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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, $P(o\text{-Tol})_3$, 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.

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].

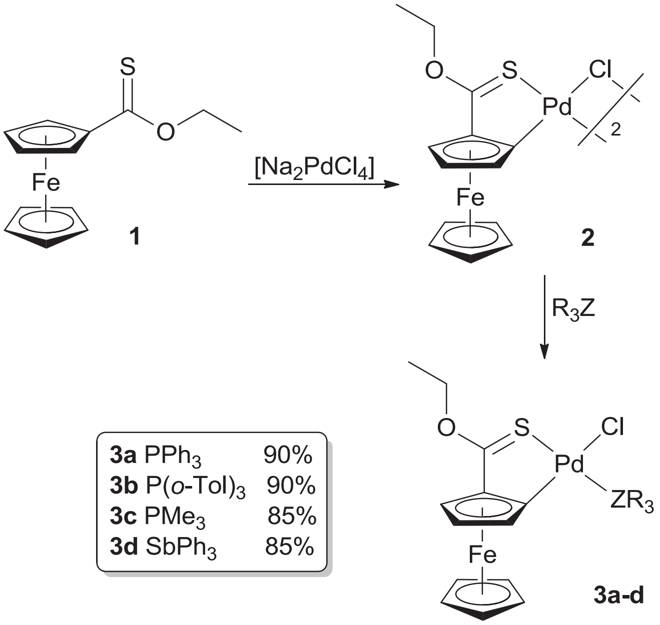
As expected, their ^{31}P NMR spectra showed that the coordinated phosphine signals are shifted to higher frequencies compared to the corresponding free phosphine, due to coordination with the Pd atom, and evidencing the cleavage of dimer **2**. The ^1H NMR spectrum of **3a** shows two multiple signals 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 C*H* 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 *transphobia 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.



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

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 $P\text{-}(o\text{-Tol})_3$ ($\theta = 194°$) 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