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(Ferrocenylthienyl)phosphines: Synthesis, electrochemistry and their use in Suzuki-Miyaura *C,C* coupling

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ABSTRACT

(Ferrocenylthienyl)phosphines of type 2-PR_2-5-Fc-^{c}C_4H_2S (R = Ph (**3a**), ^{t}Bu (**3b**)) and 2-PR_2-3,4-Fc_2-^{c}C_4HS (R = Ph (**4a**), ^{t}Bu (**4b**); Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)) and their selenium derivatives were synthesized by consecutive synthetic methodologies. The molecular structure of **3a** and **4a**,**b** in the solid state show inter- and intramolecular (*T*-shaped) $\pi-\pi$ interactions for **3a** and **4a**, resulting in dimeric and 1D polymeric structures.

Phosphines **3a**,**b** and **4a**,**b** were applied in the Pd-catalyzed Suzuki-Miyaura *C,C* cross coupling reaction of aryl halides and boronic acids yielding the respective biaryls. Compound **3b** shows a higher activity in *C,C* cross coupling reactions as compared to **3a** and previously published thiophene-based phosphines and aminophosphines. Moreover sterically hindered and deactivated aryl bromides could be coupled at Pd loadings as low as 0.05 mol-% and at temperatures between 25 °C and 50 °C. However, the application of diferrocenylthienylphosphines **4a**,**b** in Suzuki-Miyaura reactions resulted in decreased yields of the corresponding biaryls.

In the context of electrochemical investigations on these compounds, a strong dependency of the individual electrode reactions on the phosphorus substituents were found. During UV–Vis/NIR spectroelectrochemical studies, only a very limited iron-iron electronic interaction in **4a-Se**$^+$ could be detected. Thus, **4a-Se**$^+$ corresponds to a very weak coupled class II system according to the classification of Robin and Day.

1. Introduction

Palladium-catalyzed *C,C* cross coupling reactions are established as useful transformations, for example, in the synthesis of pharmaceuticals as well as agro- and fine chemicals [1–3]. As a widely used cross-coupling protocol, the Suzuki-Miyaura reaction allows the coupling of aryl boronic acids with aryl halides to biaryls at mild reaction conditions and with excellent tolerance of a broad range of functional groups. The application of electron-rich, bulky phosphines as ligands in transition metal complexes allow an efficient conversion of electron-donating and electron-withdrawing as well as sterically demanding aryl halides [4–12]. In general, heterocycle-based phosphines were studied in various aspects: in the context of a synthetical access of oligoaryl systems and phosphinolines, electrochemical investigations [13], and in coordination chemistry [14–17]. For example, thienylphosphines are of interest as ligands in transition metal-catalyzed processes such as allylation and transfer hydrogenation reactions [18], α-arylation of ketones [19] or transition metal-catalyzed hydroformylation of olefins [20]. Nevertheless, only a few reports concerning their application in the Pd-catalyzed Suzuki-Miyaura reaction are known [21,22]. Recently, we reported the synthesis of a series of (ferrocenylthienyl)phosphines of type 2-PR_2-3-Fc-^{c}C_4H_2S (R = ^{t}Bu, Ph; Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)) and their application in the Pd-catalyzed Suzuki-Miyaura *C,C* cross coupling [23].

In continuation of our work on catalysts with a ferrocene-based backbone [24–29], we present herein the synthesis, characterization and electrochemistry [30–39] of a series of ferrocenyl-substituted thienylphosphines, as well as their use as ligands in the Pd-promoted Suzuki-Miyaura *C,C* cross coupling.

2. Results and discussion

Synthesis and characterization of (ferrocenylthienyl)phosphines **3a**,**b** and **4a**,**b**.

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The synthesis of ferrocenyl-substituted thienylphosphines of type 2-PR_2-5-Fc-$^{c}C_4H_2S$ (R = Ph (**3a**), ^{t}Bu (**3b**)) and 2-PR_2-3,4-Fc_2-$^{c}C_4HS$ (R = Ph (**4a**), ^{t}Bu (**4b**); Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5)) was carried out by a consecutive reaction sequence (Scheme 1). A Negishi *C,C* cross coupling reaction of the respective bromothiophene with ferrocenyl-zinc chloride gave the appropriate ferrocenylthiophenes **1** and **2** (Scheme 1) [32,40,41]. These compounds were lithiated with ^{n}BuLi at −80 °C in tetrahydrofuran and were reacted subsequently with the respective chlorophosphines PR_2Cl (R = Ph, ^{t}Bu), yielding the appropriate (ferrocenylthienyl)phosphines **3a**,**b** and **4a**,**b** (Scheme 1). The selenophosphines of **3a**,**b** and **4a**,**b** were synthesized by an addition of a 2-fold excess of elemental selenium to a dichloromethane solution of the individual phosphine at ambient temperature (Scheme 1, Experimental Part).

(Ferrocenylthienyl)phosphines **3a**,**b** and **4a**,**b** were identified by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy, elemental analysis and mass spectrometry. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3a**,**b** and **4a**,**b** show signal patterns as typical for thienyl and ferrocenyl increments (Experimental Part). The ^{31}P{^{1}H} NMR spectra consist of signals at −18.9 and −23.4 ppm for the PPh_2-substituted thiophenes **3a** and **4a**, and at 16.3 and 27.0 for P^{t}Bu_2 derivatives **3b** and **4b**. The phosphorous-selenium coupling constant for **3a-Se** and **4b-Se** allows a quantification of the σ-donor ability of the phosphorous atom towards selenium (Table 1) [42,43].

In general, the $^{1}J_{P/Se}$ value increases with electron-withdrawing groups, indicating an increased s-character of the phosphorus orbital which is involved in the P–Se bond [42,43]. Surprisingly, the $^{1}J_{P/Se}$ value of **4a-Se** is similar as found for the P^{t}Bu_2-derivative **4b-Se**, both offer larger $^{1}J_{P/Se}$ coupling constants than **3a,b-Se**. The smallest coupling constant was found for **3b-Se**, indicating that **3b** represents the strongest σ-donating phosphine.

The molecular structures of **3a** and **4a**,**b** in the solid state were determined by single crystal X-ray diffraction analysis at temperatures of <110 K using Cu Kα (**3a**) or Mo Kα (**4a**,**b**) radiation. Suitable crystals were obtained by slow diffusion of methanol into a saturated dichloromethane solution containing **3a** or **4a**,**b** at ambient temperature. The ORTEP diagrams of **3a** and **4a**,**b** with selected bond lengths (Å), bond angles (°) and torsion angles (°) are shown in Fig. 1. The compounds crystallize in the triclinic space group *P*−1 (**3a**, **4b**) and in the monoclinic space group $P2_1/c$ (**4a**), each with one molecule in the asymmetric unit. Compound **4a** was refined disordered with two sets of sights (ratio 0.59:0.41). The cyclopentadienyls exhibit rather eclipsed conformations for all three compounds ranging from 2.58(11) ° (**3a**) to 9.30(11) ° (**4b**), except for the Fe2-bonded C_5H_5 cycle in **4a** which reveals a staggered conformation (26.1(4) °).

In **3a**, the cyclopentadienyl and the thienyl plane are nearly coplanar towards each other (7.38(14) °), whereas in **4a**,**b** a non-uniform setup is characteristic (**4a**, 32.20(12), 59.70(8); **4b**, 17.62(10), 80.40(5) °) with the ferrocenyls rotated away from each other (∠ $C_5H_4 \cdots C_5H_4$: **4a**, 43.23(11); **4b**, 89.94(5) °), due to their steric demand.

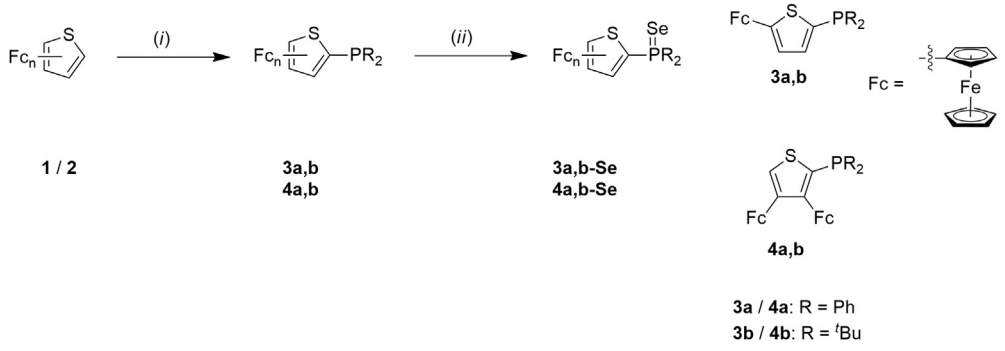
Table 1
Chemical shifts (^{31}P{^{1}H} NMR, $CDCl_3$, 25 °C) and $^{1}J_{P/Se}$ of (ferrocenylthienyl)phosphinoselenides **3a,b-Se** and **4a,b-Se**.

Compd.	δ/ppm	$^{1}J_{P/Se}$/Hz
3a-Se	21.8	732
3b-Se	69.1	702
4a-Se	26.6	741
4b-Se	70.6	746

Furthermore, the rotation of the ferrocenyls affects the substituents at the phosphorus atom. Thus, in compound **3a** both phenyl rings are virtually symmetric (48.6(2) and 59.8(2) °) above and below the thienyl plane. The electron lone pair, which is rotated away from the sulfur atom for all three compounds, is located in the thienyl plane with a slight deviation of 5.6(2) ° [44]. A similar behavior is found for **4b** (51.03(14) and 66.37(14) °) with the nearby ferrocenyl unit rotated away from the *tert*-butyl group and the lone pair, which is with 7.67(14) ° located out of the thienyl plane. However, in **4a** the ferrocenyl moiety is directed towards the phenyl rings and hence deflects from the phosphine building block (66.1(2) and 37.6(2) °), as confirmed by the rotation of the lone pair out of the thiophene plane (14.3(2) °). In phenyl substituted **3a** and **4a** inter- and intramolecular (*T*-shaped) π-π interactions are present including phenyl, thienyl and cyclopentadienyl planes causing dimeric and one dimensional polymeric structures (Supporting Information, Figures SI1, SI2 Table SI1).

2.1. Catalytic investigations

The catalytic performance of **3a**,**b** and **4a**,**b** in the Suzuki-Miyaura *C,C* cross coupling reaction was investigated by the conversion of different bromo and chloro benzenes with phenylboronic acid (Table 2). The corresponding reactions were carried out in a 1,4-dioxane-water mixture (ratio 2:1 (*v*:*v*)) at 100 °C in presence of potassium carbonate as base. The catalytic active species were generated by using 2.0 mol-% of **3a**,**b** or **4a**,**b** with 1.0 mol-% of [$Pd(OAc)_2$]. The resulting yields of thus formed biphenyls were determined by ^{1}H NMR spectroscopy with acetylferrocene as internal standard. The obtained data reveal a strong dependence of the conversion of substrates on the substitution pattern of the thiophene and at the phosphorous atom (Table 2). The use of P^{t}Bu_2-functionalized **3b** leads to high conversions of bulky, electron-rich aryl bromides and electron-deficient chloro aryls, while the PPh_2-



Scheme 1. Synthesis of (ferrocenylthienyl)phosphines **3a**,**b** and **4a**,**b** and the respective selenophosphines **3a,b-Se** and **4a,b-Se**. (Reaction conditions: (i) a) ^{n}BuLi, tetrahydrofuran, −80 °C 1 h; b) $ClPR_2$, −40 to 25 °C, 24 h (ii) 2 equiv. Se, dichloromethane, 25 °C, 24 h).