtained on a Melt-Temp II apparatus and are uncorrected. NMR spectra were measured with a JEOL Eclipse +300 and a Bruker Avance 300, using $CDCl_3$ as solvent. Chemical shifts are in ppm (δ), relative to TMS. The MS-FAB and MS-EI spectra were obtained on a JEOL SX 102A, the

values of the signals are expressed in mass/charge units (m/z), followed by the relative intensity with reference to a 100% base peak. Elemental analyses for carbon, hydrogen and sulfur atoms were performed on a Perkin Elmer 2400 elemental 35 analyzer using cystine as standard.

The equipment used for irradiation with IR energy was created by employing an empty cylindrical metal vessel in which an Osram lamp (bulb model Thera-Therm, 250 W, 125 V) was inserted [22a]. This lamp is special short-wave IR lamp (IR-A) for use in body care and wellness applications, with a maximum radiation at a wavelength of about 1100 nm. The lamp instantly emits a full thermal output as soon as it is switched on. For controlling the temperature, a Digi-Sense variable-time power controller was used. This time controller turned the output load on and off and then repeated the cycle. All the reactions were performed in open atmosphere.

Microwave irradiation experiments were performed using a Monowave 300 single-mode microwave reactor. The reaction temperature is monitored by an internal fiber-optic (FO) temperature probe (ruby thermometer) protected by a borosilicate immersion well inserted directly into the reaction mixture. Reaction times refer to the hold time at the desired set temperature and not to total irradiation time. A hydraulic sensor integrated in the swiveling cover of the instrument performs pressure sensing. The reusable 10 mL Pyrex vial is sealed with PEEK snap caps and standard PTFE coated silicone septa. Reaction cooling is performed by compressed air automatically after the heating period has elapsed. All the reactions were performed in open atmosphere.

The reactions conducted under ultrasound irradiation were carried out in a flask, suspended into the ultrasonic bath (Bransonic 2510R-MTH, 42 KHz frequency, 550 W power). A Digi-Sense variable-time power controller was used for controlling the temperature. All the reactions were performed in open atmosphere.

4.2. Structure determination by X-ray crystallography

Suitable X-ray quality crystal of **3b** was grown by slow evaporation of chloroform at room temperature. A crystal of **3b** was mounted on a glass fiber at room temperature, and then placed on a Bruker Smart Apex CCD diffractometer, equipped with Mo-Kα radiation; decay was negligible in both cases. Details of crystallographic data collected on compounds **3b** is provided in Table 5. Systematic absences and intensity statistics were used in space group determination. The structure was solved using direct methods [31]. Anisotropic structure refinements were achieved using full matrix, least-squares technique on all non-hydrogen atoms. All hydrogen atoms were placed in idealized positions, based on hybridization, with isotropic thermal parameters fixed at 1.2 times the value of the attached atom. Structure solutions and refinements were performed using SHELXTL V6.10 [32]. The experimental and refinement details of the X-ray crystallographic structure of compound **3b** can be obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk), reference code 952478.

4.3. Synthesis of fischer ethoxy ferrocenyl carbene complex and O-ethyl ferrocenylthionoester (**1**)

The preparation of these compounds was carried out using the methodology previously described elsewhere [14,22].

4.4. Synthesis of palladacycles **3**(**a**–**d**)

A suspension of palladium chloride (0.5 mmol, 86.7 mg) and sodium chloride (1 mmol, 58.5 mg) in methanol (20 mL) was stirred at room temperature, until a brown homogeneous solution was obtained. To this solution was then added, dropwise, a dichloromethane solution (5 mL) of *O*-ethyl ferrocenylthionoester **1** (0.5 mmol, 136.9 mg). The mixture reaction was stirred for 3 h at room temperature, obtaining a deep purple solid. The solvent was evaporated and the resulting crude was suspended in CH_2Cl_2 and treated with PPh_3 (0.5 mmol, 131.2 mg) at room temperature, during 2 h. The solvent was evaporated and the precipitate obtained was filtered and washed with hexane. The precipitate was purified by column chromatography on neutral alumina (eluent; hexane/CH_2Cl_2 1:1) to give **3a** (304.5 mg, 90%). A similar procedure for the preparation of **3a** was followed to synthesize **3b**, **3c** and **3d**.

3a. $C_{31}H_{28}ClFeOPdPS$. 90%, mp 162–164 °C (dec). IR_{vmax} (KBr, cm^{-1}): 3074, 2965, 2925 (C–H), 1257 (C=S). MS-FAB$^+$ m/z (rel. intensity %) 677 [M^+] (5), 642 [M^+–Cl] (26), 523 [M^+–$(C_6H_5)_2$]. ^{1}H NMR ($CDCl_3$, ppm): δ 1.54 [t, 3H, C*H*$_3$], 3.88 [br s, 6H, C*H* (Cp sub) and C*H* Cp], 4.37 [m, 1H, C*H* (Cp sub)], 4.65 (m, 3H, CH_2O and C*H* (Cp Sub)], 7.42 (br s, 9H, C$H_{arom\ m,\ p}$), 7.76 (br s, 6H, C$H_{arom\ o}$). ^{13}C NMR ($CDCl_3$, ppm): δ 14.3 [CH_3], 67.0 [*C*H (Cp sub)], 70.9 [CH_2O], 72.4 [*C*H (Cp sub)] 72.9 [*C*H, Cp], 81.2 [*C*H (Cp sub)], 89.5 [C_{ipso} C(S)], 95.5 [C_{ipso} Pd], 128.3 [d, $J_{C\text{-}P}$ = 10.4 Hz, *C*H$_{arom\ m}$], 130.7 [CH$_{arom\ p}$], 134.9 [d, $J_{C\text{-}P}$ = 47.4 Hz, C_{ipso}P], 135.2 [d, $J_{C\text{-}P}$ = 12.7 Hz, *C*H$_{arom\ o}$], 224.2 [*C*(S)OEt]. ^{31}P NMR ($CDCl_3$, ppm): δ 35.6. Elemental analysis (%): calcd for $C_{31}H_{28}ClFeOPdPS$ C, 54.94; H, 4.16; S, 4.73; found: C, 53.89; H, 3.96; S, 4.71.

3b. $C_{34}H_{34}ClFeOPdSP$. Deep purple solid, 90%, mp 148–151 °C (dec). IR_{vmax} (KBr, cm^{-1}): 3061, 2924, (C–H). 1258 (C=S). MS-FAB$^+$ m/z (rel. intensity %) 719 [M^+] (5), 683 [M^+–Cl], 415 [M^+–P(*o*-tolyl)$_3$]. ^{1}H NMR ($CDCl_3$, ppm): δ 1.54 [t, 3H, C*H*$_3$CH$_2$O], 1.68 [s, 3H, C*H*$_3$ P(*o*-tolyl)$_3$], 2.15 [s, 3H, C*H*$_3$ P(*o*-tolyl)$_3$], 3.36 [s, 3H, C*H*$_3$ P(*o*-tolyl)$_3$], 3.74 [s, 5H, C*H* Cp], 3.82 (s, 1H, C*H* (Cp sub)], 4.38 [s, 1H, C*H* (Cp sub)], 4.67 [br s, 3H, –CH_2O, C*H* (Cp sub)], 7.08–7.57 (m, 9H, C*H*$_{arom}$), 8.64 (dd, 3H, C$H_{\underline{arom}}$ $J_{H\text{-}P}$ = 18 Hz). ^{13}C NMR ($CDCl_3$, ppm): δ 15.4 [*C*H$_3$CH$_2$O–], 23.1 [*C*H$_3$, $J_{C\text{-}P}$ = 9.2 Hz], 23.8 [*C*H$_3$, $J_{C\text{-}P}$ = 9.2 Hz], 25.3 [*C*H$_3$, $J_{C\text{-}P}$ = 9.2 Hz], 66. 7 [*C*H, (Cp sub)], 70.7 [CH$_2$–O], 72.1[*C*H, (Cp sub)], 72.5 [*C*H, Cp], 80.5 [*C*H, (Cp sub)] 89.1 [C_{ipso}-C(S)], 94.7 [C_{ipso}-Pd)], 125.3 [*C*H$_{arom}$], 130.4 (*C*H$_{arom}$), 131.0(*C*H$_{arom}$), 132.9 (*C*H$_{arom}$, $J_{C\text{-}P}$ = 5.25 Hz), 143.7 (C_{ipso}P), 144.7 (C_{ipso}CH$_3$ $J_{C\text{-}P}$ = 30 Hz),

Table 5
X-ray data collection and structure refinement details for **3b**.

	3b
Formula	$C_{35}H_{36}Cl_3FeOPPdS$
MW g^{-1} mol^{-1}	804.27
Crystal size (mm^3)	0.32 × 0.21 × 0.14
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	10.128(1)
b/Å	23.854(1)
c/Å	14.183(1)
α/(°)	90
β/(°)	93.078(1)
γ/(°)	90
Volume/Å^3	3421.6(4)
Z	4
d_c/Mg m^{-3}	1.561
Θ/°	1.67 to 25.39
Index Ranges	$-12 \le h \le 12$
	$-28 \le k \le 28$
	$-17 \le l \le 17$
Reflections collected	27882
Independent reflections	6274 [R(int) = 0.0535]
Data/parameters	6274/431
Final R indices	$R1$ = 0.0332
[$I > 2\sigma(I)$]	w$R2$ = 0.0685
R indices (all data)	$R1$ = 0.0448
	w$R2$ = 0.0716
GoF(F^2)	0.938
Absorptions corrections	Semi-empirical from equivalents

224.1 [C(S)OEt]. ^{31}P NMR ($CDCl_3$, ppm): δ 31.6. Elemental analysis (%): calcd for $C_{34}H_{34}ClFeOPdSP$ C, 56.74; H, 4.73; S 4.45; found: C, 56.81; H, 4.93; S, 4.51.

3c. $C_{16}H_{22}ClFeOPdSP$. Deep purple solid, 85%, mp 151 °C (dec). IR_{vmax} (KBr, cm^{-1}): 3097, 2976 (C–H), 1260 (C=S). MS-FAB$^+$ *m/z* (rel. intensity %) 491 [M^+], 455 [M^+–Cl], 379 [M^+–$P(CH_3)_3Cl$]. ^{1}H NMR ($CDCl_3$, ppm): δ 1.53 [s, 3H, CH_3CH_2O], 1.76 [d, 9H, $J_{H\text{-}P} = 9.6$ Hz, CH_3–P], 4.23 [s, 5H, *CH* Cp], 4.65 [br s, 2H, CH_3CH_2O], 4.73 [br s, 3H, CH Cp sub]. ^{13}C NMR ($CDCl_3$, ppm): δ 14.2 [CH_3CH_2O], 17.1 [d, $J = 33$ Hz, CH_3P], 67.9 [*CH* (Cp sub)], 70.8 [CH_2O,] 72.4 [*CH*, Cp], 72.9. [*CH*, (Cp sub)] 79.3 [*CH*, (Cp sub)], 90.6 [C_{ipso}-C(S)], 92.7 [C_{ipso}-Pd], 225.1 [*C*(S)OEt]. ^{31}P NMR ($CDCl_3$, ppm): δ −5.55. Elemental analysis (%): calcd for $C_{16}H_{22}ClFeOPdSP$ C, 39.10; H, 4.48; S 6.51; found C, 40.8; H, 4.43; S 6.59.

3d. $C_{31}H_{28}ClFeOPdSbS$. Deep purple solid, 85%, mp 157 °C (dec). IR_{vmax} (KBr, cm^{-1}): 3050, 2970, (C–H), 1256 (C=S). MS-FAB$^+$ *m/z*. 767 [M^+], 732 [M^+–Cl], 416 [M^+-Sb(C_6H_5)$_3$]. ^{1}H NMR ($CDCl_3$, ppm): δ 1.56 [br s, 3H, CH_3]; 4.09 [br s, 5H, *CH* Cp]; 4.14 [m, 1H, *CH* (Cp sub)]; 4.46 [m, 2H, CH_2O]; 4.70 [m, 2H, CH (Cp sub]; 7.43 [br s, 9H $CH_{arom\ m,\ p}$]; 7.77[br s, 6H, $CH_{arom\ o}$]. ^{13}C NMR ($CDCl_3$, ppm): δ 14.3 [CH_3], 67.9 [CH_2O], 71.2 [CH (Cp sub)], 73.1 [CH (Cp sub)], 72.6 [CH Cp], 83.2 [CH (Cp sub)], 89.9 [C_{ipso}-C(S)], 90.7 [C_{ipso}-Pd], 129.3 [$CH_{arom,\ m}$], 130.3 ($CH_{arom,\ p}$), 131.7 (C_{ipso}-Sb)], 136.6 [$CH_{arom,\ o}$], 225.0 [*C*(S)OEt]. Elemental analysis (%): calcd for $C_{31}H_{28}ClFeOPdSbS$ C, 48.50; H, 3.65; S, 4.17; found. C, 48.71, H, 3.70; S, 4.26.

4.5. General procedure for Mizoroki-Heck coupling reactions

In a 10-mL round-bottomed flask, a mixture of aryl iodide (1 mmol), methyl acrylate (1.2 mmol), and base (1.2 mmol), was placed in 4 ml of DMF, then a solution of complex **3a** (0.05% mol) in 1 mL of DMF was added. The reaction mixture was refluxed for the time stated in Tables 1 and 2 at 140 °C. The reaction mixture was poured into water (20 mL) and extracted with ether or hexane (2 × 30 mL). The combined organic layers were dried over anhydrous sodium sulfate. After the removal of the solvent *in vacuo*, the resulting crude was purified by column chromatography on silica gel (hexane-ethyl acetate) to give (*E*)-methyl *p*-methyl cinnamate (The purified product was identified by means of determination of mp and by ^{1}H and ^{13}C NMR, the data obtained are consistent with literature) [33].

Note: The entire round flasks used in each coupling reaction were meticulously cleaned with aqua regia to avoid the presence of unseen palladium catalyst.

4.6. General procedure for Suzuki-Miyaura coupling reactions under microwave irradiation

A 10 mL microwave-transparent process vial was filled with aryl iodide (1 mmol), phenylboronic acid (1.2 mmol), base (1.2 mmol), 5 mL of solvent and **3a** (0.1% mol). The vial was sealed with PEEK snap caps and standard PTFE coated silicone septa. The reaction mixture was then exposed to microwave heating for the time stated in Table 3 at 90 °C. The reaction vial was thereafter cooled to room temperature and the mixture was diluted with 20 mL of water and extracted with 3 × 10 mL of ether. The combined organic layers were dried over anhydrous sodium sulfate. The crude product was finally purified by column chromatography on silica-gel to give the isolated products in yields stated in Tables 3 and 4 (The purified product was identified by means of determination of mp and by ^{1}H and ^{13}C NMR, the data obtained are consistent with literature) [34].

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