Palladiumdichloride (ferrocenylethynyl)phosphanes and their use in Pd-catalyzed Heck–Mizoroki- and Suzuki–Miyaura carbon–carbon cross-coupling reactions

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ABSTRACT

In this work the synthesis of phosphane selenides $(FcC{\equiv}C)_nPh_{3-n}P{=}Se$ (**2a**, $n = 1$; **2b**, $n = 2$; **2c**, $n = 3$; Fc = ferrocenyl, $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe)$ from $(FcC{\equiv}C)_nPh_{3-n}P$ (**1a**, $n = 1$; **1b**, $n = 2$; **1c**, $n = 3$) and selenium is described to estimate the σ-donor properties of these systems by $^{31}P\{^1H\}$ NMR spectroscopy. Progressive replacement of phenyl by ferrocenylethynyl causes a shielding of the phosphorus atom with increasing of the $^1J(^{31}P\text{-}^{77}Se)$ coupling constants.

The palladiumdichloride metal-organic complexes $[((FcC{\equiv}C)_nPh_{3-n}P)_2PdCl_2]$ (**3a**, $n = 1$; **3b**, $n = 2$; **3c**, $n = 3$) have been used as (pre)catalysts in the Suzuki–Miyaura (reaction of 2-bromo-toluene (**4a**) and 4-bromo-acetophenone (**4b**), respectively, with phenyl boronic acid (**5**) to give 2-methyl biphenyl (**6a**) and 4-acetyl biphenyl (**6b**)) and in the Heck–Mizoroki reaction (treatment of iodobenzene (**7**) with *tert*-butyl acrylate (**8**) to give *E-tert*-butyl cinnamate (**9**)).

The structures of molecules **1a**, **1c**, **2c**, and **3c** in the solid state were determined by single X-ray structure analysis showing that the structural parameters of these systems are unexceptional and correspond to those of related phosphanes, seleno phosphanes, and palladium dichloride complexes.

1. Introduction

Palladium-catalyzed carbon–carbon cross-coupling reactions such as the Suzuki–Miyaura [1] and the Heck–Mizoroki [1a–e,2] reaction are among the most essential transformations in organic and organometallic chemistry. Recently, very active organometallic and metal-organic systems have been framed amending the stability and efficiency of the palladium-based catalysts [3]. In this respect, heterocyclic carbenes, [4] *ortho*-metallated benzyl thioethers, [5] cyclometallated imine-type derivatives, [6] diverse palladacycles [7] and a series of electron-rich and, sterically hindered phosphane palladium complexes [8] were synthesized and applied as catalysts in C–C bond forming reactions. In the Heck–Mizoroki reaction weak σ-donating phosphane ligands are privileged, while in the Suzuki–Miyaura reaction strong Lewis-basic phosphanes are essential [1a].

The donor properties of phosphanes (PR_3; R = alkyl, aryl, alkoxyl) toward selenium acceptors can be quantified by the phosphorus–selenium coupling constant ($^1J(^{31}P\text{-}^{77}Se)$) as indicated by $^{31}P\{^1H\}$ NMR spectroscopy [9]. There it was found that an electron-withdrawing group at the phosphorus atom increases the coupling constant $^1J(^{31}P\text{-}^{77}Se)$ which can be explained by the increased *s* character of the phosphorus orbital involved in the P–Se bonding. Consequently, shorter bond distances between the

phosphorus and the acceptor carbon atoms are found. This electronic effect directly affects the steric demand around the phosphorus atom which causes marked changes in the behavior of the respective transition metal complexes. These feature sizes are decisive parameters for the specific design of transition metal compounds used as catalytic active species in homogeneous catalysis.

In this paper we report the synthesis of (ferrocenylethynyl)phosphane selenides and the use of (ferrocenylethynyl)phosphane palladium-dichlorides of type $[((FcC{\equiv}C)_nPh_{3-n}P)_2PdCl_2]$ (Fc = ferrocenyl, $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe)$ as (pre)catalysts in the Heck–Mizoroki (the reaction of iodobenzene with *tert*-butyl acrylate) and Suzuki–Miyaura reaction (reaction of 2-bromo-toluene or 4-bromo-acetophenone with phenylboronic acid). The influence of the electronic ($^1J(^{31}P\text{-}^{77}Se)$) and steric (Tolman cone angle) effects on the catalytic activity of the appropriate organometallic compounds will be discussed. The basic idea of this work was to synthesize with the (ferrocenylethynyl)phosphane ligands more stable phosphane-palladium catalysts for C–C cross-coupling reactions in comparison with, for example, "$(Ph_3P)_2Pd$" which only shows low stability and activity during the catalytic cycle.
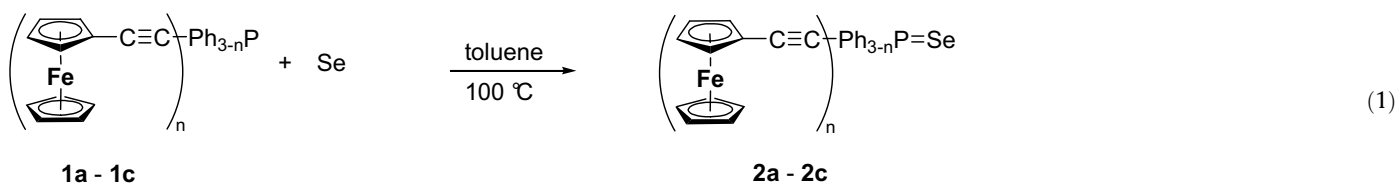
2. Results and discussion

The synthesis of the (ferrocenylethynyl)phosphanes $(FcC{\equiv}C)_nPh_{3-n}P$ and the respective palladium complexes $[((FcC{\equiv}C)_nPh_{3-n}P)_2PdCl_2]$ ($n = 1, 2, 3$; Fc = $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe)$

were recently reported by Baumgartner et al. [10] and our group [11]. Whereas the Baumgartner group is interested in the use of the latter molecules as precursors in the formation of super-molecular assemblies and in the investigation of these systems toward materials applications, our aim is to make use of these organometallic compounds as (pre)catalysts in carbon–carbon cross-coupling reactions.

To verify the donor ability of $(FcC\equiv C)_nPh_{3-n}P$ (**1a**, $n = 1$; **1b**, $n = 2$; **1c**, $n = 3$) these compounds were converted to the corresponding phosphane selenides $(FcC\equiv C)_nPh_{3-n}P=Se$ (**2a**, $n = 1$; **2b**, $n = 2$; **2c**, $n = 3$) by the reaction of **1a–1c** with elemental selenium in toluene at 100 °C (Reaction (1)) (see Section 4). After appropriate work-up, **2a–2c** could be isolated as orange to red solids in quantitative yield.

The crystal structures of **1a**, **1c**, and **2c** are set-up by one (**1a**) or three (**1c**, **2c**) ferrocenyl ethynyl moieties with somewhat deformed P–C≡C–Fc units (Figs. 1–3). The carbon–carbon triple bond distances are between 1.176(19) and 1.210(10) Å and are typical for this type of molecules [10–12]. The two cyclopentadienyl rings of the ferrocenyl fragments of **1a** (1.57, 1.78°), **1c** (0.76, 1.19, 2.63°), and **2c** (0.26°) are almost parallel oriented with D−Fe−D′ separations between 1.6352(1) and 1.6618(3) Å (D = centroid of the cyclopentadienyl ring C_5H_5, D′ = centroid of the cyclopentadienyl ring C_5H_4).

The phosphorus–carbon bond separations are in the range of 1.743(3) to 1.772(3) Å and are representative for P–C≡C units [10,11,12c]. The other structural parameters are unexceptional and correspond to those of related compounds [10–12].

$$(1)$$

1a - 1c + Se $\xrightarrow[\text{100 °C}]{\text{toluene}}$ **2a - 2c**

The identities of phosphanes **1a–1c** [10,11] and the respective phosphane selenides **2a–2c** have been confirmed by elemental analysis, IR and NMR spectroscopy (see Section 4).

The molecular solid state structures of **1a**, **1c**, and **2c** were additionally solved by single X-ray structure analysis. Suitable crystals were obtained by slow diffusion of *n*-hexane into a concentrated dichloromethane solution containing either **1a**, **1c** or **2c** at room temperature. ORTEP diagrams, selected bond distances (Å) and angles (°) are shown in Fig. 1 (**1a**), Fig. 2 (**1c**), and Figs. 3 and 4 (**2c**). The crystal and structure refinement data are presented in Section 4 (Table 4).

The overall structure of **2c** conforms to a chandelier (Fig. 3), whereby the P=Se unit is in accordance with the socket and the ferrocenyl moieties correspond to the candles. This means that all ferrocene units are positioned on the site of the phosphorus–selenium bond. Compound **2c** thereby possesses the molecular symmetry C_{3h}. Molecule **2c** crystallizes in the rhombohedral non-centrosymmetric space group $R3m$ and its absolute conformation was ascertained by refinement of the Flack parameter 0.013(10) [13]. The ferrocenyl units form a 1D polymer by π–π interactions between C_5H_4 (D1) and C_5H_5 (D2′) (Fig. 4). The distance of the centroid of the cyclopentadienyl rings D and D′ is 3.704 Å and is typical
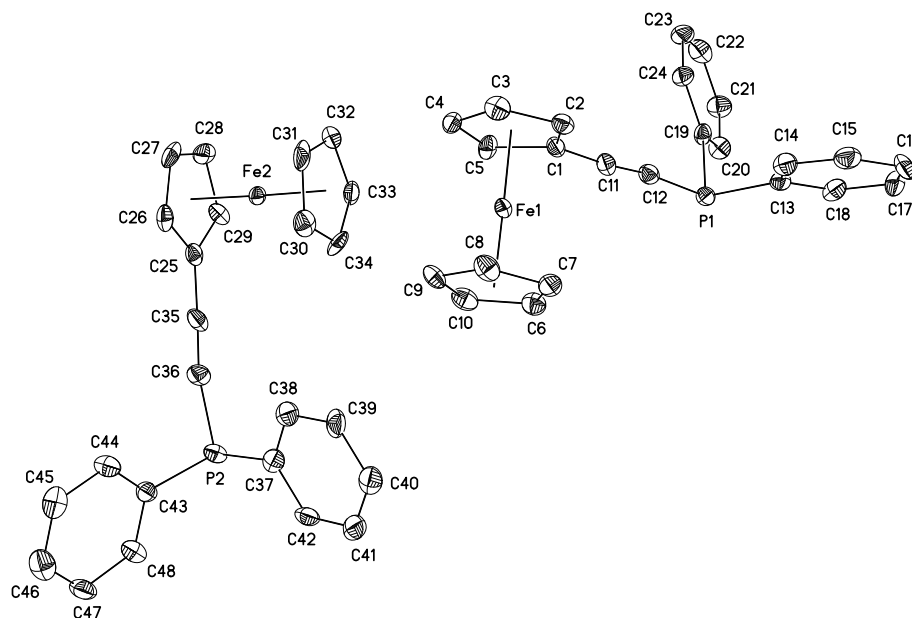

Fig. 1. ORTEP diagram (50% probability level) of **1a** with the atom numbering scheme. (Hydrogen atoms are omitted for clarity.) The asymmetric unit of **1a** consists of two crystallographically independent molecules (molecules **A** (right) and **B** (left)). Selected bond distances (Å) and angles (°): Molecule **A**: P1–C12 1.757(7), P1–C13 1.840(8), P1–C19 1.833(7), C11–C12 1.210(10), D1–Fe1 1.6488(3), D2–Fe1 1.6521(3); P1–C12–C11 173.7(7), C12–C11–C1 175.3(8), C12–P1–C13 102.4(3), C12–P1–C19 102.4(3), C13–P1–C19 102.6(3). Molecule **B**: P2–C36 1.760(8), P2–C3 1.848(8), P2–C43 1.839(8), C35–C36 1.203(11), D3–Fe2 1.6618(3), D4–Fe2 1.6427(3); P2–C36–C35 169.2(7), C36–C35–C25 176.1(8), C36–P2–C37 99.4(4), C36–P2–C43 103.3(4), C37–P2–C43 101.0(3) (D1 = centroids of C1–C5, D2 = centroids of C6–C10, D3 = centroids of C25–C29, D4 = centroids of C30–C34). Standard uncertainties of the last significant digit(s) are shown in parenthesis.
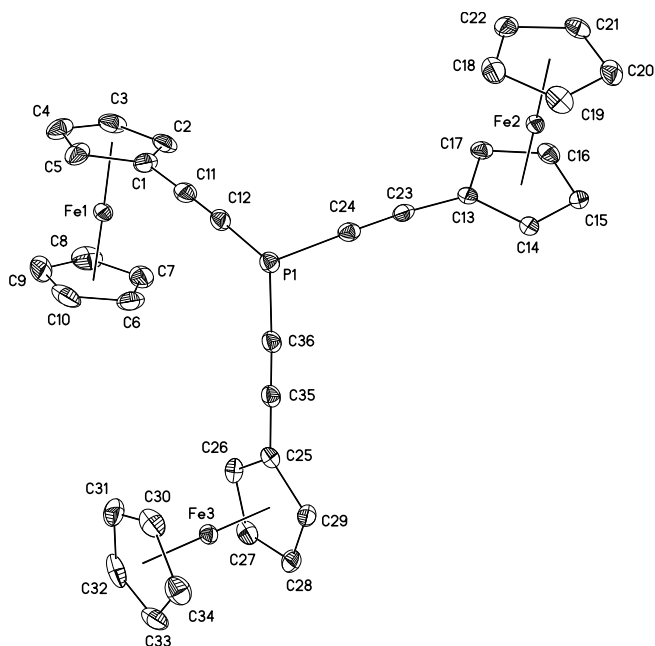
Fig. 2. ORTEP diagram (50% probability level) of **1c** with the atom numbering scheme. (Hydrogen atoms are omitted for clarity.) Selected bond distances (Å) and angles (°): P1–C12 1.766(3), P1–C24 1.767(3), P1–C36 1.772(3), C11–C12 1.197(4), C23–C24 1.198(3), C35–C36 1.193(4), D1–Fe1 1.6398(2), D2–Fe1 1.6342(2), D3–Fe2 1.6496(2), D4–Fe2 1.6447(1), D5–Fe3 1.6470(2), D6–Fe3 1.6421(1); P1–C12–C11 175.6(3), P1–C24–C23 176.5(2), P1–C36–C35 173.6(2), C12–C11–C1 177.9(3), C24–C23–C13 174.7(3), C36–C35–C25 176.4(3), C12–P1–C24 98.92(12), C12–P1–C36 99.40(12), C24–P1–C36 99.76(12) (D1 = centroids of C1–C5, D2 = centroids of C6–C10, D3 = centroids of C13–C17, D4 = centroids of C18–C22, D5 = centroids of C25–C29, D6 = centroids of C30–C34). Standard uncertainties of the last significant digit(s) are shown in parenthesis.

for parallel-displaced geometries [14]. Characteristic for **2c** is the P–Se bond with 2.0991(11) Å, which is identical to that of other phosphane selenides, for example, tris(*m*-trifluoromethylphenyl) phosphane selenide [15] and tris(2-furyl)phosphane selenide
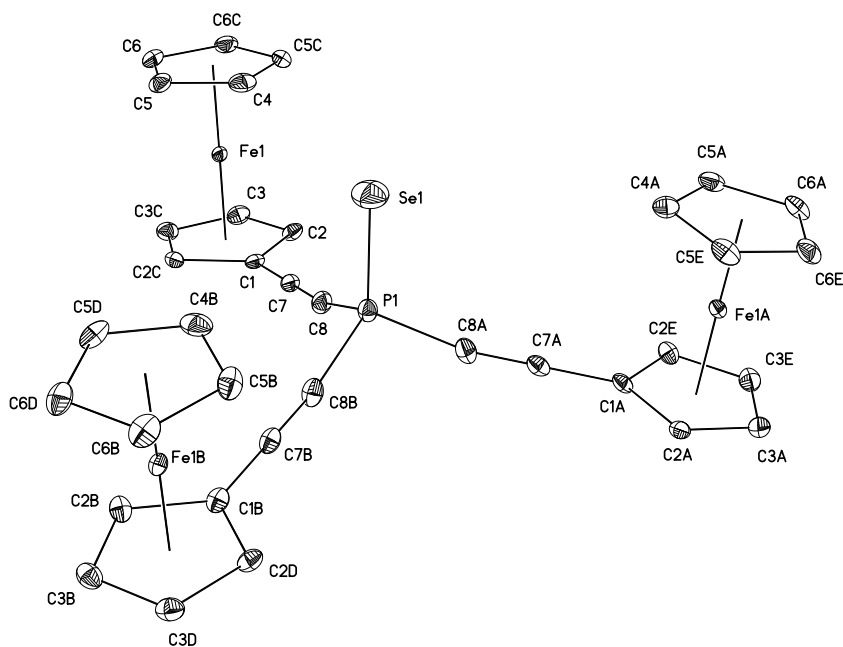

Fig. 4. ORTEP diagram (50% probability level) of a (selected) part of the polymeric structure of **2c** formed by π–π interactions between the cyclopentadienyl rings D1–D2' (3.704 Å; D1 = centroid of C_5H_4, D2' = centroid of C_5H_5 of the second molecule). (Hydrogen atoms were omitted for clarity). All cyclopentadienyl rings are perfectly parallel oriented with C–C separations ranging from 3.635 to 3.712 Å. (Label' refers to a second, label" refers to a third molecule of **2c**.)

Fig. 3. ORTEP diagram (50% probability level) of the molecular structure of **2c** with the atom numbering scheme. (Hydrogen atoms are omitted for clarity.) Symmetry transformations used to generate equivalent atoms (indicated with the suffixes A, B, C, D, and E): A: 1 − y, 1 + x − y, z; B: −x + y, 1 − x, z; C: −x + y, y, z; D: x, 1 + x − y, z; E: 1 − y, 1 − x, z. Selected bond distances (Å) and angles (°): P1–Se1 2.0991(11), P1–C8 1.743(3), C7–C8 1.204(4), D1–Fe1 1.6566(2), D2–Fe1 1.6499(2); P1–C8–C7 167.9(2), C8–C7–C1 180.0(3), C8–P1–Se1 113.64(9), C8–P–C8A 105.00(10). D1 = centroid of C1–C2–C3–C2(C)–C3(C); D2 = centroid of C4–C5–C6–C5(C)–C6(C). Standard uncertainties of the last significant digit(s) are shown in parenthesis.
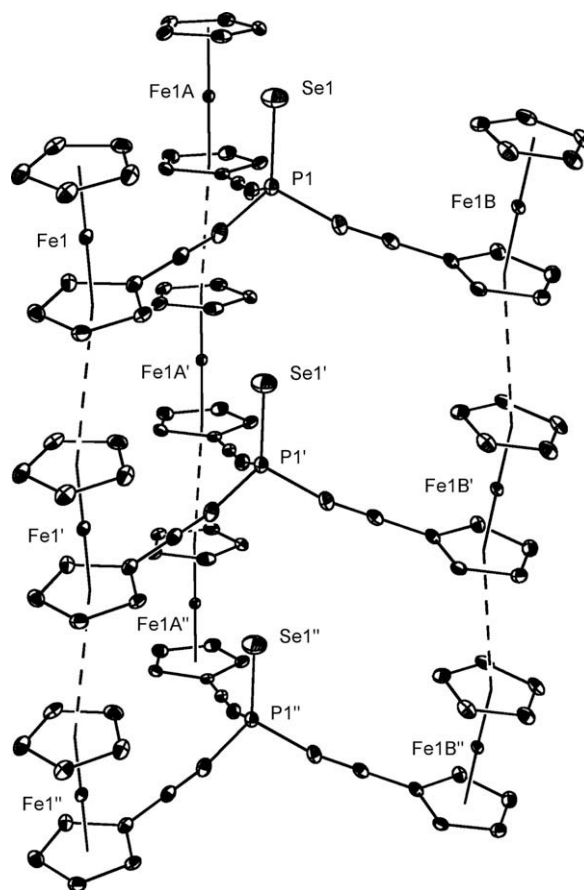
Table 1
Chemical shifts and ^{31}P–^{77}Se coupling constants of **2a**–**2c,** and Ph$_3$P=Se for comparison.

Compd.	δ [ppm]	$^1J(^{31}$P–^{77}Se) [Hz]
Se=PPh$_3$ [9c]	35.9	732
2a	4.3	746
2b	−31.3	757
2c	−71.3	765

[9d], respectively, containing σ-electron-withdrawing substituents. As result thereof, the s character of the phosphorus orbital involved in bonding to the selenium atom is increased (see below). The C–P–C inter-valence angles at P1 (Fig. 3) are in the typical range for tertiary phosphane selenides [15].

The ^{31}P{^{1}H} NMR data together with the $^1J(^{31}$P–^{77}Se) coupling constant for the phosphane selenides **2a**–**2c** are summarized in Table 1.

Following trends can be seen from Table 1. Progressive replacement of phenyl by ferrocenylethynyl causes a shielding of the phosphorus atom with increasing of the $^1J(^{31}$P–^{77}Se) coupling constants. The latter observation shows that the ferrocenylethynyl building blocks act as electron-withdrawing units in phosphane selenides. Considering the $^1J(^{31}$P–^{77}Se) coupling constants in Table 1 these values suggest that in the series of the ferrocenylethynyl phosphanes, compound **1a** in its palladium-complexed form should be best suited for the Suzuki–Miyaura reaction, while phosphane **1c** with its more electron-withdrawing character is supposed to be better for the Heck–Mizoroki reaction (vide supra).

In order to explore the possibility of using the palladium-complexed ferrocenylethynyl phosphanes **1a**–**1c** in the Suzuki–Miyaura and Heck–Mizoroki reaction, the appropriate coordination compounds had to be prepared. The synthesis of these systems succeeds in a straightforward manner by the reaction of **1a**–**1c** with [(Et$_2$S)$_2$PdCl$_2$] in the molar ratio of 2:1 in dichloromethane as solvent at room temperature (Reaction (2)). [10,11] After appropriate work-up, complexes [((FcC≡C)$_n$Ph$_{3-n}$P)$_2$PdCl$_2$] (**3a**, n = 1; **3b**, n = 2; **3c**, n = 3) were obtained as dark red solids in excellent yield.
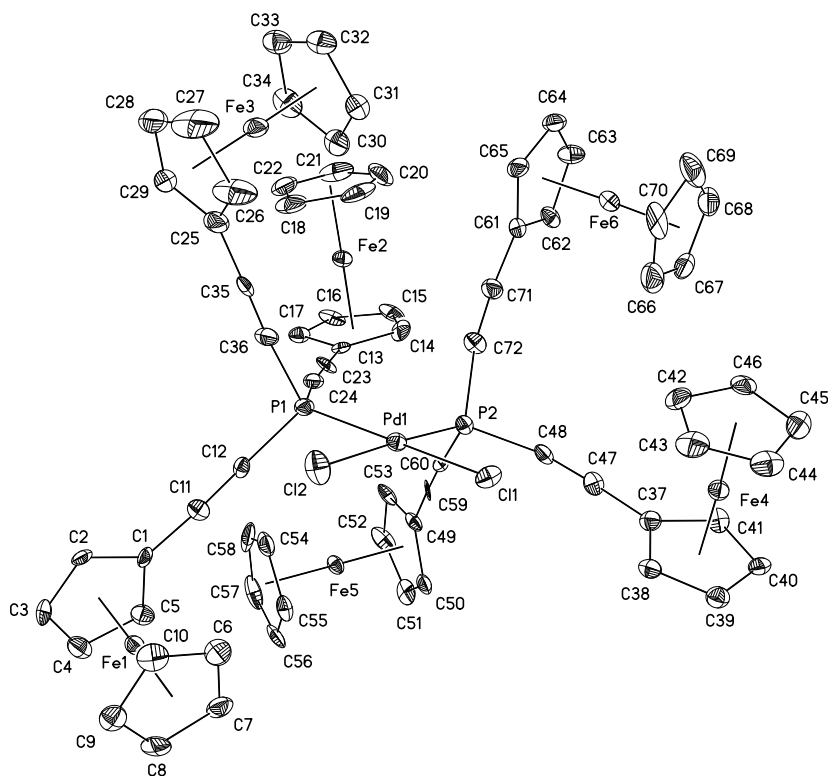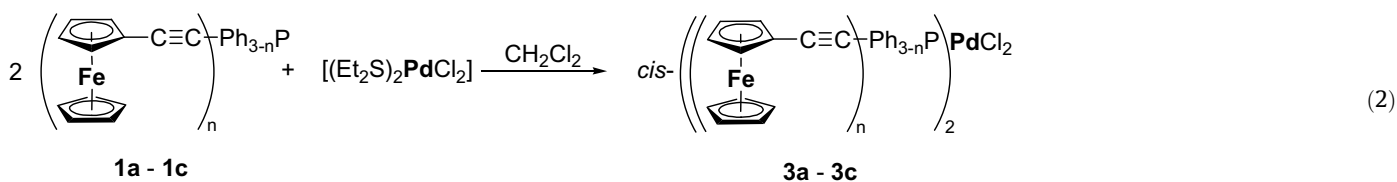

(2)

Fig. 5. ORTEP diagram (50% probability level) of **3c** with the atom numbering scheme. (Hydrogen atoms and two molecules of trichloromethane are omitted for clarity.) Selected bond distances (Å) and angles (°): Pd1–Cl1 2.238(4), Pd1–Cl2 2.322(4), Pd1–P1 2.238(4), Pd1–P2 2.251(4), P1–C12 1.738(14), P1–C24 1.732(15), P1–C36 1.760(15), P2–C48 1.730(14), P2–C60 1.752(14), P2–C72 1.750(14), C11–C12 1.203(19), C23–C24 1.184(19), C35–C36 1.176(19), C47–C48 1.205(19), C59–C60 1.199(19), C71–C72 1.20(2), D1–Fe1 1.6325(7), D2–Fe1 1.6290(6), D3–Fe2 1.6603(7), D4–Fe2 1.6357(6), D5–Fe3 1.6395(7), D6–Fe3 1.6415(8), D7–Fe4 1.6390(6), D8–Fe4 1.6371(6), D9–Fe5 1.6431(6), D10–Fe5 1.6348(6), D11–Fe6 1.6466(8), D12–Fe6 1.6308(7); P1–C12–C11 177.4(13), C12–C11–C1 176.8(15), P1–C24–C23 172.8(14), C24–C23–C13 178.9(14), P1–C36–C35 175.6(14), C36–C35–C25 176.5(18), P2–C48–C47 165.1(13), C48–C47–C37 177.2(16), P2–C60–C59 177.3(12), C60–C59–C49 177.6(16), P2–C72–C71 169.4(14), C72–C71–C61 174.9(17) (D1 = centroid of C1–C5, D2 = centroid of C6–C10, D3 = centroid of C13–C17, D4 = centroid of C18 – C22, D5 = centroid of C25–C29, D6 = centroid of C30–C34, D7 = centroid of C37–C41, D8 = centroid of C42–C46, D9 = centroid of C49–C53, D10 = centroid of C54–C58, D11 = centroid of C61–C65, D12 = centroid of C66–C70; Standard uncertainties of the last significant digit(s) are shown in parenthesis).
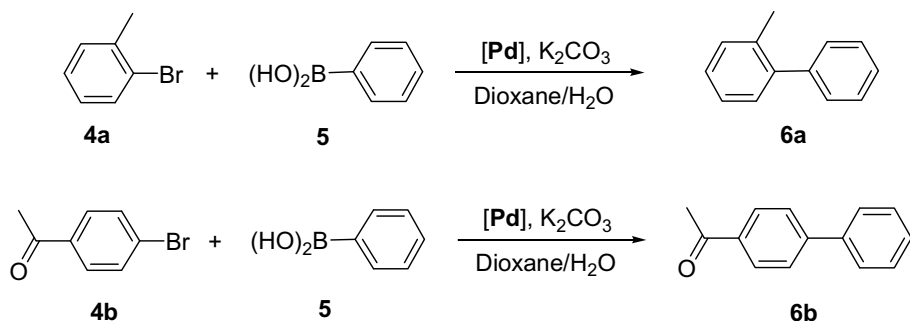
From complex **3c** single crystals suitable for X-ray diffraction studies could be grown from slow diffusion of petroleum ether into a dichloromethane solution containing **3c** at 25 °C.

The structure of **3c** in the solid state (Fig. 5) indicates a *cis*-configuration which is the most favored arrangement in ferrocenylethynyl phosphane and phenylethynyl phosphane palladium dichloride chemistry, *i.e.* [((FcC≡C)Ph₂P)₂PdCl₂] and [((PhC≡C)Ph₂P)₂PdCl₂]. [10,16] The P–C–C angles are with 165.1(13)–177.4(13)° essentially linear (Fig. 5) which differs from [((FcC≡C)Ph₂P)₂PdCl₂] in which angles of 157.3(6) and 170.7(6)° are typical and have been explained by the increased steric bulkiness within the complex [10]. The ferrocenylethynyl moieties are not coplanar arranged with the P₂PdCl₂ plane (r. m. s. deviation 0.0629 Å). All other structural parameters (Fig. 5) correspond to those of related palladium dichloride complexes [10,16].

Heterobimetallic complexes [((FcC≡C)ₙPh₃₋ₙP)₂PdCl₂] (**3a**, n = 1; **3b**, n = 2; **3c**, n = 3) with different electronic and steric properties were used as (pre)catalysts in the aforementioned carbon–carbon cross-coupling reactions.

2.1. Suzuki–Miyaura reaction

In a model reaction we studied the combination of 2-bromo-toluene (**4a**) and 4-bromo-acetophenone (**4b**), respectively, with phenyl boronic acid (**5**, 1.3 equivalents) in the presence of **3a–3c** (loading of 0.05–0.5 mol% Pd, Table 2), potassium carbonate (3.0 equiv.) as base and a 2:1 mixture of dioxane-water as solvent to give the cross-coupled products 2-methyl biphenyl (**6a**) and 4-acetyl biphenyl (**6b**), respectively, under inert gas atmosphere (Reaction (3)). The catalytic reactions were carried out at 100 °C in analogy to literature procedures for comparison [3g]. In all reactions complexes **3b** and **3c** showed an initial reaction period of 5–20 min to generate the catalytic active species.

tration. Quantitative conversion is found for trimetallic Fe₂Pd **3a** at a Pd loading of 0.25 mol%, while **3b** and **3c** show their highest activities at 0.1 mol%, respectively 0.05 mol% (Table 2). However, for the common Suzuki catalyst [Pd(OAc)₂/PPh₃] (**10**) [17] used as a reference system best results were obtained with 0.5 mol% (Table 2).

From Table 2 and Fig. 7 it is obvious that in the carbon–carbon cross-coupling reaction of **4b** with **5** always a quantitative conversion is found, which originates from the higher reactivity of **4b** compared with **4a**. A decrease of reactivity from **3a** to **3c** is also observed.

In summary, an efficient and general catalytic protocol for the carbon–carbon cross-coupling of 2-bromo-toluene (**4a**) and 4-bromo-acetophenone (**4b**) with phenyl boronic acid (**5**) and complexes **3a–3c** as palladium (pre)catalysts was established. Compared with other catalytic active systems in the Suzuki–Miyaura reaction including the catalysts developed by Beller, Buchwald, and Herrmann complexes **3a–3c** are less active [19–21]. Nevertheless, for all three tested complexes it is obvious that they reach quantitative conversion during 1 h.

Electron-donating phosphane complexes are better suited as catalytic active systems in the Suzuki–Miyaura reaction [1a]. This is confirmed by Tables 1 and 2 as well as Figs. 6 and 7, and is verified in the series **3a** > **3b** > **3c**. As outlined earlier (Table 1) the σ-donor ability of phosphanes can be evaluated by measuring the magnitude of $^1J(^{31}P-^{77}Se)$ in the ^{31}P NMR spectra [9a,b]. The coupling constants listed in Table 1 nicely correlate with the conversion numbers presented in Table 2 and are in agreement with the σ-donor ability increasing in the order of **3c** > **3b** > **3a**. This allows in a simple way to decide if individual phosphane palladium coordination complexes are suitable (pre)catalysts in the Suzuki–Miyaura reaction by only determining the magnitude of the $^{31}P-^{77}Se$ coupling constants of the respective phosphane selenides.

(3)

All palladium complexes **3a–3c** are active in the cross-coupling of **4a** and **4b** with **5** and show high productivities, especially at low catalyst concentrations (TONs up to 2000, TON = *t*urnover *n*umber). It is obvious that **3a** as well as **3b** show optimum performance at catalyst concentrations of 0.25 and 0.1 mol%, respectively. While **3a** is more tolerant toward increased palladium loadings (0.5 vs. 0.25 mol%), **3b** shows high activities even at reduced palladium concentrations (0.1 vs. 0.05 mol%). In contrast, **3c** shows an unexpected behavior, its productivity is significantly increased with decreasing palladium loadings.

Kinetic investigations (Fig. 6) with **3a–3c** in the Suzuki–Miyaura cross-coupling of **4a** and **4b** with **5** showed that **3b** and **3c** need somewhat longer induction periods to form the active catalyst. From Fig. 6 it can be seen that the lower the concentration, the higher the activity/conversion up to the optimally catalyst concen-

The classification of the appropriate catalyst by considering sterical arguments (Tolman cone angle) is outlined below.

2.2. Heck–Mizoroki reaction

To appreciate the performance of complexes **3a–3c** in the Heck–Mizoroki carbon–carbon coupling reaction the rate of conversion and systematic kinetic studies were carried out. As a model reaction we chose the coupling between iodobenzene (**7**) and *tert*-butyl acrylate (**8**) to give *E*-*tert*-butyl cinnamate (**9**) following the method described by Boyes and Butler [22]. Thus, **7** and **8** were reacted in toluene and acetonitrile mixtures of ratio 1:1 between 65 and 100 °C in the presence of NEt^{i}Pr₂ as a base and [CuI] as reducing agent with catalyst loadings of 0.25, 0.50, 0.75 and 1.0 mol% (Reaction (4), Table 3, Fig. 8) to test the productivity of the appropriate

catalytic systems. In addition to these studies, reactions with the conventional monodendate triphenylphosphane ligands were carried out under similar conditions, so that direct comparison might be achieved.

As summarized in Table 3 the reactions carried out at higher temperature produce higher conversion numbers, for example, the best results were obtained at 100 °C for all compounds. Nevertheless, the determination of the optimum reaction conditions is
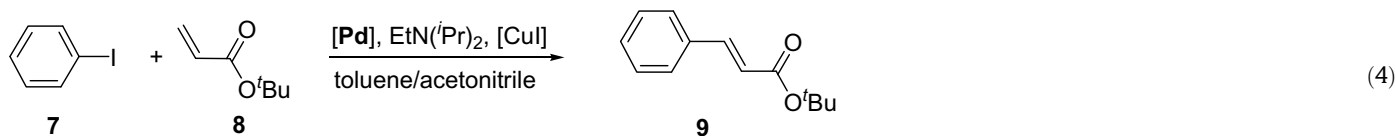
$$\text{7} + \text{8} \xrightarrow[\text{toluene/acetonitrile}]{\text{[Pd], EtN(}^i\text{Pr)}_2\text{, [CuI]}} \text{9} \tag{4}$$

Table 2
Conditions of the Suzuki–Miyaura C–C cross-coupling of **4a** and **4b** with **5** by complexes **3a–3c,** and [Pd(OAc)$_2$/PPh$_3$] (**10**) [17] for comparison.

Compd.	Conc. [mol%]	Yield biphenyls [%][a]		TON[b]	
		6a	**6b**	**6a**	**6b**
10	0.5	76.7		153	
3a	0.5	86.2		172	
3b	0.5	40.7		81	
3c	0.5	32.4		65	
10	0.25	35.1		139	
3a	0.25	100		395	
3b	0.25	98.1		387	
3c	0.25	66.2		261	
3a	0.1	100	100	1000	1000
3b	0.1	100	100	1000	1000
3c	0.1	71.9	100	719	1000
3a	0.05	48.0	100	960	2000
3b	0.05	94.2	100	1884	2000
3c	0.05	83.1	100	1662	2000

[a] Yields are determined by ^{1}H NMR spectroscopy with acetyl ferrocene as a standard relative to **6a** and **6b**, respectively; 60 min.
[b] (Mol product/mol [Pd]).

not predictable since individual catalysts show a unique behavior, for example, catalyst **3a** has its highest productivity at a palladium loading of 0.25, **3b** at 0.75, and **3c** at 0.75 and 0.25 mol% at 100 °C (Table 3). The maximal possible conversion amounts to ca. 92% (Table 3). As consequence of the data presented in Table 3 it can be concluded that the highest productivity is obtained with the catalyst possessing the highest Lewis-basic and lowest electron-withdrawing phosphane ligands. This effect is not consistent with the electronic argumentation used in the Suzuki–Miyaura reaction (vide supra) and hence, must be different originated. Apart from electronic effects also steric arguments (Tolman cone angle) must be considered since these effects are responsible for changing the molecular properties or parts of it.

The Tolman cone angle is the apex angle of a cylindrical cone centered 2.28 Å from the center of the phosphorus atom which touches the van-der-Waals radii of the outermost atoms [23]. Increasing the angle between the phosphane substituents will decrease the percentage of the *s* character in the phosphorus lone-pair. The Tolman cone angle of PPh$_3$ with 145° was published by Tolman [24]. The Tolman cone angel for compound **1a** was calcu-
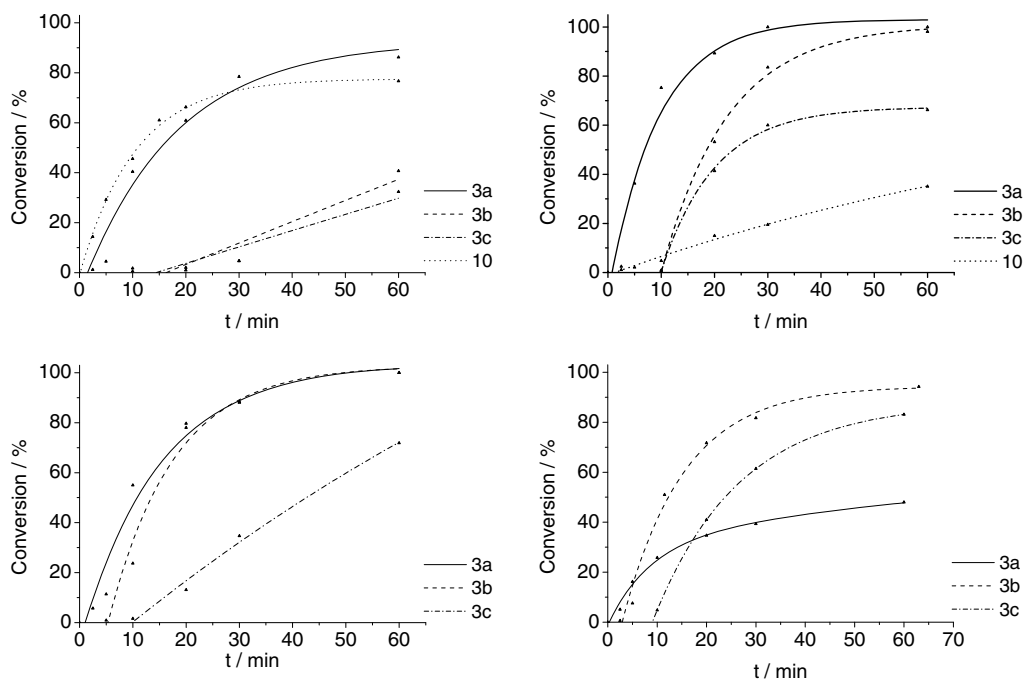

Fig. 6. Kinetic investigation of **3a–3c** in the Suzuki–Miyaura carbon–carbon cross-coupling reaction of **4a** with **5** to give **6a**. (Top: left, 0.5 mol%; right, 0.25 mol%; bottom: left, 0.1 mol%, right, 0.05 mol% (pre)catalyst.)
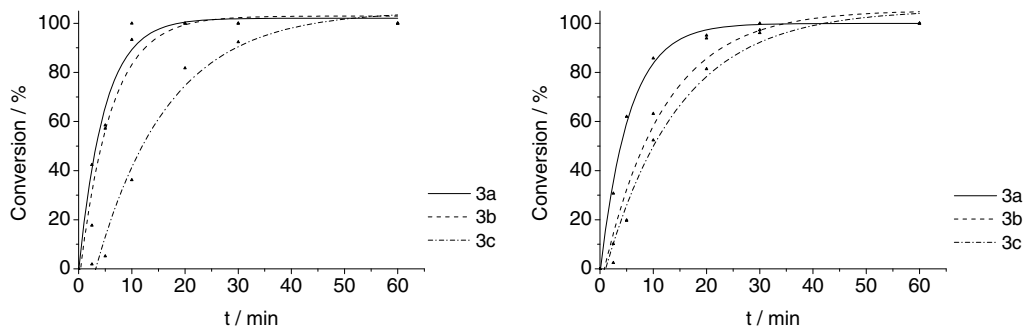
Fig. 7. Kinetic investigation of **3a**–**3c** in the Suzuki–Miyaura carbon–carbon cross-coupling reaction of **4b** with **5** to give **6b**. (Left, 0.1 mol%; right, 0.05 mol% (pre)catalyst.)

Table 3
Conditions of the Heck–Mizoroki C–C cross-coupling reaction of **7** with **8** by complexes **3a**–**3c,** and [Pd(OAc)₂/2 PPh₃/[CuI]]ᵃ (**10**) for comparison.

Compd.	Conc. [mol%]	65 °C	100 °C
		Yield of **9** [%]ᵇ	
10	1.0	53.7	31.0
3a		38.2	83.4
10	0.75	56.1	70.3
3a		36.1	68.5
3b		11.4	54.9
3c		0	4.3
10	0.5	53.6	81.1
3a		22.7	91.1
3b		8.0	43.9
3c		0.5	0
10	0.25	34.2	47.1
3a		22.0	91.8
3b		7.6	18.6
3c		0	4.3

ᵃ According to the method described by Boyes and Butler [22].
ᵇ Yields are determined by ¹H NMR spectroscopy with acetyl ferrocene as standard relative to **9**; reaction time 32 h.

Fig. 8. Schematic view of the different orientations of the ferrocene subunits in **3a**–**3c**.

lated to 168° and for **1c** to 175°. Thus, electronic and steric effects are intimately related [24].

The $^1J(^{31}P–^{77}Se)$ coupling constant (**3a**, 746 Hz; **3c**, 765 Hz) shows that **3c** possesses a higher electron deficiency as **3a**. Considering this, coordination complex **3c** should be the better catalyst. As discussed earlier, however, metal-organic **3a** evinces a higher productivity. This contrary behavior most probably is attributed to the different orientations of the sandwich substructures present in the appropriate phosphane ligands, which finally influences the Tolman cone angle (Fig. 8). From Fig. 8 it can be seen that, when the sandwich units are positioned to the outside they are not influencing the angle between the phosphorus substituents, but signifi-
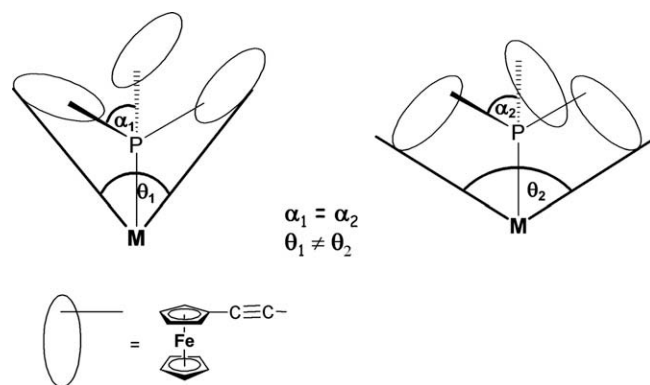
cantly are responsible for a larger Tolman cone angle (**3a**, 168; **3c**, 175°; for comparison, PPh₃ 145° [24]). This emphasizes that the s character in the phosphorus lone-pair will not be increased in **3c** as stated above, rather the phosphane group acts as an electron deficient Lewis-base ligand. These results indicate that presumably the reason for the contrary catalytic behavior of **3a** vs. **3c** is owed to the higher shielding in **3c** resulting in a more hindered attack of the substrates to the catalytic active centre.

The kinetic studies carried out with **3a**–**3c**, and [Pd(OAc)₂/2 PPh₃/[CuI]] (**10**) [22] for comparison in a mixture of toluene/acetonitrile of ratio 1:1 at 80 °C and in presence of 0.5 mol% of palladium are shown in Fig. 9. From these graphs it is obviously that, as outlined earlier, **3a** is by far the most active and productive catalyst in the reaction of **7** with **8** to give **9**. The conversion rate is 70%. Complexes **3b** and **3c** show, due to their steric bulkiness, lower activities. Therefore, we repeated the catalytic reactions once more by
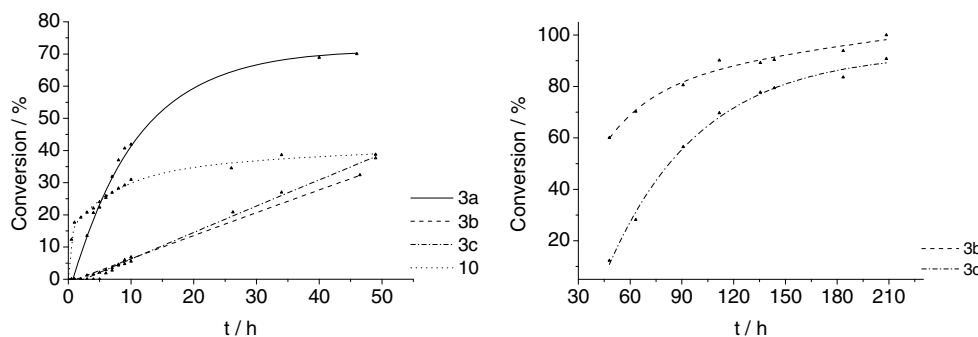

Fig. 9. Kinetic investigations of **3a**–**3c** in the Heck–Mizoroki carbon–carbon cross-coupling reaction of **7** with **8**. (0.5 mol% (pre)catalyst; left, conversion time 0–50 h; right, conversion time 45–210 h.)

starting from 45 h. After 210 h the conversion rate for **3c** is 91%, while for **3b** a quantitative conversion is typical (Fig. 9, right). However, the catalyst systems reported by, for example, Fu, [25] Herrmann, [26] and Reetz, [27] are much more active than **3a**–**3c** and even can be used for less reactive aryl halides under mild conditions.

3. Conclusion

Within this report, the synthesis of phosphane selenides $(FcC{\equiv}C)_nPh_{3-n}P{=}Se$ (n = 1; 2; 3; Fc = ferrocenyl, $(\eta^5$-$C_5H_4)(\eta^5$-$C_5H_5)Fe$) from $(FcC{\equiv}C)_nPh_{3-n}P$ and selenium is described to estimate the σ-donor properties of these systems by $^{31}P\{^1H\}$ NMR spectroscopy. Progressive replacement of phenyl by ferrocenylethynyl causes a shielding of the phosphorus atom with increasing of the $^1J(^{31}P-^{77}Se)$ coupling constants. The appropriate palladiumdichloride complexes $[((FcC{\equiv}C)_nPh_{3-n}P)_2PdCl_2]$ are accessible by treatment of $(FcC{\equiv}C)_nPh_{3-n}P$ with $[(Et_2S)_2PdCl_2]$. Single X-ray structure analysis confirms the *cis*-configuration of these molecules.

It could be shown that complexes $[((FcC{\equiv}C)_nPh_{3-n}P)_2PdCl_2]$ can successfully be used as (pre)catalysts in Suzuki–Miyaura and Heck–Mizoroki carbon–carbon cross-coupling reactions. Compared with the $[Pd(OAc)_2/PPh_3]$ standard system they show significantly higher activities and productivities. Although, they are less active than the catalyst systems reported earlier with any combination of N-heterocyclic carbenes, bulky, electron-rich chelating bis(phosphines), palladacycles, secondary phosphates or phosphonium salts. The obtained catalytic results can be correlated with electronic ($^1J(^{31}P-^{77}Se)$ coupling constants from $^{31}P\{^1H\}$ NMR spectroscopy) and steric parameters (Tolman cone angle vs. angle between the phosphorus substituents) of the appropriate phosphane selenides and palladiumdichloride (ferrocenylethynyl)phosphane systems. In general, electron-withdrawing phosphane ligands increase the rate of reaction in the Heck–Mizoroki reaction which may be attributed to the nucleophilic attack at the more electrophilic phosphorus atom. In contrast, the Suzuki–Miyaura carbon–carbon cross-coupling reaction electron-rich and more bulky phosphanes are favored and show the best results.

4. Experimental

4.1. General data

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Toluene, petroleum ether, *n*-pentane and *n*-hexane were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations.

4.2. Instruments

Infrared spectra were recorded with a Thermo Electron Corporation FT-IR spectrometer Nicolet IR 200. ^1H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; $^{13}C\{^1H\}$ NMR spectra were recorded at 62.860 MHz; $^{31}P\{^1H\}$ NMR spectra were recorded at 101.249 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^1H NMR: CDCl$_3$ 99.8%, δ = 7.26. $^{13}C\{^1H\}$ NMR: CDCl$_3$ (99.8%), δ = 77.16. $^{31}P\{^1H\}$ NMR: rel. H$_3$PO$_4$ (85%), δ = 0.0; rel. P(OMe)$_3$, δ = 139.0; external). The abbreviation *pt* in the ^1H NMR spectra corresponds to pseudo-triplet. Microanalyses were performed with the C, H, N analyzer FLASHEA 1112 Series (Thermo company).

4.3. Reagents

2-Bromo-toluene (**4a**), 4-bromo-acetophenone (**4b**), phenyl boronic acid (**5**) iodobenzene (**7**), *tert*-butyl acrylate (**8**), and selenium were purchased by ACROS Organics and were used as received. The ferrocenylethynyl phosphanes and the respective palladium(II)chloride complexes (**3a**–**3c**) were synthesized as described in Ref. [11]. Reagents $[(Et_2S)_2PdCl_2]$ [28] and acetylferrocene [29] were prepared in analogy to the respective synthesis protocol.

4.3.1. Synthesis of $(FcC{\equiv}C)Ph_2P{=}Se$ (2a)

150 mg (0.38 mmol) of (ferrocenylethynyl)diphenyl phosphane (**1a**) were dissolved in toluene (30 mL) and 60 mg (0.76 mmol) of selenium were added. After 12 h of stirring at 100 °C, all volatiles were removed in *oil-pump* vacuum and the brown residue was dissolved in 20 mL of dichloromethane and filtered through a pad of Celite. The title compound could be isolated as an orange, chewy oil by concentrating the solution to 10 mL and addition of petroleum ether. Yield: 170 mg (0.36 mmol, 94%).

Anal. Calc. for C$_{24}$H$_{19}$FePSe (473.97): C, 60.76; H, 4.04. Found: C, 60.74; H, 4.02%. **IR** (KBr, cm^{-1}): 2156 (m, $\nu_{C{\equiv}C}$), 559 (m, $\nu_{P{=}Se}$). **^1H NMR** (δ, CDCl$_3$): 4.27 (s, 5 H, C$_5$H$_5$), 4.34 (pt, J_{HH} = 1.9 Hz, 2 H, H$^\beta$/C$_5$H$_4$), 4.62 (pt, J_{HH} = 1.9 Hz, 2 H, H$^\alpha$/C$_5$H$_4$), 7.45–7.53 (m, 6 H, C$_6$H$_5$), 7.95–8.07 (m, 4 H, C$_6$H$_5$). **$^{13}C\{^1H\}$ NMR** (δ, CDCl$_3$): 60.8 (d, J_{CP} = 4 Hz, C^i/C$_5$H$_4$), 70.5 (C$_5$H$_5$), 72.7 (C$^\alpha$/C$_5$H$_4$), 72.7 (C$^\beta$/C$_5$H$_4$), 77.9 (C${\equiv}$C), 109.4 (d, J_{CP} = 26 Hz, C${\equiv}$C), 128.8 (d, J_{CP} = 14 Hz, C^o/C$_6$H$_5$), 131.4 (d, J_{CP} = 11 Hz, C^m/C$_6$H$_5$), 131.9 (d, J_{CP} = 3 Hz, C^P/C$_6$H$_5$), 133.2 (d, J_{CP} = 26 Hz, C^i/C$_6$H$_5$). **$^{31}P\{^1H\}$ NMR** (δ, CDCl$_3$): 4.3 ($J_{31P-77Se}$ = 746 Hz).

4.3.2. Synthesis of $(FcC{\equiv}C)_2PhP{=}Se$ (2b)

Compound **2b** was synthesized in the same manner as **2a**, whereby 150 mg (0.30 mmol) of di(ferrocenylethynyl)phenyl phosphane (**1b**) were reacted with 45 mg (0.57 mmol) of selenium. After appropriate work-up, **2b** was obtained as an orange solid. Yield: 160 mg (0.26 mmol, 93%).

Anal. Calc. for C$_{30}$H$_{23}$Fe$_2$PSe (605.94): C, 59.41; H, 3.83. Found: C, 59.77; H, 3.77%. **M.p.** 142 °C. **IR** (KBr, cm^{-1}): 2153 (m, $\nu_{C{\equiv}C}$), 557 (w, $\nu_{P{=}Se}$). **^1H NMR** (δ, CDCl$_3$): 4.29 (s, 10 H, C$_5$H$_5$), 4.33 (pt, J_{HH} = 1.9 Hz, 4 H, H$^\beta$/C$_5$H$_4$), 4.61 (pt, J_{HH} = 1.9 Hz, 4 H, H$^\alpha$/C$_5$H$_4$), 7.48–7.56 (m, 3 H, C$_6$H$_5$), 8.13–8.22 (m, 2 H, C$_6$H$_5$). **$^{13}C\{^1H\}$ NMR** (δ, CDCl$_3$): 60.7 (d, J_{CP} = 5 Hz, C^i/C$_5$H$_4$), 70.3 (d, J_{CP} = 16 Hz, C$^\alpha$/C$_5$H$_4$), 70.5 (C$_5$H$_5$), 72.7 (C$^\beta$/C$_5$H$_4$), 79.5 (C${\equiv}$C), 106.3 (d, J_{CP} = 8 Hz, C${\equiv}$C), 128.9 (d, J_{CP} = 15 Hz, C^o/C$_6$H$_5$), 129.4 (C^m/C$_6$H$_5$), 130.8 (d, J_{CP} = 14 Hz, C^P/C$_6$H$_5$), 132.3 (C^i/C$_6$H$_5$). **$^{31}P\{^1H\}$ NMR** (δ, CDCl$_3$): −31.3 ($J_{31P-77Se}$ = 757 Hz).

4.3.3. Synthesis of $(FcC{\equiv}C)_3P{=}Se$ (2c)

Compound **2c** was synthesized in the same manner as **2a**, whereby 150 mg (0.23 mmol) of tri(ferrocenylethynyl)phenyl phosphane (**1c**) were reacted with 45 mg (0.57 mmol) of selenium. After appropriate work-up, **2b** could be isolated as an orange solid. Yield: 145 mg (0.20 mmol, 86%).

Anal. Calc. for C$_{36}$H$_{27}$Fe$_3$PSe (737.91): C, 58.54; H, 3.69. Found: C, 58.76; H, 3.69%. **M.p.** 178 °C. **IR** (KBr, cm^{-1}): 2148 (w, $\nu_{C{\equiv}C}$), 556 (w, $\nu_{P{=}Se}$). **^1H NMR** (δ, CDCl$_3$): 4.34 (s, 15 H, C$_5$H$_5$), 4.35 (pt, J_{HH} = 1.9 Hz, 6 H, H$^\beta$/C$_5$H$_4$), 4.66 (pt, J_{HH} = 1.9 Hz, 6 H, H$^\alpha$/C$_5$H$_4$). **$^{13}C\{^1H\}$ NMR** (δ, CDCl$_3$): 60.4 (d, J_{CP} = 5 Hz, C^i/C$_5$H$_4$), 70.4 (d, J_{CP} = 23 Hz, C$^\alpha$/C$_5$H$_4$), 70.6 (C$_5$H$_5$), 72.7 (d, J_{CP} = 2 Hz, C$^\beta$/C$_5$H$_4$), 78.9 (C${\equiv}$C), 105.1 (d, J_{CP} = 40 Hz, C${\equiv}$C). **$^{31}P\{^1H\}$ NMR** (δ, CDCl$_3$): −71.3 ($J_{31P-77Se}$ = 765 Hz).

4.3.4. Suzuki–Miyaura reaction of 2-bromo-toluene (**4a**) and 4-bromo-acetophenone (**4b**), respectively, with phenyl boronic acid (**5**)

4.3.4.1. Kinetic investigations.
2-Bromotoluene (500 mg, 2.92 mmol), phenylboronic acid (470 mg, 3.85 mmol), K_2CO_3 (1.21 g, 8.76 mmol) and 222 mg (0.97 mmol) of acetylferrocene were dissolved in 10 mL of a dioxane/water mixture (2:1, v/v). After addition of the appropriate amount (0.5, 0.25, or 0.1 mol%) of the respective (pre)catalyst (**3a**–**3c**, or **10**), the reaction mixture was stirred for 1 h at 100 °C. After 2.5, 5, 10, 20, 30, and 60 min, samples (1 mL) were taken for characterization, chromatographed on silica gel with diethyl ether as eluent, and all volatiles were evaporated under reduced pressure. The conversions were determined by ^1H NMR spectroscopy.

4-Bromo-acetophenone (995 mg, 5.0 mmol), phenylboronic acid (726 mg, 6.0 mmol), K_2CO_3 (1.21 g, 8.76 mmol), and acetylferrocene (114 mg, 0.5 mmol) were dissolved in 10 mL of a dioxane/water mixture (2:1, v/v). After addition of the appropriate (pre)catalyst (**3a**–**3c**) (0.1 or 0.05 mol%), the reaction mixture was stirred for 1 h at 100 °C. After 2.5, 5, 10, 20, 30, and 60 min, samples (1 mL) were taken for characterization, chromatographed on silica gel with diethyl ether as eluent, and all volatiles were evaporated under reduced pressure. The conversions were determined by ^1H NMR spectroscopy.

4.3.5. Heck–Mizoroki reaction of iodobenzene (**7**) with tert-butyl acrylate (**8**)

4.3.5.1. Conversion dependency on the concentration of the (pre)catalyst.
Iodobenzene (612 mg, 3.0 mmol), tert-butylacrylate (397 mg, 3.1 mmol), EtN^{i}Pr$_2$ (415 mg, 3.2 mmol), and acetylferrocene (228 mg, 1.0 mmol) were dissolved in 10 mL of a toluene/acetonitrile mixture (1:1, v/v). After loading with the appropriate (pre)catalyst (0.25, 0.5, 0.75, and 1.0 mol%) and addition of two equivalents of [CuI], the suspension was stirred for 16 h at 65 and 100 °C, respectively. Afterward, a sample (2 mL) was taken, chromatographed on silica gel with diethyl ether as eluent and all volatiles were evaporated under reduced pressure. The conversions were determined by ^1H NMR spectroscopy.

4.3.5.2. Kinetic investigations.
Iodobenzene (654 mg, 5.1 mmol), tert-butylacrylate (672 mg, 5.2 mmol), EtN^{i}Pr$_2$ (672 mg, 5.2 mmol), and acetylferrocene (114 mg, 0.5 mmol) were dissolved in 20 mL of a toluene/acetonitrile mixture (1:1, v/v) and loaded with 0.5 mol% of the respective (pre)catalyst (**3a**–**3c**, and **10**). Two equivalents of [CuI] were added in a single potion. The reaction suspension was stirred at 80 °C and samples (1 mL) were taken in periods of 1 h. In addition, for (pre)catalysts **3b** and **3c** the kinetic investigations were performed by sampling (sample 1 mL) over a period of 208.5 h (at 48.0, 63.35, 90.75, 117.75, 135.5, 143.5, 183.5, and 208.5 h). The samples were chomatographed on silica gel with diethyl ether as eluent. All volatiles were evaporated from there samples under reduced pressure. The conversions were determined by 1H NMR spectroscopy.

5. Crystal structure determinations

The crystal and intensity collection data for **1a**, **1c**, **2c**, and **3c** are summarized in Table 4. All data were collected on a Oxford Gemini S diffractometer with graphite monochromatized Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 100 K (**1a**, **1c**, **2c**) and graphite mono-chromatized Cu K$_\alpha$ radiation ($\lambda = 1.54$ Å) at 110 K (**3c**) using oil-coated shock-cooled crystals [30]. The structures were solved by direct methods using SHELXS-97 [31] and refined by full-matrix least-square procedures on F^2 using SHELXL-97 [32]. All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions.

6. Supplementary material

CCDC 680846, 680847, 680848 and 680845 contain the supplementary crystallographic data for **1a**, **1c**, **2c**, and **3c**. These data can

Table 4
Crystal and intensity collection data for **1a**, **1c**, **2c** and **3c**.

	1a	1c	2c	3c
Formula weight	788.42	658.10	737.06	1732.23
Chemical formula	$C_{48}H_{38}Fe_2P_2$	$C_{36}H_{27}Fe_3P$	$C_{36}H_{27}Fe_3PSe$	$C_{72}H_{54}Cl_2Fe_6P_2Pd$ 2CHCl$_3$
Crystal system	Triclinic	Monoclinic	Rhombohedral	Monoclinic
Space group	$P\bar{1}$	$P2_1/a$	$R3m$	$P2_1/a$
a (Å)	5.9812(4)	13.2158(7)	18.76270(10)	22.9481(6)
b (Å)	12.2705(10)	11.0527(6)	18.76270(10)	12.3827(2)
c (Å)	25.979(2)	19.0908(13)	6.9440(2)	24.0250(3)
α (°)	99.613(7)	90	90	90
β (°)	92.641(6)	92.130(5)	90	92.780(2)
γ (°)	99.733(6)	90	120	90
V (Å^3)	1847.4(2)	2786.7(3)	2117.05(6)	6818.9(2)
ρ_{calc} (g cm^{-3})	1.417	1.569	1.734	1.687
$F(000)$	816	1344	1110	3472
Crystal dimensions (mm)	$0.3 \times 0.2 \times 0.05$	$0.4 \times 0.2 \times 0.1$	$0.4 \times 0.3 \times 0.2$	$0.1 \times 0.05 \times 0.03$
Z	2	4	3	4
Max. and min. transmission	1.04440, 0.94207	1.00000, 0.87219	1.00000, 0.85363	1.00000, 0.15934
Absorption coefficient (λ, mm^{-1})	0.907	1.624	2.894	15.696
Scan range (°)	3.18–26.09	3.08–26.11	3.19–26.06	3.68–60.72
Index ranges	$-7 \leqslant h \leqslant 7$, $-15 \leqslant k \leqslant 15$, $-32 \leqslant l \leqslant 32$	$-16 \leqslant h \leqslant 16$, $-13 \leqslant k \leqslant 13$, $-23 \leqslant l \leqslant 23$	$-23 \leqslant h \leqslant 14$, $-18 \leqslant k \leqslant 23$, $-8 \leqslant l \leqslant 7$	$-24 \leqslant h \leqslant 25$, $-13 \leqslant k \leqslant 13$, $-27 \leqslant l \leqslant 27$
Total reflections	18098	26707	958	10141
Unique reflections	7286	5531	0.0127	0.1508
R_{int}	0.0314	0.0482	958/1/73	10141/582/820
Data/restraints/parameters	7286 /0/469	5531/0/361	1.052	1.085
Goodness-of-fit on F^2	1.220	1.019	0.0151, 0.0393	0.0917, 0.2271
R_1[a], wR_2[a] [I $2\rho(I)$]	0.0825, 0.2018	0.0298, 0.0644	0.0153, 0.0395	0.1408, 0.2543
R_1[a], wR_2[a] (all data)	0.0969, 0.2057	0.0520, 0.0768	0.013(10)	–
Largest differences in peak and hole peak in final Fourier map (e Å^{-3})	1.291, −1.305	0.539, −0.317	0.425, −0.246	2.900, −0.979

[a] $R_1 = [\Sigma(||F_o| - |F_c|)/\Sigma|F_o|]$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$. $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. n = number of reflections, p = parameters used.

be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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