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Planar Chiral Ferrocenes

Evaluation of the Transferability of the "Flexible Steric Bulk" Concept from N-Heterocyclic Carbenes to Planar-Chiral Phosphinoferrocenes and their Electronic Modification

Marcus Korb,[a][‡] Dieter Schaarschmidt,[a][‡‡] Martin Grumbt,[a] Matthias König,[a] and Heinrich Lang*[a]

Abstract: The concept of "flexible steric bulk" is discussed at 2-phenylvinyl-1-phosphinoferrocenes. The introduction of freely rotatable 1'-silyl groups increases the catalytic productivity within the synthesis of tri-*ortho*-substituted biaryls by Suzuki–Miyaura *C,C* cross-coupling reactions, giving higher yields with 1/4 of catalyst concentration than for the *non*-silylated derivatives. Electronic modification of the P and the vinyl donor functionalities was investigated by introducing substituents in the *para* positions of both groups. Therein, electron-withdrawing phosphines increased the yield from 78 to 91 % for a given biaryl, by changing from a diphenylphosphino to the P(*p*-CN-$C_6H_4)_2$ unit. Opposite results, obtained from electron-donating and sterically demanding phosphines, were in accordance with the $^1J(^{31}P,^{77}Se)$ values. However, the electron density of the ferrocenyl backbone, expressed by the redox potential of the first ferrocenyl-related redox process, cannot be correlated with the donor-properties at the P atom. Changing from a PPh_2-substituted ferrocene to a (R_A)-1,1′-binaphthyl-containing phosphonite, a complex interaction between the axial- and the planar-chiral motifs occurs, resulting a change of the absolute biaryl configuration.

Introduction

In the last decades, *C,C* bond formation reactions (e.g., the Suzuki–Miyaura reaction)[1] have emerged as a powerful tool in synthetic chemistry.[2] However, the synthesis of sterically congested biaryls, i.e. bearing three or four *ortho*-substituents is still a challenging task.[3] In the field of N-heterocyclic carbenes (NHCs) the concept of "flexible steric bulk",[4] which has been developed by Glorius and co-workers, has proven to prepare tetra-*ortho*-substituted biaryls in a straightforward way.[5] They used IBiox-based (= imidazolium bioxazoline) ligand systems bearing additional cycloalkane substituents (**A**, Figure 1).

The conformational flexibility within these IBiox systems allows to adapt onto the different steric requirements within the catalytic cycle, thus increasing the stability of the catalyst without affecting its productivity negatively. Increase of the steric demand of these groups resulted in a further increase of the yield of a sterically super-crowded tetra-*ortho*-substituted biaryl coupling product, ranging from 18 % for $IBiox_6$ and 96 % for $IBiox_{12}$ fragments (**B**, Figure 1). Classical rigid NHCs, bearing adamantyl- (IAd) or mesityl-based (IMes) imidazoles, instead, did not result in the respective coupling product, which proved that flexibility is the key for the synthesis of sterically congested biaryls.

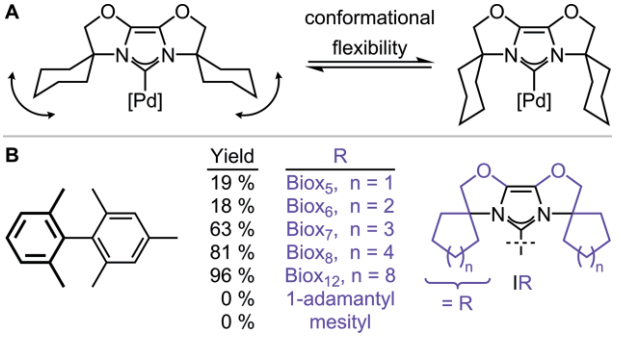

Figure 1. The concept of the "flexible steric bulk", invented by Glorius et al., shown for IBiox-based (imidazole bioxazoline) catalysts (**A**) and correlation between the yield of a tetra-*ortho*-substituted biaryl and the steric demand of the cycloalkyl rings (**B**). The biaryl was derived from chloro aryl (bold) and boronic acid coupling partners.[5]

The almost barrier-free rotation of the ferrocene cyclopentadienyl ligands may allow transferring the concept of "flexible

[a] *Dr. M. Korb, Dr. D. Schaarschmidt, M. Grumbt, M. König, Prof. H. Lang*
Technische Universität Chemnitz,
Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry,
09107 Chemnitz, Germany
E-mail: heinrich.lang@chemie.tu-chemnitz.de
[‡] Current address: Dr. Marcus Korb
The University of Western Australia,
Faculty of Sciences, School of Molecular Sciences,
35 Stirling Highway, Crawley, Perth, Western Australia 6009, Australia
[‡‡] Current address: Dr. Dieter Schaarschmidt
Universität Hamburg,
Department of Chemistry, Institute of Inorganic and Applied Chemistry,
Martin-Luther-King-Platz 6, 20146 Hamburg, Germany
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.202000414.

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steric bulk" from NHCs[5] to phosphinoferrocenes (Figure 2). 1-(Diphenylphosphino)-2-alkenylferrocenes have been chosen as model compounds, since they have already successfully been applied in the synthesis of tri-*ortho*-substituted biaryls and for atroposelective coupling reactions.[6,7] A tuning of the electronic and hence donor properties of the vinyl group is superior as compared to other hemilabile ligands.[8] To evaluate the transferability of the "flexible steric bulk" concept, chemically inert silyl substituents of different steric demand ($SiMe_3$, $SiEt_3$, Si*t*BuMe$_2$, $SiPh_3$, Si*i*Pr$_3$, Si*t*BuPh$_2$) have been introduced in 1′-position at 1-(diphenylphosphino)-2-alkenylferrocenes.

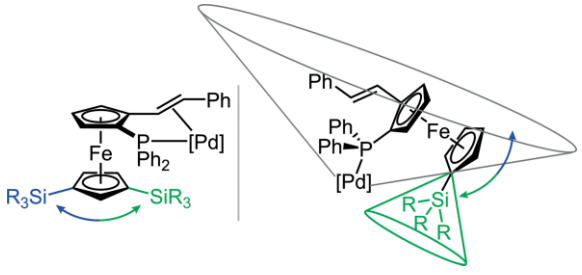


Figure 2. Concept of the "flexible steric bulk" adopted for ferrocene chemistry by introducing 1′-silyl substituents (left) and the formed cone angles of the potential ligand system (right).

Within this contribution, we present the influence of the silyl substituent onto the ability to synthesize tri- and tetra-*ortho*-substituted biaryls.

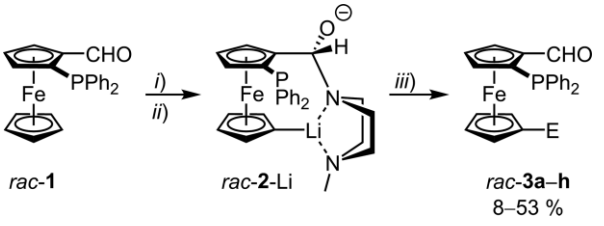
Results and Discussion

Introduction of Substituents in 1′-Position

The respective silyl functionalities SiR_2R' were introduced by applying the *N*-methylpiperazine route based on a regioselective lithiation protocol developed by Manoury and Balavoine (Scheme 1).[9] Silyl groups have been chosen, due to their availability in various steric demands, without affecting the electronic properties of the ferrocenyl backbones. In addition, they are not known to interact with neither the catalytic active species, nor the substrates and hence do not affect the mechanism, compared to a hydrogen atom. They were obtained by treating formylferrocene **1** with lithium *N*-methylpiperazide, forming the hemi-aminal anion, which on subsequent addition of *t*BuLi resulted in the exclusive lithiation of the hitherto unfunctionalized cyclopentadienyl ring, which is in line with the directing effect of the piperazine moiety. Addition of the appropriate chlorosilanes ClE (for E, see Table 1) or formamides gave the 1′-substituted ferrocenes **3a**–**h** in yields of 8–53 % (Scheme 1).

The presence of the PPh_2 group compared to ferrocenecarbaldehyde itself increased the selectivity between the 1′-functionalization and an *ortho*-silylation product from 9:1 to 100 %, although the yield is slightly reduced.[9]

The yields within **3a**–**f** decrease with increasing size of the silyl substituent (cf. cone angles,[10] Table 1). The successful silylation was, *inter alia*, verified by single-crystal X-ray diffraction analysis of **3a**,**b**,**e** (Figures 3 and S4, S5).

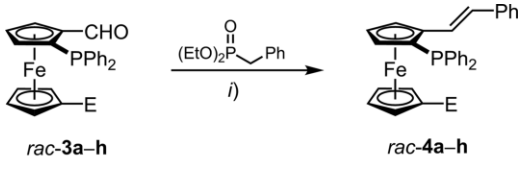


Scheme 1. Synthesis of *ortho*-diphenylphosphino-1′-triorganylsilyl formylferrocenes **3a**–**h**. (Yields are based on **1**; *i*) 1-methylpiperazine, *t*BuLi, THF, 25 °C; *ii*) *t*BuLi, 0 °C; *iii*) ClE (**a**: $ClSiMe_3$, **b**: $ClSiEt_3$, **c**: ClSi*t*BuMe$_2$, **d**: $ClSiPh_3$, **e**: ClSi*i*Pr$_3$, **f**: ClSi*t*BuPh$_2$, **g**: $ClSnBu_3$, **h**: NFP (= *N*-formylpiperidine).).

Table 1. Electrophiles used in the synthesis of **3a**–**h** together with cone angles.[a]

Electrophile	Compd.	Yield[b]	Cone angle
$ClSiMe_3$	**3a**	49 % (69 %[b])	118 °
$ClSiEt_3$	**3b**	53 %	132 °
ClSi*t*BuMe$_2$	**3c**	16 %	139 °
$ClSiPh_3$	**3d**	20 %	145 °
ClSi*i*Pr$_3$	**3e**	18 %	160 °
ClSi*t*BuPh$_2$	**3f**	8 %	157 °
$ClSnBu_3$	**3g**	48 % (56 %[b])	132 °
NFP[d]	**3h**	46 % (17 %[b,c])	–[e]

[a] The cone angles refer to the respective M–PR_3 phosphines by Tolman.[10] [b] Yields of literature reported derivatives without bearing an *ortho*-diphenylphosphino group are given in brackets. [c] DMF (dimethylformamide) was used instead of NFP (= *N*-formylpiperidine). [d] Hydrolysis results in a formyl group. [e] No comparable P analogue.



4a (E = $SiMe_3$)	85 %	**4e** (E = Si^{i}Pr$_3$)	94%
4b (E = $SiEt_3$)	86 %	**4f** (E = Si^{i}BuPh$_2$)	71%
4c (E = Si^{i}BuMe$_2$)	58%	**4g** (E = $SnBu_3$)	82%
4d (E = $SiPh_3$)	82%	**4h** (E = CH=CHPh)	38%

Scheme 2. Synthesis of 1′-silylated vinylferrocenyl phosphines **4a**–**h**. (*i*) THF, –78 °C, diethyl benzylphospho-nate, BuLi, **3a**–**h**, 60 °C. Yields are based on **3a**–**h**. All vinyl groups were obtained with an (*E*)-configuration.).

By reacting formylferrocenes **3a**–**h** with diethyl benzylphosponate in Horner–Wadsworth-Emmons (*HWE*) reactions, the respective (*E*)-phenylvinyl derivatives **4a**–**h** were obtained (Scheme 2). The yields range between 58–94 % and seem not to be influenced by the size of the silyl substituents. In case of ferrocene **3h** the *HWE* reaction proceeds at both aldehyde functionalities to give compound **4h** in 38 % yield. The high stereoselectivity and the *E*-configuration of the vinyl moieties was, *inter alia*, verified by ^{1}H NMR spectroscopy, where doublets with a $^3J_{H,H}$ coupling constant of 16 Hz along the newly formed C=C double bond were observed. Furthermore, the identity of ferrocenes **4a**,**b** was confirmed by single-crystal X-ray diffraction analysis (Figures 3 and SI2).

The molecular structures of formyl ferrocenes **3a**,**b**,**e** in the solid state exhibit an *anti*-clinal conformation (**3a**,**b**,**e**;

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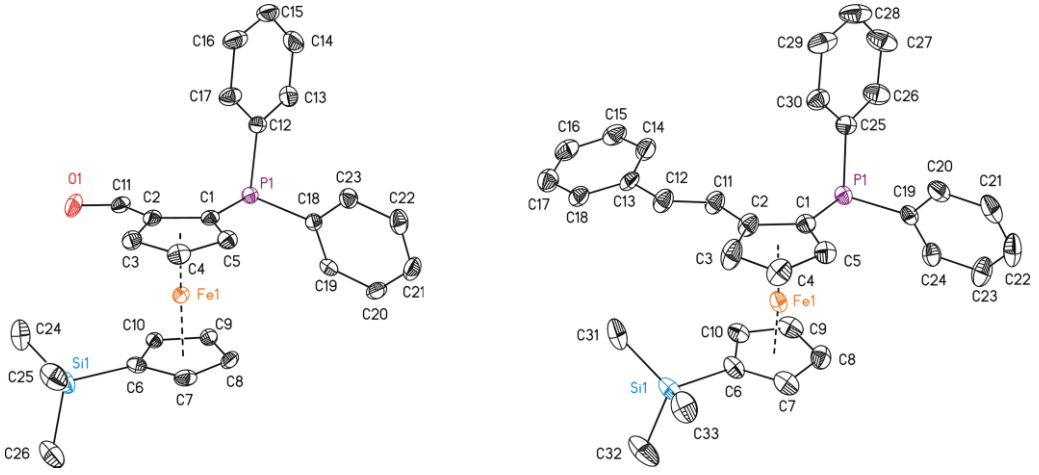


Figure 3. ORTEP (50 % probability level) of the molecular structures of **3a** (left) and **4a** (right) with their atom numbering schemes. Hydrogen atoms and disordered parts in **4a** have been omitted for clarity. Selected bond lengths Å and torsion angles ° for **3a**: C11=O1 1.215(2), C1–C2–C11–O1 –179.62(19); for **4a**: C11=C12 1.333(3), C1–C2–C11–C12 174.3(2).

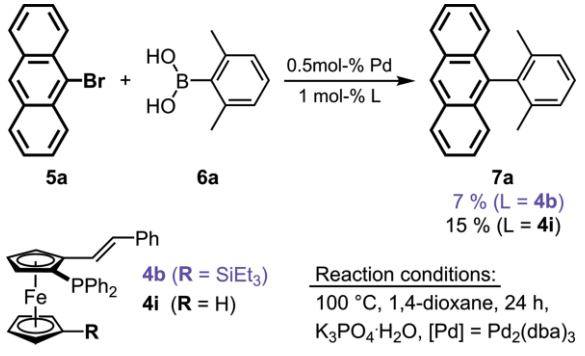
147.89(17)–154.14(14) °) and their phenyl-vinyl derivatives **4a**,**b** show a rather *anti*-periplanar orientation (**4a**,**b**; 165.4(5)–167.58(13) °) of the silyl groups towards the phosphinyl substituents.

Compound **3e** oxidized during the crystallization process and thus the solid-state structure co-crystallized with the respective phosphine oxide in 9 %. The C=O bond lengths of formyl ferrocenes **3a**,**b**,**e** (1.215(2)–1.216(2) Å) and the C=C distances in **4a**,**b** (1.333(3)–1.334(2) Å) are in the range of compounds reported in literature and seem not to be influenced by the presence and size of the silyl substituents.[11]

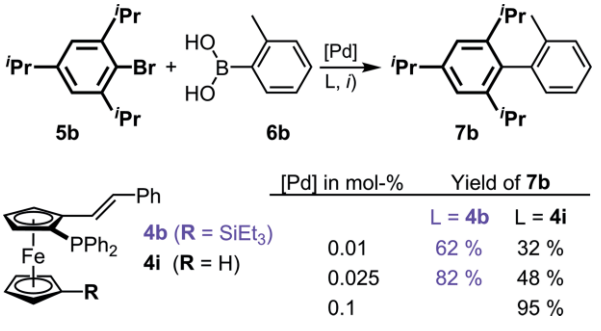
However, a rotation of the C=O fragment[12] out of the C_5H_3 cyclopentadienyl co-planarity rises from 5.9(2) (**3a**) to 6.97(18) (**3b**) and 15.2(3) ° (**3e**), while increasing the steric demand of the silyl group in 1′-position. A similar behavior is observed for the vinyl planes, where the bending increases from 5.9(2) (**4a**) to 8.16(14) (**4b**) by changing from $SiMe_3$ to $SiEt_3$.

Ferrocenes **4a**–**f** were applied as ligands in palladium-catalyzed Suzuki–Miyaura *C*,*C* cross-coupling reactions for the synthesis of tri- and tetra-*ortho*-substituted biaryls. For the latter, the reaction of 9-bromoanthracene (**5a**) with 2,6-dimethylphenylboronic acid (**6a**) was chosen, using **4a–f** as ligands (Scheme 3). However, 9-(2,6-dimethylphenyl)anthracene (**7a**) was only be formed in yields of up to 7 % while using **4b** (Figure S1). Contrary, **4i** gave the tetra-*ortho*-substituted biaryl **7a** in 15 % (Table S1). Sterically less (**4a**) and more (**4c**–**f**) demanding silyl groups resulted in lower yields of **7a**. A higher catalyst concentration also affected the yield negatively and instead increased the yield of hydro-dehalogenation product anthracene (Figure S1).

In contrast, the synthesis of the tri-*ortho*-substituted biaryls, e.g. **7b** proceeds smoothly with **4b** at 70 °C (Scheme 4). Silylated **4b** and *non*-silylated **4i** differ distinctively in their ability to perform this coupling reaction at very low catalyst concentrations. $SiEt_3$-substituted **4b** gives the coupling product **7b** in 62 % yield with a 0.01 mol-% [Pd] loading, whereas with *non*-silylated **4i** only 32 % yield could be achieved under identical reaction conditions (Scheme 4).



Scheme 3. Comparison of silylated **4b** and *non*-silylated **4i** for the synthesis of the tetra-*ortho*-substituted biaryl **7a**.



Scheme 4. Comparison of **4b** and *non*-silylated **4i** for the synthesis of the tri-*ortho*-substituted biaryl **7b** at different catalyst loadings. (*i*) 0.5 mmol **5b**, 0.75 mmol **6b**, 1.5 mmol $K_3PO_4{\cdot}H_2O$, $Pd_2(dba)_3$/**4b** (Pd/L = 1:2), 5 mL of toluene, 70 °C, 24 h. Yields are based on **5b**.

It seems that the introduction of the silyl-substituent at the hitherto unsubstituted cyclopentadienyl moiety increases the catalytic productivity of the phosphinoferrocenes in the synthesis of tri-*ortho*-substituted biaryls. This might be explained by a temporary or permanent shielding of the palladium atom by the silyl group.

The activation barrier for the synthesis of sterically shielded **7b** was determined using **4i**, in order to optimize the reaction

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temperature towards a high activity/productivity (Figure 4). Running the reaction at 60, 70 and 100 °C reveals a reaction of first order with an activation energy of 80.2 ± 1 kJ/mol (Figure S2). Comparison with literature values is hardly possible, due to the lack of experimental kinetic data for Suzuki–Miyaura *C,C* cross-coupling reactions for the synthesis of sterically hindered (triple-*ortho*-substituted) biaryls. Herein, the first results for activation energies of ferrocenyl-based ligands are given. The value of 80.2 ± 1 kJ/mol is similar to pincer-based systems (59–84 kJ/mol), whereby a sterically less demanding substrate was chosen.[13]

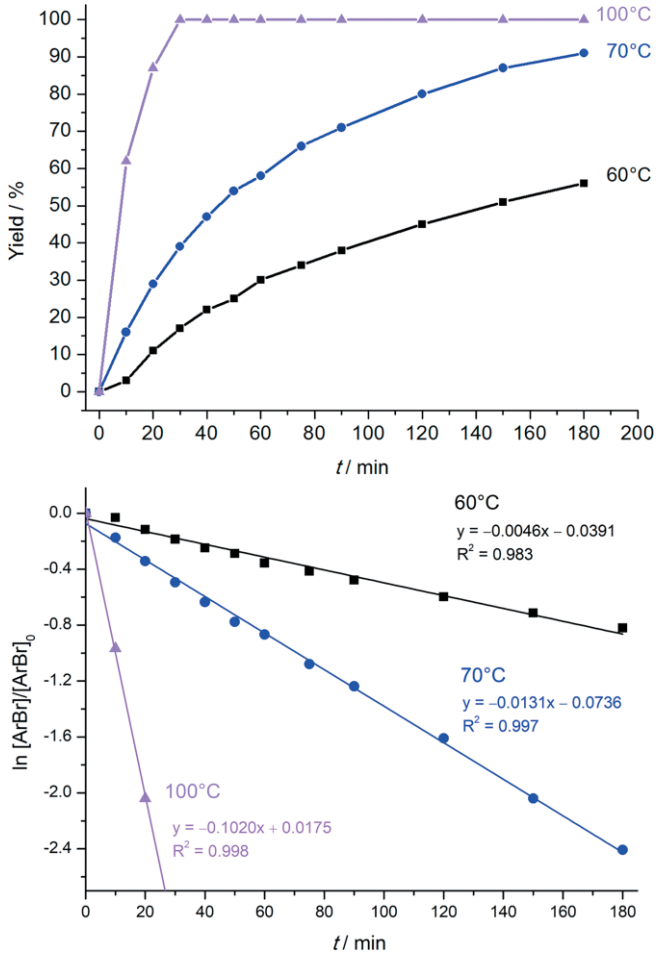
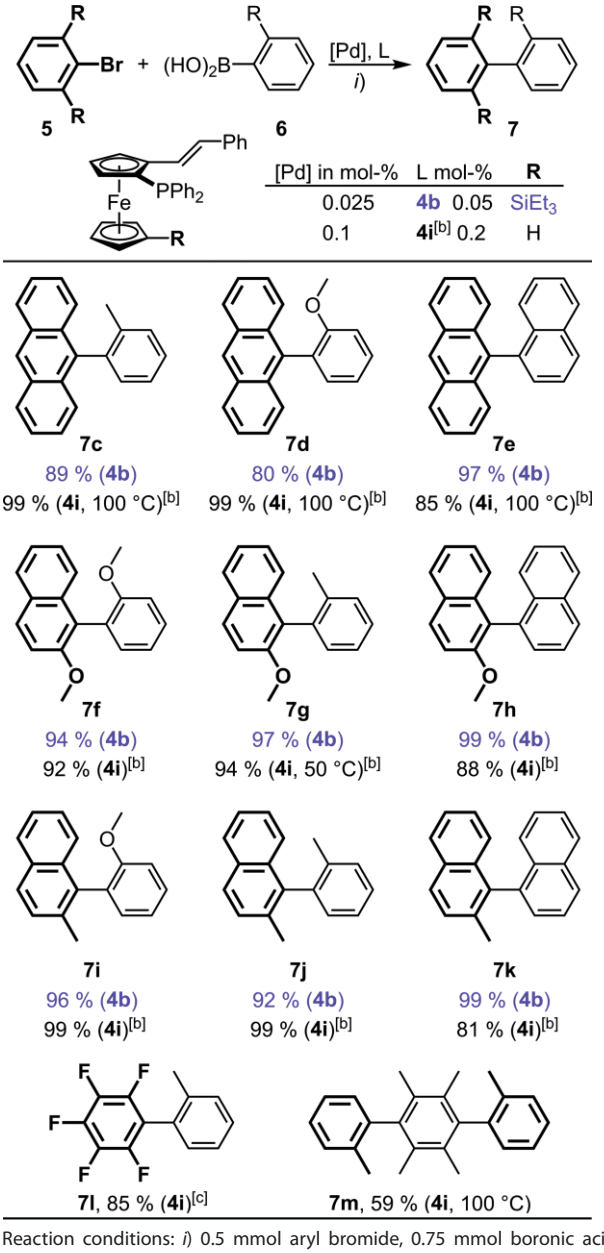


Figure 4. Temperature-dependent formation of **7b**, using **4i** as the ligand (top) and determination of the rate constants (bottom). (Reaction conditions are given in Scheme 4, 0.1 mol-% [Pd], 0.2 mol-% **4i**, toluene. Determined via GC–MS using acenaphthene as an internal standard.).

The synthesis of other biaryls (**7c**–**m**) with sterically demanding substituents in *ortho*-position to the biaryl axis, while applying phosphinoferrocenes **4b** and **4i**, confirms the results obtained for biaryl **7b** (Table 2). By applying 1/4 of the catalyst concentration for **4b** compared to **4i** similar or even higher yields for the respective biaryls could be achieved. It can therefore be concluded that the introduction of a silyl group in 1′-position of 1-(diphenylphosphino)-2-alkenyl-ferrocenes does not affect the ability to synthesize tri-*ortho*-substituted biaryls, however, it increases the kinetic stability of the catalyst towards degradation and therefore allows for a significant reduction of the catalyst loading in the synthesis of tri-*ortho*-substituted biaryls.

Table 2. Comparison of the catalytic productivity of silylated **4b** and *non*-silylated **4i** for the synthesis of tri-*ortho*-substituted biaryls **7c**–**m**.[a]



[a] Reaction conditions: *i*) 0.5 mmol aryl bromide, 0.75 mmol boronic acid, 1.5 mmol $K_3PO_4 \cdot H_2O$, $[Pd_2(dba)_3]$ and **4b**/**i**, 5 mL of toluene, 70 °C, 24 h. Isolated yields based on an average of two runs. [b] Values derived from ref.[6] [c] The respective aryl chloride was used.

Functionalization of the Phenyl-Vinyl Fragment

A further possibility to influence the catalytic performance of vinyl ferrocenyl phosphines is their functionalization at the vinyl (**8a**,**b**) or the phosphine (**9a**–**d**) groups. Their preparation has recently been described by our working group[7] and is similar

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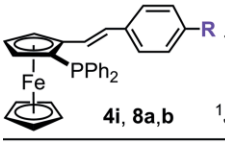
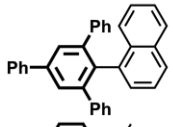
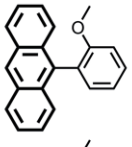
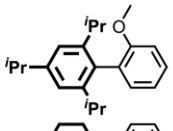
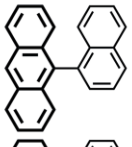
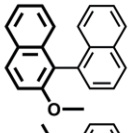
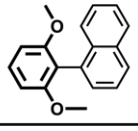
to the synthesis of **4a**–**f**, whereby either the benzylphosphonate for the *HWE* reaction or the phosphinyl electrophile was altered.

The introduction of electron-donating (**8a**, OMe) or electron-withdrawing substituents (**8b**, CN) in *para*-position of the phenylvinyl-substituent changes the electron density at the vinyl moiety and hence the ferrocenyl backbone, which was monitored by cyclic voltammetry of the respective phosphine sulfides **4i**-**S** and **8a**,**b**-**S** (Table 3). The analytical data of the latter two compounds[7] are completed by results of single-crystal X-ray diffraction measurements (Figures S6, S7). Determination of the σ-donor properties of the phosphine can be achieved by comparing the $^1J(^{31}P,^{77}Se)$ coupling constants of the respective P^V-selenides **8a**,**b**-**Se** (Table 3). The coupling constants reflect the hybridization and electron density of the lone pair of electrons at the P atom.[14] Higher values, and thus a lower donor σ-ability, correspond to P orbitals with an increased *s*-character, caused by electron-withdrawing substituents, vice versa for donating groups. Sterically demanding groups force the phosphine into a flat geometry, which changes the hybridization and also lowers the *s*-character of the lone pair of electrons, accompanied with a decreased $^1J(^{31}P,^{77}Se)$ coupling constant. For compounds **8a**,**b**-**Se**, these values are equal, proving that the σ-donor properties of the phosphines in their parent compounds **8a**,**b** are not influenced by the electronic properties of the phenylvinyl-substituent (Table 3).

Table 3. Impact of an electronic modification of the vinyl moiety in ferrocenes **4i** and **8a**,**b** within the synthesis of biaryls **7d**,**e**,**h**,**n**–**p** represented by their yields (in %).[a]

	Compd.	8a	4i	8b
	R	OMe	H	CN
	$E^{o'}$ / mV[b]	165	200	260
4i, 8a,b	^1J ($^{31}P,^{77}Se$)[c]	730.4	731.1	730.7
 7n	time			
	3 h	–	–	–
	24 h	76[d]	76[d,e]	76[d]
 7d	3 h	100	94	54
	24 h	100	100	99
 7o	3 h	80	75	72
	24 h	80	75	72
 7e	3 h	96	85	85
	24 h	98	84	83
 7h	3 h	100	84	–
	24 h	100	84	–
 7p	3 h	100	62	–
	24 h	100	62	–

[a] Reaction conditions for the synthesis of the shown biaryls: 0.1 mol-% [Pd] from $[Pd_2(dba)_3]$, 0.2 mol-% **4i**/**8a**,**b**, 70 °C. Determined via GC–MS using acenaphthene as an internal standard. [b] Formal potential of the ferrocenyl-based redox process, obtained from the respective thiophosphines **4i**-**S** and **8a,b**-**S**, reported against FcH/FcH^+; for conditions see the Supporting Information. [c] Obtained from the respective selenated derivatives **8a**,**b**-**Se**; reported in Hz. [d] Isolated yields. [e] Derived from ref.[7]

This is reflected within the synthesis of biaryl **7n**, using ligands **8a**,**b**, where equal yields (76 %, Table 3) were obtained for the biaryl as well as for side products, e.g. hydro-dehalogenation and homo-coupled biaryls (Figure S3). It can therefore be concluded that the catalytic productivity corresponds with the σ-donor strength of the phosphine and is therefore not influenced by an electronic modification of the phenyl-vinyl fragment.

Comparison of the yields of various biaryls after 3 h (Table 3) reveals that conversion is close to completeness for electron-rich **8a**, whereas electron deficient **8d** exhibits a lower catalytic activity, represented within the formation of **7d**. Similarly, after a reaction time of 24 h **8a** gives slightly higher yields of the biaryls, revealing a somewhat positive impact of increased electron density at the vinyl group. The results support the assumption that the transmetalation is rate determining, since the yields are moreover influenced by the boronic acid.[6]

This is in accordance with recent findings for bisferrocenyl-based ligand systems, where the inversion of the bromide and boronic acid coupling partner dramatically reduced the yield, if the latter became sterically more demanding.[15]

Steric and Electronic Modification of the Phosphine

In contrast, a modification at the phosphine group significantly affects the yield of **7n** (Table 4). The use of sterically demanding PR_2 groups (**9a**, R = *o*-tolyl; **9b**, R = cyclohexyl (Cy)) resulted in a very low conversion of 2-bromo-1,3,5-triphenylbenzene (**9a**: 14 %, **9b**: 24 %), compared to ferrocene **4i** (R = Ph, 76 %). In both cases the halide was recovered and by-products were not detected (Table S2). The catalytic productivity could be increased by the introduction of electron-withdrawing substituents at the PPh_2 moiety. Phosphino alkenylferrocenes **9d** (R = *m*-Cl-C_6H_4) and **9e** (R = *p*-NC-C_6H_4) gave biaryl **7n** in yields of 81 and 91 %, respectively. For a better comparison of the σ-donor properties at the phosphorus atom, the $^1J(^{31}P,^{77}Se)$ coupling constants were determined (Table 4).[16] In case of sterically equally demanding **4i** and **9d**,**e** (cf. cone angles, Table 4), the less donating phosphine **9e** gave the highest yield.

An opposite behavior is observed for **9a** and **9b** where a higher $^1J(^{31}P,^{77}Se)$ value resulted in lower yields, due to the increased size of the phosphine group in **9a**. In general, a low σ-donor character of the phosphine is beneficial for the formation of **7n**. The values reveal that a combination of electronic and steric effects are decisive for the yield of **7n**. It also indicates that the oxidative addition is not rate determining, since this step is usually facilitated by sterically demanding phosphines.[17] It should be noted that, although a high amount of the starting aryl bromide remained unreacted in case of **9a** (Table S2), this is not an indicator for the oxidative addition to

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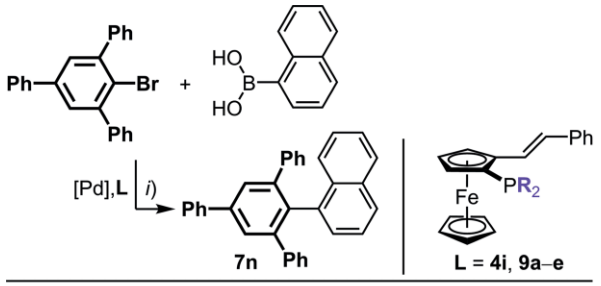
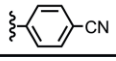
Table 4. Impact of an electronic modification of the phosphinyl-moiety in ferrocenes **4i** and **9a**–**e** within the synthesis of biaryl **7n**.[a]



L	R	Yield of **7n**[b]	θ of R[c]	^1J (^{31}P,^{77}Se)[d]	σ	$E^{o'}$ in mV[e]
9a		14 %	194 °	710.5 Hz[f]	–	170
9b		22 %	170 °	696.5 Hz	–0.15[h]	170
9c		75 %	–	749.6 Hz	0.02[h]	180
4i		76 %	145 °	731.1 Hz[g]	0.00	200[g]
9d		81 %	145 °	748.0 Hz	0.37	240
9e		91 %	145 °	760.2 Hz	0.59	300

[a] Reaction conditions: 0.1 mol-% [Pd] from $[Pd_2(dba)_3]$, 0.2 mol-% L, 1.5 mmol $K_3PO_4{\cdot}H_2O$, 1.0 mmol aryl bromide, 1.5 mmol boronic acid, 5 mL of toluene, 70 °C, 24 h. NMR yields, determined using acenaphthene as internal standard. [b] Yields are based on the bromoarene. [c] The cone angles (Θ) refer to the respective M–PR_3 phosphines by Tolman.[10] [d] Corresponding $^{31}P\{^1H\}$ values of the selenophosphines (ppm): **9a**-**Se**, 26.6; **9b**-**Se**, 47.2; **9c**-**Se**, –7.3; **9d**-**Se**, 30.3, **9e**-**Se**, 31.0 ppm; the values of their parent P^{III} species can be found in ref.[7] [e] Formal potential ($E^{o'}$) of the ferrocenyl-based redox process given against FcH/FcH^+, obtained from the respective thiophosphines **9a**–**e**-**S**. [f] The respective selenophosphine showed broad signals of the respective doublet. Thus, a fitted spectrum was used to calculate the coupling constant. [g] Derived from ref.[7] [h] The values refer to phenyl-bonded derivatives.[10]

be rate determining. It could instead be shown that this step becomes reversible, especially for sterically demanding phosphines.[18] However, if this fact plays a role cannot unambiguously be verified herein.

To prove, if an electronic modification at the phosphorus atom affects the redox properties at the ferrocenyl backbone, the electrochemical properties of **9a**–**e** were investigated by cyclic voltammetry. Thus, compounds **9a**–**e** were oxidized with elemental sulfur to the respective phosphine sulfides to avoid side reactions during the electrochemical measurements.[7,19] Compared to **4i**-**S** (R = H) and **8b**-**S** (R = CN), where a difference of the redox potential of 60 mV occurred, the introduction of a *p*-CN functionality at the PPh_2 group in **9e**-**S** gave a difference of 100 mV relative to **4i**-**S**. The lowest redox potentials, and hence the highest electron densities of the ferrocenyl backbones, are observed for **9a,b**-**S** (170 mV). An increase of the electron-withdrawing character of the phosphines increases the redox potentials accordingly from **9c**-**S** to **9e**-**S**. This trend corresponds well with the $^1J(^{31}P,^{77}Se)$ coupling constants and the σ-Hammett constants, as well as with literature values.[20] The identity of **9e** (Figure 6) and **9a**-**S** (Figure S8) could also be verified by using single-crystal X-ray diffraction analysis. Compared to silylated derivatives **3a**,**b**,**e** and **4a**,**b**, where the vinyl functionality was rotated out of the C_5H_3 plane by 5.9(2)–15.2(3) °, **9e** gave a value of 3.6(5) °, due to the absence of the sterically demanding silyl substituent.

The question arises, if the lower yield of **7n** in case of electron-rich **9b** and also **9c** may be caused by a lower catalytic activity and therefore a too short reaction time.

Hence, the catalytic reaction was monitored for 180 min, revealing a significantly higher activity for **4i** compared to **9b**,**c** (Figure 5). The latter compounds reveal a similar activity within the starting period (up to 40 min). After 60 min the catalytic reaction has terminated for electron-rich **9b**, whereas **9c** remains active. The low catalytic activity and productivity of cyclohexyl substituents, that usually enhance the oxidative addition,[17] therefore imply that this step is not rate determining. After 3 h, the reaction with ligand **4i** has almost finished, whereby **9c** showed less than 50 % conversion, which is steadily increasing. It should be noted that compound **9c** reveals an ambiguous behavior. Although the comparably high $^1J(^{31}P,^{77}Se)$ value suggests low σ-donor properties, usually accompanied with an withdrawing character, it reveals a lower redox potential as the PPh_2 derivative **4i**, indicating an electron-rich ferrocenyl backbone (Table 4). Although the monitoring reveals that a reaction time of 3 h is slightly too short for most of the ligand systems, it illustrates that the parent compound **4i** almost reaches complete conversion, which is in accordance to the results, obtained for other biaryls (Table 3). It can thus be excluded that the low yields of birayl **7n** in combination with ligands **9a**,**b** are caused by unadjusted reaction times.

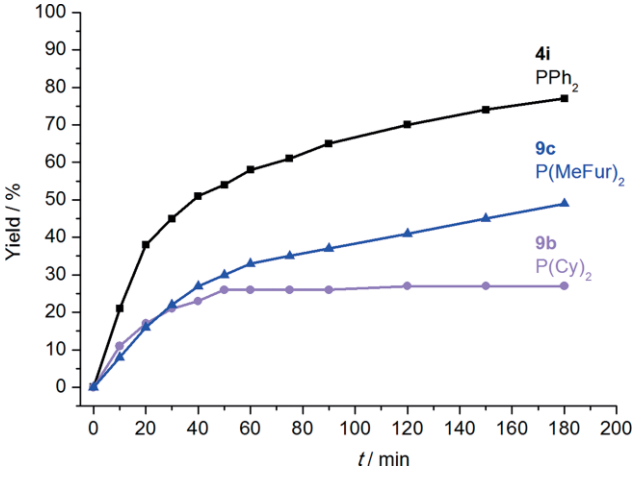
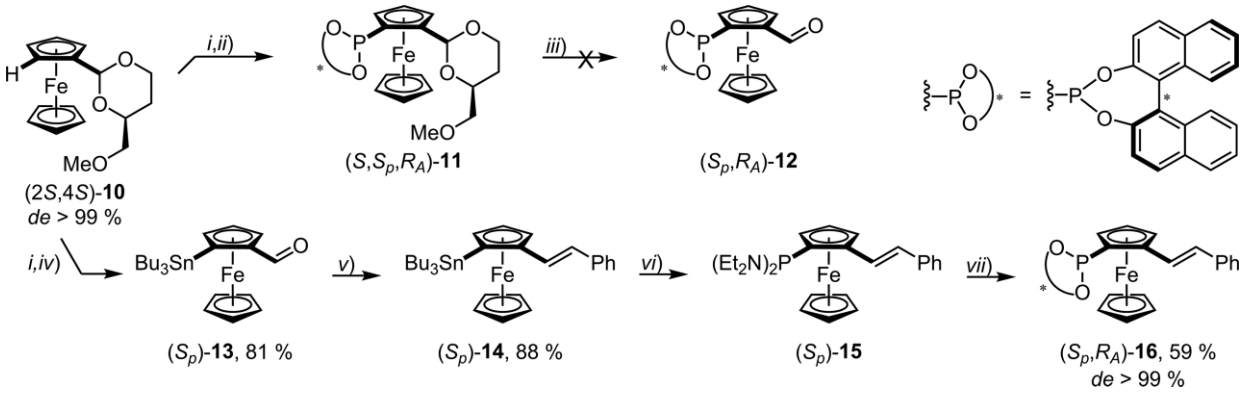


Figure 5. Reaction monitoring of the synthesis of **7n** by using **4i**, **9b**,**c** as ligands according to Table 4.

Chirality at the Phosphine

Vinyl-functionalized ferrocenyl phosphines have already been used in atroposelective Suzuki couplings where biaryls with up to 36 % *ee* could be obtained.[6] Since it could herein be shown that the catalytic productivity is predominately affected by a functionalization at the phosphorus atom, rather than at the



Scheme 5. Pathways for the synthesis of BINOL-substituted (S_p,R_A)-**16**. (*i*) (*S*)-**10**, *t*BuLi, Et_2O, –80 °C, 15 min, 25 °C, 2 h; *ii*) –30 °C, ClP-(R_A)-BINOL, Et_2O, 15 min, 25 °C, 12 h; *iii*) CH_2Cl_2, *p*TsOH/H_2O, 25 °C, 24 h; *iv*) 1st $ClSnBu_3$, –30 °C, Et_2O, 15 min, 25 °C, 12 h, 2nd CH_2Cl_2, *p*TsOH/H_2O, 25 °C, 24 h; yield based on (*S*)-**10**; *v*) P(O)(OEt)$_2$Bn, BuLi, THF, –80 °C, 30 min, (S_p)-**13**, 25 °C, 90 min, 60 °C, 12 h; yield based on (S_p)-**13**; *vi*) BuLi, THF, –80 °C, 30 min, ClP(NEt$_2$)$_2$, 25 °C, 12 h; *vii*) (R_A)-BINOL, toluene, 110 °C, 72 h; yield is based on (S_p)-**14**. Bn = benzyl).

hemi-labile bonded vinyl group, introduction of further chiral elements should occur at the phosphine donor, in order to study the effect onto the enantioselectivity of atroposelective biaryl couplings. A (R_A)-BINOL functionality (BINOL = 1,1′-bi-2-naphthol) was chosen, since it was already applied in asymmetric catalysis[21] and rearrangement reactions,[22] where almost enantiopure products could be obtained. Further, it could be shown that large π-systems, as present in BINOL fragments, play an essential role in the catalytic cycle and interact with aromatic substrates via attractive dispersion interactions that prioritize different conformations.[23]

The chiral acetal (2*S*,4*S*)-**10** was used as the starting material, which can diastereoselectively be lithiated in *ortho*-position (*de* > 99 %), using literature established protocols (Scheme 5).[24a] Reaction of the thus obtained lithiated species with a (R_A)-BINOL-chlorophosphite electrophile, did unfortunately not give formyl ferrocene (S_p,R_A)-**12**, upon cleavage of the chiral acetal group in (S,S_p,R_A)-**11**, probably due to a simultaneous cleavage of the formed phosphonite (Scheme 5). Replacement of the chloride by a phenoxy leaving group in the respective BINOL reagent[25] failed to give (S,S_p,R_A)-**11** upon reaction with (*S*)-**10**-Li. As an alternative pathway, ferrocene (S_p)-**13**[24b] was synthesized and subsequently converted into vinyl ferrocene (S_p)-**14** by applying a *HWE* reaction (Scheme 5). The $SnBu_3$ functionality was replaced by the reaction of (S_p)-**14** with BuLi and subsequent addition of ClP(NEt$_2$)$_2$. The P–N bonds within these phosphoramidates can easily be protonated and thus, (R_A)-BINOL was added, giving (S_p,R_A)-**16** in 59 % yield. Although this procedure is well established for phenyl-based phosphoramidates,[26] the first example in ferrocene chemistry is presented herein. The use of the isomeric (S_A)-BINOL derivative did not give the desired phosphonite, probably caused by a *mismatch* interaction.

Single crystals of (S_p,R_A)-**16** were analyzed by X-ray diffraction (Figure 6), which confirmed the absolute configuration of the described stereogenic elements. The main difference is the orientation of the planar phenyl-vinyl fragment towards the *P* moiety that is usually rotated away from the *ortho*-substituent, as observed for compounds **3a**,**b**,**e**, **4a**,**b** and **9e**. However, in compound **16** it reveals the opposite orientation and directs toward

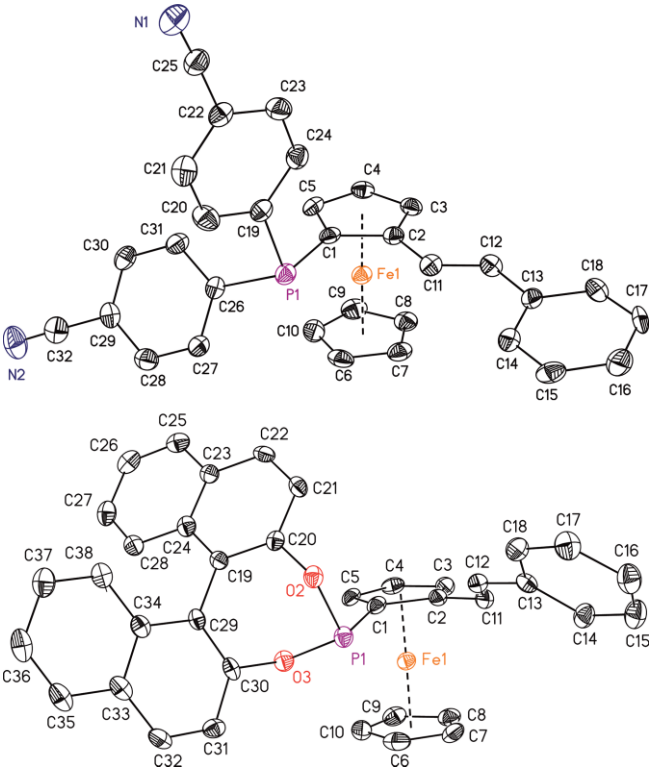


Figure 6. ORTEP (50 % probability level) of the molecular structures of **9e** (top) and (S_p,R_A)-**16** (bottom) with the atom numbering schemes. All hydrogen atoms have been omitted for clarity. Selected bond lengths Å and torsion angles ° for **9e**: C11=C12 1.327(4), C25≡N1 1.137(3), C32≡N2 1.130(4), C1–C2–C11–C12 –178.4(3); **16**: C11=C12 1.337(5), C1–C2–C11–C12 –28.9(6).

the P-substituent (Figure 6). The latter species reveals a rotation of the vinyl group out of the C_5H_3 co-planarity by 30.3(4) °, probably due to a steric interaction of the lone pair of the phosphorus atom and the C12-bonded hydrogen atom. Figure 6 also gives an explanation for the unsuccessful formation of the (S_A)-epimer of **16**, since an inverted configuration at the BINOL backbone would cause steric interactions of the lower naphthyl substituent with the unsubstituted cyclopentadienyl.

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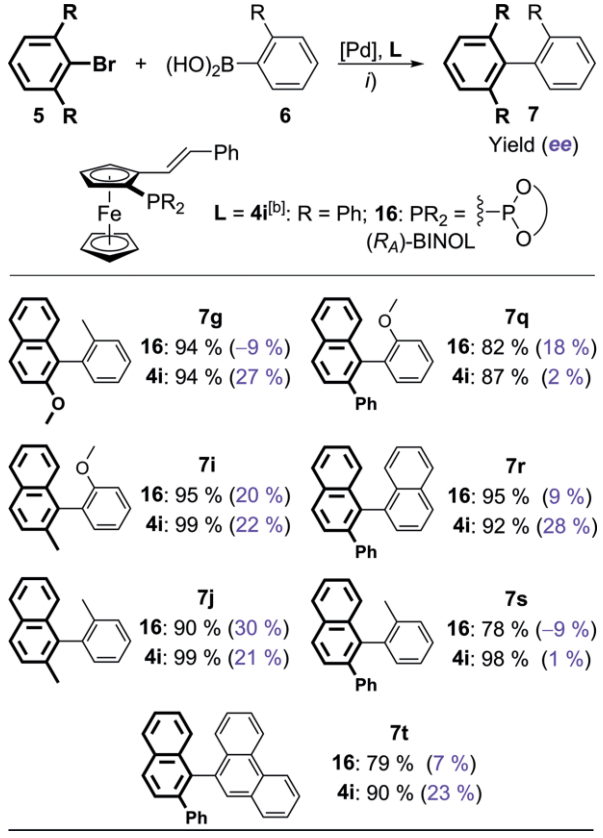
Phosphonite **16** was applied in Suzuki–Miyaura *C,C* cross-coupling reactions and compared with the results of **4i** under similar reaction conditions and catalyst loadings (Table 5). The *ee* of the obtained biaryls ranges between 9 and 30 %, whereas neither a trend of the substitution pattern of the aryl halide, nor the boronic acid seems to be obvious. A higher *ee* than for **4i** was observed for **7j**,**q**,**s**, whereby biaryls **7g**,**n**,**r**,**t** reveal an opposite behavior. Thus, a positive and negative interaction between BINOL and the planar-chiral ferrocenylvinyl functionality can be concluded, making it difficult to predict the influence of additional chirality within the catalytic cycle. Comparison of the area ratios of the obtained isomers (Table S3) of each biaryl, revealed an opposed relative configuration of the main isomer in case of **7g**,**o**, which is expressed by a negative *ee* value. With regard to **7g**, where a change of the *ee* from 27 to –9 % occurred, a superior influence of the BINOL moiety compared to the planar-chirality can be concluded.

Table 5. Comparison of the catalytic productivity (yield) and the enantiomeric excess (*ee*) between phosphine **4i** and phosphonite **16**.[a]



[a] All *ee* calculations refer to the area ratios of each biaryl using **4i**. An inverted stereoselectivity, caused by **16**, can therefore result in negative *ee* values; see Table S3. *i*) 1.0 mmol aryl bromide, 1.5 mmol boronic acid, 3.0 mmol K_3PO_4·H_2O, toluene, 0.25 mol-% [$Pd_2(dba)_3$], 1.0 mol-% **16**, 70 °C, 24 h. Isolated yields, average of two runs. [b] 0.1 mol-% [Pd], 0.2 mol-% **4i**.

The overall smaller *ee* of **7g** most probably results from a *mismatch* case of both configurations. However, since the synthesis of the (S_A)-epimer of **16** failed, the *match* case cannot be proven. The non-predictable and complex dependency of substrate and *ee* has also been observed for different ferrocene-based ligand systems, where a range between 3 % and 69 % occurred.[27]

Computational methods also revealed a contribution of all three steps of the catalytic cycle to the final *ee*, which corresponds with the results herein.[28]

Conclusion

The concept of "flexible steric bulk" was adopted in ferrocene chemistry by introducing sterically demanding silyl substituents at a hitherto *non*-substituted cyclopentadienyl in planar-chiral 2-phenylvinyl-1-diphenylphosphino ferrocenes. The C_5H_4-SiR_3 fragment can freely rotate around the C_5H_3–Fe–C_5H_4 axis and may therefore shield the Pd atom within the catalytic cycle, if required. This behavior increased the catalytic productivity for the synthesis of tri-*ortho*-substituted biaryls within Suzuki–Miyaura *C,C* cross-coupling reactions. By lowering the catalyst concentration to 0.025 mol-% still similar or higher yields than with 0.1 mol-% for the non-silylated derivative were observed, showing a slightly positive influence of the additional "flexible steric bulk". Furthermore, the effect of an electronic modification of the phosphine and the vinyl donor functionalities was investigated. The introduction of a substituent in *para* position of the phenylvinyl moiety did not show an effect on the catalytic productivity, whereby an electronic effect on the redox potential at the ferrocenyl backbone and hence the electronic properties of the vinyl group could be observed. However, an electronic modification at the phenylvinyl group does not affect the donor properties of the phosphine, confirmed by equal $^1J(^{31}P,^{77}Se)$ coupling constants of the respective selenophosphines. In contrast, modification of the phosphine fragment significantly affected the yield of the chosen biaryl. Therein, electron-withdrawing substituents increased the yield from 78 to 91 %, while changing from a PPh_2 to a P(*p*-CN-C_6H_4)$_2$ bearing derivative. Electron-donating cyclohexyl and sterically demanding *o*-tolyl phosphines reduced the yield to 22 and 14 %, respectively. This was in accordance with the $^1J(^{31}P,^{77}Se)$ coupling constants, revealing the lowest σ-donor ability for the P(*p*-CN-C_6H_4)$_2$ substituted ferrocene. By functionalization of the phosphine moiety a higher impact on the redox potential of the ferrocenyl backbone was achieved, compared to a phenylvinyl substitution. The use of a ferrocene, which contains phosphorus- and planar-chiral elements revealed a complex interaction between both motifs, whereby a positive and negative influence of the *ee*, compared to the PPh_2 derivative, was observed depending on the substitution pattern.

Experimental Section

General. All reactions were carried out under an atmosphere of argon by using standard Schlenk techniques. For column chromatography, either silica with a particle size of 40–60 μm [230–400 mesh (ASTM)] or alumina with a particle size of 90 μm was used.

Reagents. *t*BuLi (1.9 *M* in pentane), BuLi (2.5 *M* in hexane) and all other starting materials were obtained from commercial suppliers and used without further purification. 2-Formyl-1-diphenylphosphi-

noferrocene (*rac*)-**1**,[6,7] (*S*)-2-ferrocenyl-1,3-dioxane (*S*)-**10**,[29] 2-formyl-1-(tributyl-stannyl)ferrocene (S_p)-**13**,[24b] 2-phenylvinyl-1-(tributyl-stannyl)ferrocene (*rac*)-**14**[7] and vinylferrocenes **8a**,**b** and **9a**–**d**[7] were synthesized according to previously published procedures. Within the synthesis of phosphine sulfides **8a**-**S** and **8b**-**S** according to literature,[7] single crystals were obtained, whose results are presented in Figures S6–8.

Instruments. NMR spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for ^{1}H, 125.7 MHz for ^{13}C, 99.4 MHz for ^{29}Si, 202.5 MHz for ^{31}P and 186.6 MHz for ^{119}Sn nuclei). Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane (δ = 0.00 ppm) with the solvent as reference signal (^{1}H NMR: $CHCl_3$, δ = 7.26; C_6HD_5, δ = 7.16; $CHDCl_2$: δ = 5.32; ^{13}C{^{1}H} NMR: $CDCl_3$, δ = 77.16; CD_2Cl_2, δ = 54.00; C_6D_6, δ = 125.06; ^{29}Si{^{1}H} NMR: $SiMe_4$, δ = 0.00; ^{31}P{^{1}H} NMR: standard external rel. 85 % H_3PO_4, δ = 0.0; $P(OMe)_3$, δ = 139.0; ^{119}Sn{^{1}H} NMR: standard external $SnMe_4$, δ = 0.0) or by the ^{2}H solvent lock signal.[30] The melting points were determined using a Gallenkamp MFB 595 010 M melting point apparatus. Elemental analyses were measured with a Thermo FlashEA 1112 instrument. High-resolution mass spectra were recorded with a Bruker Daltonik micrOTOF-QII spectrometer.

Single crystal X-ray diffraction analysis

Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from diethyl ether/*n*-hexane mixtures at ambient temperature. Data were collected with an Oxford Gemini S diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) and a D8 Venture, using micro-focused Cu $K\alpha$ radiation (λ = 1.54184 Å). The structures were solved by direct methods and refined by full-matrix least- squares procedures on F^2.[31,32] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions.

Deposition Number(s) 1879366 (for **3a**), 1879367 (for **3b**), 1879368 (for **3e**), 1879369 (for **4a**), 1879370 (for **4b**), 1879371 (for **9e**), 1879372 (for **16**), 1879373 (for **8a**-**S**), 1879374 (for **8b**-**S**), 1879375 {for (**9a**-**S**)$_2$•2$CHCl_3$} contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

General procedure for 1′-directed lithiation of 2-(diphenylphosphino)formylferrocene (**1**).

N-Methylpiperazine (1.3 equiv.) suspended in anhydrous tetrahydrofuran (6 mL/mmol) was treated dropwise with *t*BuLi (1.1 equiv.) at ambient temperature. After 15 min of stirring at this temperature a suspension of 2-(diphenylphosphino)formylferrocene (**1**, 1.0 equiv.) in anhydrous tetrahydrofuran (10 mL/mmol) was added dropwise within 10 min and the reaction solution was stirred for 2 h. The reaction solution was cooled to 0 °C. *t*BuLi (1.3 equiv.) was added dropwise and stirring was continued for 1 h at this temperature. After cooling the reaction mixture to –78 °C the electrophile ($ClSiR_3$, 3 equiv.) was added dropwise over 10 min and after stirring for 30 min at –78 °C the reaction mixture was warmed to ambient temperature and stirred overnight at 25 °C. The products were purified by column chromatography (silica, 2.5 × 12 cm column size) using a 1:4 hexane/diethyl ether mixture (*v*/*v*).

Synthesis of 1′-trimethylsilyl-2-(diphenylphosphino)formylferrocene (3a). The title compound was synthesized according to the general procedure using $ClSiMe_3$ (413 mg, 3.8 mmol) as the electrophile. After evaporation of all volatiles, compound **3a** was obtained as an orange solid.

Yield: 287 mg (0.61 mmol, 49 % based on **1**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 66.39; H, 5.79; found C, 66.09; H, 5.83. Mp. 155 °C. ^{1}H NMR ($CDCl_3$, δ): 0.13 (s, 9H, CH_3), 3.85 (ddd, $^3J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 1.1, 1.3 Hz, 1H, C_5H_4), 4.05 (ddd, $^3J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.4 Hz, $^3J_{P,H}$ = 1.2 Hz, 1H, C_5H_3), 4.28 (ddd, $^3J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 1.1, 1.3 Hz, 1H, C_5H_4), 4.34 (ddd, $^3J_{H,H}$ = 2.4, 2.4 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.59 (ddd, $^3J_{H,H}$ = 2.4, 2.4 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.63 (dd, $^3J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 5.04 (ddd, $^3J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.4 Hz, $^4J_{P,H}$ = 1.1 Hz, 1H, C_5H_3), 7.13–7.18 (m, 2H, Ph), 7.23–7.27 (m, 3H, Ph), 7.39–7.45 (m, 3H, Ph), 7.54–7.60 (m, 2H, Ph), 10.19 (d, $^4J_{P,H}$ = 2.8 Hz, 1H, CHO). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): –0.4 (CH_3), 72.0 (d, $J_{P,C}$ = 2.0 Hz, C_5H_3), 74.1 (d, $J_{P,C}$ = 2.2 Hz, C_5H_4), 74.4 (C_5H_3), 74.9 (d, $J_{P,C}$ = 2.7 Hz, C_5H_4), 75.0 (C_5H_4), 75.3 ($^qC_5H_4$), 75.9 (C_5H_4), 76.3 (d, $J_{P,C)}$ = 4.4Hz, C_5H_3), 80.5 (d, $J_{P,C}$ = 17.2 Hz, $^qC_5H_3$), 83.3 (d, $J_{P,C}$ = 13.8 Hz, $^qC_5H_3$), 128.4 (Ph), 128.5 (d, $J_{P,C}$ = 6.8Hz, Ph), 128.6 (d, $J_{P,C}$ = 7.5Hz, Ph), 129.8 (Ph), 132.3 (d, $J_{P,C}$ = 18.6Hz, Ph), 135.3 (d, $J_{P,C}$ = 21.4Hz, Ph), 136.5 (d, $J_{P,C}$ = 10.5Hz, ^{q}Ph), 139.3 (d, $J_{P,C}$ = 10.3 Hz, ^{q}Ph), 193.4 (d, $^3J_{P,C}$ = 11.0 Hz, CHO). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –23.0 (s). HRMS: *m*/*z*: calcd. for $C_{26}H_{27}FeOPSi$: 470.0918, found 470.0926 $[M]^+$.

Crystal data: $C_{26}H_{27}FeOPSi$, M = 470.38 g mol^{-1}, crystal dimensions 0.40 × 0.20 × 0.04 mm, monoclinic, *C*2/*c*, λ = 0.71073 Å, a = 24.9239(15) Å, b = 8.6167(4) Å, c = 24.1441(15) Å, β = 112.926(7) °, V = 4775.6(5) Å^3, Z = 8, ρ_{calcd} = 1.308 Mg m^{-3}, μ = 0.764 mm^{-1}, T = 106(3) K, θ range 2.910–25.498°, 14852 reflections collected, 4427 independent reflections (R_{int} = 0.0380), R_1 = 0.0346, wR_2 = 0.0792 [$I > 2\sigma(I)$].

Synthesis of 1′-triethylsilyl-2-(diphenylphosphino)formylferrocene (3b). The title compound was synthesized according to the general procedure using $ClSiEt_3$ (573 mg, 3.8 mmol) as the electrophile. After evaporation of all volatiles **3b** was obtained as an orange solid.

Yield 341 mg (0.67 mmol, 53 % based on **1**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 67.97; H, 6.49; found C, 67.97; H, 6.68. Mp. 133 °C. ^{1}H NMR ($CDCl_3$, δ): 0.61 (q, $^3J_{H,H}$ = 8.0 Hz, 3H, CH_2), 0.62 (q, $^3J_{H,H}$ = 8.0 Hz, 3H, CH_2), 0.92 (t, $^3J_{H,H}$ = 8.0 Hz, 9H, CH_3), 3.82 (ddd, $^3J_{H,H}$ = 2.2 Hz, $^4J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 4.05 (ddd, $^3J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.3 Hz, $^3J_{P,H}$ = 1.3 Hz, 1H, C_5H_3), 4.26 (ddd, $^3J_{H,H}$ = 2.2 Hz, $^4J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 4.38 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_3), 4.59 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.64 (dd, $^3J_{H,H}$ = 2.6, 2.6 Hz, 1H, C_5H_3), 5.05 (ddd, $^3J_{H,H}$ = 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, $^4J_{P,H}$ = 1.1 Hz, 1H, C_5H_3), 7.12–7.19 (m, 2H, Ph), 7.21–7.28 (m, 3H, Ph), 7.37–7.45 (m, 3H, Ph), 7.53–7.60 (m, 2H, Ph), 10.20 (d, $^4J_{P,H}$ = 2.8 Hz, 1H, CHO). ^{13}C{^{1}H} NMR ($CDCl_3$, δ) 4.0 (CH_2), 7.3 (CH_3), 72.0 (d, $^3J_{P,C}$ = 2.2 Hz, C_5H_3), 73.0 ($^qC_5H_4$), 74.1 (d, $J_{P,C}$ = 2.1 Hz, C_5H_4), 74.6 (C_5H_3), 74.7 (d, $J_{P,C}$ = 2.3 Hz, C_5H_4), 75.6 (C_5H_4), 76.3 (C_5H_4), 76.4 (d, $^2J_{P,C}$ = 4.4 Hz, C_5H_3), 80.5 (d, $^1J_{P,C}$ = 17.2 Hz, $^qC_5H_3$), 83.2 (d, $^2J_{P,C}$ = 13.7 Hz, $^qC_5H_3$), 128.7 (Ph), 128.8 (d, $^3J_{P,C}$ = 6.4 Hz, Ph), 128.9 (d, $^3J_{P,C}$ = 7.7 Hz, Ph), 130.1 (Ph), 132.6 (d, $^2J_{P,C}$ = 18.8 Hz, Ph), 135.7 (d, $^2J_{P,C}$ = 21.7 Hz, Ph), 136.9 (d, $^1J_{P,C}$ = 10.8 Hz, ^{q}Ph), 139.8 (d, $^1J_{P,C}$ = 10.5 Hz, ^{q}Ph), 194.2 (d, $^3J_{P,C}$ = 12.0 Hz, CHO). ^{31}P{^{1}H} NMR ($CDCl_3$, δ) –24.1 (s). HRMS: *m*/*z*: calcd. for $C_{29}H_{33}FeOPSi$: 512.1388, found 512.1418 $[M]^+$.

Crystal data: $C_{29}H_{33}FeOPSi$, M = 512.46 g mol^{-1}, crystal dimensions 0.40 × 0.40 × 0.25 mm, triclinic, $P\bar{1}$, λ = 0.71073 Å, a = 8.5783(5) Å, b = 13.2205(12) Å, c = 13.2517(9) Å, α = 108.022(7) °, β = 101.602(5) °, γ = 108.279(6) °, V = 1280.91(18) Å^3, Z = 2, ρ_{calcd} = 1.329 Mg m^{-3}, μ = 0.718 mm^{-1}, T = 110.00(10) K, θ range 2.915–25.997°, 9656 reflections collected, 5005 independent reflections (R_{int} = 0.0268), R_1 = 0.0363, wR_2 = 0.0790 [$I > 2\sigma(I)$].

Synthesis of 1′-*tert*-butyldimethylsilyl-2-(diphenylphos-phino)-formylferrocene (3c). The title compound was synthesized accord-

ing to the general procedure using $ClSitBuMe_2$ (573 mg, 3.8 mmol) as the electrophile. After evaporation of all volatiles compound **3c** was obtained as an orange solid.

Yield 106 mg (0.21 mmol, 16 % based on **1**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 67.97; H, 6.49; found C, 68.14; H, 6.76. Mp. 126 °C. ^1H NMR ($CDCl_3$, δ): 0.03 (s, 3H, CH_3), 0.22 (s, 3H, CH_3), 0.74 (s, 9H, $C(CH_3)_3$), 3.82 (ddd, $^3J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 4.04 (ddd, $^3J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.3 Hz, $^3J_{P,H}$ = 1.3 Hz, 1H, C_5H_3), 4.26 (ddd, $^3J_{H,H}$ = 2.3 Hz, $^4J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 4.33 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.61 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.62 (dd, $^3J_{H,H}$ = 2.6, 2.6 Hz, 1H, C_5H_3), 5.03 (ddd, $^3J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.2 Hz, $^4J_{P,H}$ = 1.2 Hz, 1H, C_5H_3), 7.12–7.20 (m, 2H, Ph), 7.22–7.28 (m, 3H, Ph), 7.38–7.45 (m, 3H, Ph), 7.53–7.60 (m, 2H, Ph), 10.19 (d, $^4J_{P,H}$ = 2.8 Hz, 1H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): –6.3 (CH_3), –6.2 (CH_3), 16.7 ($^qC(CH_3)_3$), 26.0 ($C(CH_3)_3$), 72.1 (d, $^3J_{P,C}$ = 1.7 Hz, C_5H_4), 72.7 ($^qC_5H_4$), 74.2 (d, $J_{P,C}$ = 1.8 Hz, C_5H_4), 74.5 (C_5H_3), 75.0 (d, $J_{P,C}$ = 2.3 Hz, C_5H_4), 75.6 (C_5H_4), 76.4 (d, $^2J_{P,C}$ = 4.3 Hz, C_5H_3), 76.7 (C_5H_4), 80.5 (d, $^1J_{P,C}$ = 17.2 Hz, $^qC_5H_3$), 83.4 (d, $^2J_{P,C}$ = 14.0 Hz, $^qC_5H_3$), 128.7 (Ph), 128.8 (d, $^3J_{P,C}$ = 6.8 Hz, Ph), 128.9 (d, $^3J_{P,C}$ = 7.9 Hz, Ph), 130.1 (Ph), 132.7 (d, $^2J_{P,C}$ = 18.9 Hz, Ph), 135.7 (d, $^2J_{P,C}$ = 21.9 Hz, Ph), 136.9 (d, $^1J_{P,C}$ = 10.8 Hz, ^{q}Ph), 139.7 (d, $^1J_{P,C}$ = 10.7 Hz, ^{q}Ph), 194.1 (d, $^3J_{P,C}$ = 12.1 Hz, CHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –24.1 (s). HRMS: *m/z*: calcd. for $C_{29}H_{33}OFePSi$: 512.1388, found 512.1290 $[M]^+$.

Synthesis of 1′-triphenylsilyl-2-(diphenylphosphino)formylferrocene (3d). The title compound was synthesized according to the general procedure using $ClSiPh_3$ (1.12 g, 3.8 mmol) as the electrophile. After evaporation of all volatiles in vacuo **3d** was obtained as an orange solid.

Yield: 160 mg (0.24 mmol, 20 % based on **1**). Mp. 180 °C (decomp.). ^1H NMR ($CDCl_3$, δ): 3.73–3.76 (m, 1H, C_5H_3), 3.89–3.92 (m, 1H, C_5H_4), 4.07 (dd, $^3J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 4.43–4.46 (m, 1H, C_5H_4), 4.53–4.57 (m, 1H, C_5H_4), 4.68–4.72 (m, 1H, C_5H_4), 4.79–4.83 (m, 1H, C_5H_3), 7.08–7.14 (m, 2H, PPh), 7.19–7.25 (m, 3H, PPh), 7.35 (t, $^3J_{H,H}$ = 7.3Hz, 6H, SiPh), 7.32–7.53 (m, 6H, PPh/SiPh), 7.32–7.53 (m, 6H, SiPh), 7.32–7.53 (m, 2H, PPh), 10.04 (d, $^4J_{P,H}$ = 2.6 Hz, 1H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 69.4 ($^qC_5H_4$), 72.8 (d, $J_{P,C}$ = 2.1 Hz, C_5H_3), 75.6 (d, $J_{P,C}$ = 1.5 Hz, C_5H_4), 75.7 (d, $J_{P,C}$ = 3.7 Hz, C_5H_4), 75.9 (C_5H_3), 77.0 (C_5H_4), 77.1 (d, J(P,C) = 4.4 Hz, C_5H_3), 77.7 (C_5H_4), 80.7 (d, J(P,C) = 17.3 Hz, $^qC_5H_3$), 83.3 (d, J(P,C) = 13.7 Hz, $^qC_5H_3$), 128.4 (SiPh), 128.7 (d, J(P,C) = 6.1 Hz, PPh), 128.8 (PPh), 128.9 (d, $J_{P,C}$ = 7.7 Hz, PPh), 130.0 (PPh), 130.2 (SiPh), 132.7 (d, $J_{P,C}$ = 18.5 Hz, PPh), 135.1 (^{q}SiPh), 135.5 (d, $J_{P,C}$ = 21.5 Hz, PPh), 136.3 (SiPh), 136.9 (d, $J_{P,C}$ = 11.2 Hz, ^{q}PPh), 139.4 (d, $J_{P,C}$ = 10.3 Hz, ^{q}PPh), 194.4 (d, $J_{P,C}$ = 9.8 Hz, CHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –24.0 (s). HRMS: *m/z*: calcd. for $C_{41}H_{33}OFePSi$: 656.1388, found 656.1341 $[M]^+$.

Synthesis of 1′-triisopropylsilyl-2-(diphenylphosphino)formylferrocene (3e). The title compound was synthesized according to the general procedure using $ClSiiPr_3$ (733 mg, 3.8 mmol) as the electrophile. After evaporation of all volatiles compound **3e** was obtained as an orange solid.

Yield 123 mg (0.33 mmol, 18 % based on **1**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 69.31; H, 7.09; found C, 69.78; H, 7.55. Mp. 139 °C; ^1H NMR ($CDCl_3$, δ): 1.00 (d, $^3J_{H,H}$ = 7.2 Hz, 9H, CH_3), 1.04 (d, $^3J_{H,H}$ = 7.1 Hz, 9H, CH_3), 1.07–1.17 (m, 3H, CH), 3.80 (ddd, $^3J_{H,H}$ = 2.2 Hz, $^4J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 4.05 (ddd, $^3J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 1.1 Hz, $^3J_{P,H}$ = 1.1 Hz, 1H, C_5H_3), 4.32 (ddd, $^3J_{H,H}$ = 2.2 Hz, $^4J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 4.53 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.62 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, C_5H_4), 4.66 (dd, $^3J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 5.06 (ddd, $^3J_{H,H}$ = 2.3 Hz, $^4J_{H,H}$ = 1.2 Hz, $^4J_{P,H}$ = 1.2 Hz, 1H, C_5H_3), 7.14–7.21 (m, 2H, Ph), 7.23–7.29 (m, 3H, Ph), 7.37–7.46 (m, 3H, Ph), 7.54–7.62 (m, 2H, Ph), 10.23 (d, $^4J_{P,H}$ = 2.7 Hz, 1H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 11.4 (CH), 18.5 (CH_3), 18.6 (CH_3), 71.3 ($^qC_5H_4$), 72.3 (d, $^3J_{P,C}$ = 1.8 Hz, C_5H_3), 74.4 (d, $J_{P,C}$ = 4.0 Hz, C_5H_4), 74.5 (C_5H_4), 75.6 (C_5H_3), 76.7 (C_5H_4), 76.8 (C_5H_4), 77.0 (d, $^2J_{P,C}$ = 4.4 Hz, C_5H_3), 80.4 (d, $^1J_{P,C}$ = 17.1 Hz, $^qC_5H_3$), 83.0 (d, $^2J_{P,C}$ = 13.7 Hz, $^qC_5H_3$), 128.7 (Ph), 128.8 (d, $^3J_{P,C}$ = 6.7 Hz, Ph), 128.9 (d, $^3J_{P,C}$ = 7.7 Hz, Ph), 130.1 (Ph), 132.7 (d, $^2J_{P,C}$ = 18.6 Hz, Ph), 135.6 (d, $^2J_{P,C}$ = 21.2 Hz, Ph), 136.9 (d, $^1J_{P,C}$ = 10.8 Hz, ^{q}Ph), 139.6 (d, $^1J_{P,C}$ = 10.3 Hz, ^{q}Ph), 194.4 (d, $^3J_{P,C}$ = 10.4 Hz, CHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –24.1 (s). HRMS: *m/z*: calcd. for $C_{32}H_{39}FeOPSi$: 554.1857, found 554.1912 $[M]^+$.

Crystal data: $C_{32}H_{39}FeO_{1.09}PSi$, M = 555.91 g mol^{-1}, crystal dimensions 0.40 × 0.40 × 0.40 mm, triclinic, $P\bar{1}$, λ = 0.71073 Å, a = 9.5926(5) Å, b = 12.2607(5) Å, c = 13.3543(6) Å, α = 71.229(4) °, β = 74.424(4) °, γ = 76.127(4) °, V = 1412.08(12) Å^3, Z = 2, ρ_{calcd} = 1.307 Mg m^{-3}, μ = 0.657 mm^{-1}, T = 110.00(10) K, θ range 3.041–26.000°, 19490 reflections collected, 5525 independent reflections (R_{int} = 0.0335), R_1 = 0.0321, wR_2 = 0.0777 [$I > 2\sigma(I)$].

Synthesis of 1′-*tert*-butyldiphenylsilyl-2-(diphenylphos-phino)-formylferrocene (3f). The title compound was synthesized according to the general procedure using $ClSitBuPh_2$ (1.04 g, 3.8 mmol) as the electrophile. After evaporation of all volatiles compound **3f** was obtained as an orange solid to yield 59.6 mg (0.19 mmol, 8 % based on **1**) Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 73.58; H, 5.86; found C, 73.03; H, 6.04 (best match). Mp. 153 °C. ^1H NMR ($CDCl_3$, δ): 1.01 (s, 9H, CH_3), 3.67 (ddd, $^3J_{H,H}$ = 2.6 Hz, $^4J_{H,H}$ = 1.3 Hz, $^3J_{P,H}$ = 1.3 Hz, 1H, C_5H_3), 3.77 (ddd, $^3J_{H,H}$ = 2.3 Hz, $^4J_{H,H}$ = 1.0, 1.0 Hz, 1H, C_5H_4), 4.07 (dd, $^3J_{H,H}$= 2.6, 2.6 Hz, 1H, C_5H_3), 4.42 (ddd, $^3J_{H,H}$ = 2.1 Hz, $^4J_{H,H}$ = 0.9, 0.9 Hz, 1H, C_5H_4), 4.51 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, C_5H_4), 4.67 (ddd, $^3J_{H,H}$ = 2.4, 2.4 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.74 (ddd, $^3J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.2 Hz, $^4J_{P,H}$ = 1.2 Hz, 1H, C_5H_3), 7.06–7.12 (m, 2H, PPh), 7.17–7.24 (m, 3H, PPh), 7.27–7.31 (m, 2H, SiPh), 7.31–7.44 (m, 7H, PPh/SiPh), 7.45–7.49 (m, 2H, PPh), 7.50–7.54 (m, 2H, SiPh), 7.65–7.68 (m, 2H, SiPh), 10.00 (d, $^4J_{P,H}$ = 2.6 Hz, 1H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 18.3 ($^qC(CH_3)_3$), 27.9 (CH_3), 69.7 ($^qC_5H_4$), 72.9 (d, $^3J_{P,C}$ = 2.2 Hz, C_5H_3), 75.3 (d, $J_{P,C}$ = 3.7 Hz, C_5H_4), 75.4 (d, $J_{P,C}$ = 2.2 Hz, C_5H_4), 76.1 (C_5H_3), 77.1 (d, $^2J_{P,C}$ = 4.4 Hz, C_5H_3), 77.4 (C_5H_4), 77.5 (C_5H_4), 80.4 (d, $^1J_{P,C}$ = 17.3 Hz, $^qC_5H_3$), 83.2 (d, $^2J_{P,C}$ = 13.6 Hz, $^qC_5H_3$), 127.9 (SiPh), 128.1 (SiPh), 128.6 (PPh), 128.7 (d, $^3J_{P,C}$ = 5.9 Hz, PPh), 128.8 (d, $^3J_{P,C}$ = 7.9 Hz, PPh), 129.8 (PPh), 129.9 (SiPh), 130.0 (SiPh), 132.6 (d, $^2J_{P,C}$ = 18.9 Hz, PPh), 135.2 (^{q}SiPh), 135.3 (^{q}SiPh), 135.4 (d, $^2J_{P,C}$ = 21.2 Hz, PPh), 136.6 (SiPh), 136.7 (SiPh), 137.0 (d, $^1J_{P,C}$ = 10.9 Hz, ^{q}PPh), 139.5 (d, $^1J_{P,C}$ = 10.3 Hz, ^{q}PPh), 194.4 (d, $^3J_{P,C}$ = 9.9 Hz, CHO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –23.8 (s). HRMS: *m/z*: calcd. for $C_{39}H_{37}OFePSi$: 636.1701, found 636.1677 $[M]^+$.

Synthesis of 1′-tri-*n*-butylstannyl-2-(diphenylphosphino)formylferrocene (3g). The title compound was synthesized according to the general procedure using $ClSnBu_3$ (1.24 g, 3.8 mmol) as the electrophile. After evaporation of all volatiles in vacuo compound **3g** was obtained as an orange solid.

Yield 418 mg (0.61 mmol, 48 % based on **1**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 61.17; H, 6.60; found C, 61.31; H, 6.72. Mp. 67 °C. ^1H NMR ($CDCl_3$, δ): 0.89 (t, $^3J_{H,H}$ = 7.3 Hz, 9H, CH_3), 0.86 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, $SnCH_2$), 0.87 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, $SnCH_2$), 1.23 (sext, $^3J_{H,H}$ = 7.3 Hz, 6H, CH_2CH_3), 1.44–1.52 (m, 6H, $CH_2CH_2CH_3$), 3.71–3.76 (m, 1H, C_5H_4), 4.02 (ddd, $^3J_{H,H}$ = 2.4 Hz, $^4J_{H,H}$ = 1.1 Hz, $^3J_{P,H}$ = 1.2 Hz, 1H, C_5H_3), 4.18–4.23 (m, 1H, C_5H_4), 4.42 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 0.9 Hz, 1H, C_5H_4), 4.58 (dd, $^3J_{H,H}$ = 2.6, 2.6 Hz, 1H, C_5H_3), 4.60 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 0.9 Hz, 1H, C_5H_4), 4.99–5.03 (m, 1H, C_5H_3), 7.13–7.19 (m, 2H, Ph), 7.23–7.27 (m, 3H, Ph), 7.38–7.45 (m, 3H, Ph), 7.53–7.59 (m, 2H, Ph), 10.20 (d, $^4J_{P,H}$ = 2.8 Hz, 1H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 9.9 ($^1J_{117Sn,13C}$ = 334.5 Hz,

$^{1}J_{119Sn,13C}$ = 349.9 Hz, $SnCH_2$), 13.4 (CH_3), 27.1 ($^{3}J_{119Sn,13C}$ = 57.5 Hz, CH_2CH_3), 28.9 ($^{2}J_{119Sn,13C}$ = 20.0 Hz, $CH_2CH_2CH_3$), 71.6 (d,$^{3}J_{P,C}$ = 1.7 Hz, C_5H_3), 72.0 ($^{1}J_{117Sn,13C}$ = 344.3 Hz, $^{1}J_{119Sn,13C}$ = 360.7 Hz, $^{q}C_5H_4$), 74.2 (d, $J_{P,C}$ = 2.6 Hz, $^{3}J_{119Sn,13C}$ = 30.9 Hz, C_5H_4), 74.3 (C_5H_3), 74.6 (d, $J_{P,C}$ = 2.0 Hz, $^{3}J_{119Sn,13C}$ = 30.9 Hz, C_5H_4), 76.2 (d, $^{2}J_{P,C}$ = 4.4 Hz, C_5H_3), 76.8 ($^{2}J_{119Sn,13C}$ = 37.6 Hz, C_5H_4), 77.3 ($^{2}J_{119Sn,13C}$ = 36.8 Hz, C_5H_4), 80.3 (d, $^{1}J_{P,C}$ = 16.6 Hz, $^{q}C_5H_3$), 83.3 (d, $^{2}J_{P,C}$ = 13.8 Hz, $^{q}C_5H_3$), 128.7 (Ph), 128.8 (d, $^{3}J_{P,C}$ = 6.3 Hz, Ph), 128.9 (d, $^{3}J_{P,C}$ = 8.1 Hz, Ph), 130.0 (Ph), 132.7 (d, $^{2}J_{P,C}$ = 18.7 Hz, Ph), 135.6 (d, $^{2}J_{P,C}$ = 21.2 Hz, Ph), 137.0 (d, $^{1}J_{P,C}$ = 10.7 Hz, ^{q}Ph), 139.8 (d, $^{1}J_{P,C}$ = 10.8 Hz, ^{q}Ph), 194.2 (d, $^{3}J_{P,C}$ = 10.6 Hz, CHO). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): –23.9 (s). HRMS: *m/z*: calcd. for $C_{35}H_{45}OFePSn$: 688.1579, found 688.1634 $[M]^+$.

General procedure for the Horner–Wadsworth-Emmons reaction (HWE) of formylferrocenes **3a**–**h** and diethyl benzylphosphonates to **4a**–**h**.

According to a reaction procedure published previously,[7] diethyl benzylphosphonate (3 equiv.) was dissolved in anhydrous tetrahydrofuran (4 mL/mmol) and dropwise treated with BuLi (2.0 equiv.) at –78 °C within 10 min. Stirring at this temperature was continued for 30 min. Afterwards, the respective formylferrocenes **3a**–**h** (1.0 equiv.) dissolved in anhydrous tetrahydrofuran (10 mL/mmol) were slowly added to the cooled reaction mixture over 3 min, which was afterwards warmed to ambient temperature. The reaction mixture was stirred for 90 min at 25 °C and for 12 h at 60 °C followed by the addition of 10 mL of water. Stirring was continued for additional 15 min. The organic solvent was removed under reduced pressure. The residual mixture was extracted trice with 20 mL of dichloromethane each and the combined organic phases were washed with 30 mL of brine thrice. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified via column chromatography (silica, 2.5 × 12 cm column size) using a 1:9 hexane/diethyl ether mixture (*v*:*v*) as the eluent.

1′-Trimethylsilyl-1-(2-*(E)*-phenylvinyl)-2-(diphenylphosphino)-ferrocene (4a). Compound **4a** was synthesized according to the general procedure using diethyl benzylphosphonate (0.58 g, 2.6 mmol) and **3a** (0.40 g, 0.85 mmol). After evaporation of all volatiles, **4a** was obtained as a dark orange solid.

Yield 395 mg (0.73 mmol, 85 % based on **3a**) Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 72.79; H, 6.11; found C, 73.24; H, 6.61. Mp. 124 °C. ^{1}H NMR ($CDCl_3$, δ): 0.12 (s, 9H, CH_3), 3.71–3.74 (m, 1H, C_5H_4), 3.83–3.86 (m, 1H, C_5H_3), 4.07–4.10 (m, 1H, C_5H_4), 4.20 (ddd, $^{3}J_{H,H}$ = 3.2, 3.2 Hz, $^{4}J_{H,H}$ = 1.6 Hz, 1H, C_5H_4), 4.35 (ddd, $^{3}J_{H,H}$ = 2.2, 2.2 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.38 (dd, $^{3}J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 4.82–4.85 (m, 1H, C_5H_3), 6.76 (d, $^{3}J_{H,H}$ = 16.1 Hz, 1H, *CH*Ph), 7.13–7.25 (m, 7H, *CH*CH*Ph*, PPh), 7.29 (t, $J_{H,H}$ = 7.6 Hz, 2H, CH*Ph*), 7.39 (d, $J_{H,H}$ = 7.4 Hz, 2H, CH*Ph*), 7.41–7.44 (m, 3H, PPh), 7.58–7.65 (m, 2H, PPh). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): –0.7 (CH_3), 68.0 (d, $^{3}J_{P,C}$ = 3.3 Hz, C_5H_3), 71.0 (C_5H_3), 72.4 (d, $^{2}J_{P,C}$ = 3.5 Hz, C_5H_3), 73.3 (d, $J_{P,C}$ = 1.6 Hz, C_5H_4), 73.4 ($^{q}C_5H_4$), 73.6 (C_5H_4), 75.3 (d, $J_{P,C}$ = 1.8 Hz, C_5H_4), 76.1 (d, $^{1}J_{P,C}$ = 9.0 Hz, $^{q}C_5H_3$), 76.2 (C_5H_4), 88.8 (d, $^{2}J_{P,C}$ = 20.9 Hz, $^{q}C_5H_3$), 125.8 (d, $^{3}J_{P,C}$ = 12.0 Hz, *C*HCHPh), 126.5 (CH*Ph*), 127.3 (CH*Ph*), 127.7 (d, $^{4}J_{P,C}$ = 1.3 Hz, CHCHPh), 128.2 (PPh), 128.6 (d, $^{3}J_{P,C}$ = 5.6 Hz, PPh), 128.7 (d, $^{3}J_{P,C}$ = 7.8 Hz, PPh), 129.0 (CH*Ph*), 129.8 (PPh), 132.5 (d, $^{2}J_{P,C}$ = 17.8 Hz, PPh), 135.9 (d, $^{2}J_{P,C}$ = 21.5 Hz, PPh), 137.7 (d, $^{1}J_{P,C}$ = 8.4 Hz, ^{q}PPh), 138.3 (^{q}CH*Ph*), 140.5 (d, $^{1}J_{P,C}$ = 10.4 Hz, ^{q}PPh). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): –23.3 (s). HRMS: *m/z*: calcd. for $C_{33}H_{33}FePSi$: 544.1439, found 544.1417 $[M]^+$.

Crystal data: $C_{33}H_{33}FePSi$, M = 544.50 g mol^{-1}, crystal dimensions 0.35 × 0.12 × 0.03 mm, monoclinic, $P2_1/c$, λ = 0.71073 Å, a = 9.3096(3) Å, b = 32.5093(11) Å, c = 9.3297(3) Å, β = 90.464(2) °, V = 2823.53(16) Å^3, Z = 4, ρ_{calcd} = 1.281 Mg m^{-3}, μ = 0.653 mm^{-1}, T = 107(1) K, θ range 3.142–25.999°, 30674 reflections collected, 5539 independent reflections (R_{int} = 0.0390), R_1 = 0.0356, wR_2 = 0.0778 [$I > 2\sigma(I)$].

1′-Triethylsilyl-1-(2-*(E)*-phenylvinyl)-2-(diphenylphosphino)ferrocene (4b). Compound **4b** was synthesized according to the general procedure using diethyl benzylphosphonate (0.83 g, 3.6 mmol) and **3b** (0.62 g, 1.21 mmol). After evaporation of all volatiles in vacuo **4b** was obtained as a dark orange solid.

Yield 587 mg (1.06 mmol, 86 % based on **3b**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 73.71; H, 6.70; found C, 73.53; H, 6.73. Mp. 72 °C. ^{1}H NMR ($CDCl_3$, δ): 0.61 (q, $^{3}J_{H,H}$ = 8.0 Hz, 3H, CH_2), 0.62 (q, $^{3}J_{H,H}$ = 8.0 Hz, 3H, CH_2), 0.92 (t, $^{3}J_{H,H}$ = 8.0 Hz, 9H, CH_3), 3.71 (ddd, $^{3}J_{H,H}$ = 2.2 Hz, $^{4}J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 3.84–3.86 (m, 1H, C_5H_3), 4.09 (ddd, $^{3}J_{H,H}$ = 2.2 Hz, $^{4}J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 4.24 (ddd, $^{3}J_{H,H}$ = 2.4, 2.4 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.33 (ddd, $^{3}J_{H,H}$ = 2.3, 2.3 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.40 (dd, $^{3}J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 4.82–4.85 (m, 1H, C_5H_3), 6.77 (d, $^{3}J_{H,H}$ = 16.1 Hz, 1H, *CH*Ph), 7.13–7.25 (m, 7H, PPh, *CH*CH*Ph*), 7.29 (t, $J_{H,H}$ = 7.6 Hz, 2H, CH*Ph*), 7.39 (d, $J_{H,H}$ = 7.3 Hz, 2H, CH*Ph*), 7.41–7.45 (m, 3H, PPh), 7.59–7.65 (m, 2H, PPh). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 4.2 (CH_2), 7.4 (CH_3), 68.0 (d, $^{3}J_{P,C}$ = 3.0 Hz, C_5H_3), 71.0 ($^{q}C_5H_4$), 71.2 (C_5H_3), 72.5 (d, $^{2}J_{P,C}$ = 3.5 Hz, C_5H_3), 73.2 (d, $J_{P,C}$ = 1.7 Hz, C_5H_4), 74.3 (C_5H_4), 75.3 (d, $J_{P,C}$ = 1.5 Hz, C_5H_4), 76.0 (d, $^{1}J_{P,C}$ = 9.0 Hz, $^{q}C_5H_3$), 76.5 (C_5H_4), 88.7 (d, $^{2}J_{P,C}$ = 21.0 Hz, $^{q}C_5H_3$), 125.8 (d, $^{3}J_{P,C}$ = 12.2 Hz, *C*HCHPh), 126.5 (CH*Ph*), 127.3 (CH*Ph*), 127.7 (d, $^{4}J_{P,C}$ = 1.3 Hz, *C*HPh), 128.2 (PPh), 128.6 (d, $^{3}J_{P,C}$ = 5.6 Hz, PPh), 128.7 (d, $^{3}J_{P,C}$ = 8.0 Hz, PPh), 129.0 (CH*Ph*), 129.8 (PPh), 132.5 (d, $^{2}J_{P,C}$ = 17.4 Hz, PPh), 135.9 (d, $^{2}J_{P,C}$ = 21.5 Hz, PPh), 137.7 (d, $^{1}J_{P,C}$ = 8.4 Hz, ^{q}PPh), 138.3 (^{q}CH*Ph*), 140.5 (d, $^{1}J_{P,C}$ = 10.3 Hz, ^{q}PPh). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): –23.2 (s). HRMS: *m/z*: calcd. for $C_{36}H_{39}FePSi$: 586.1908, found 586.1883 $[M]^+$.

Crystal data: $C_{36}H_{39}FePSi$, M = 586.58 g mol^{-1}, crystal dimensions 0.38 × 0.38 × 0.12 mm, triclinic, $P\bar{1}$, λ = 0.71073 Å, a = 8.7195(4) Å, b = 12.2585(6) Å, c = 15.5536(6) Å, α = 110.738(4) °, β = 91.874(3) °, γ = 95.725(4) °, V = 1542.88(13) Å^3, Z = 2, ρ_{calcd} = 1.263 Mg m^{-3}, μ = 0.603 mm^{-1}, T = 110.00(10) K, θ range 2.896–26.000°, 22105 reflections collected, 6043 independent reflections (R_{int} = 0.0301), R_1 = 0.0302, wR_2 = 0.0753 [$I > 2\sigma(I)$].

1′-*tert*-Butyldimethylsilyl-1-(2-*(E)*-phenylvinyl)-2-(diphenylphosphino)ferrocene (4c). Compound **4c** was synthesized according to the general procedure using diethyl benzylphosphonate (0.14 g, 0.61 mmol) and **3c** (0.11 g, 0.20 mmol). After evaporation of all volatiles **4c** was obtained as a dark orange oil.

Yield 70 mg (0.12 mmol, 58 % based on **3c**). ^{1}H NMR ($CDCl_3$, δ): 0.04 (s, 3H, $SiCH_3$), 0.23 (s, 3H, $SiCH_3$), 0.74 (s, 9H, $C(CH_3)_3$), 3.70 (ddd, $^{3}J_{H,H}$ = 2.3 Hz, $^{4}J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 3.83–3.86 (m, 1H, C_5H_3), 4.05–4.07 (m, 1H, C_5H_4), 4.19 (ddd, $^{3}J_{H,H}$ = 2.2, 2.2 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.34–4.37 (m, 1H, C_5H_4), 4.37 (dd, $^{3}J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 4.79–4.84 (m, 1H, C_5H_3), 6.77 (d, $^{3}J_{H,H}$ = 16.1 Hz, 1H, *CH*Ph), 7.14–7.25 (m, 7H, PPh, *CH*CH*Ph*), 7.29 (t, $J_{H,H}$ = 7.6 Hz, 2H, CH*Ph*), 7.37–7.45 (m, 5H, PPh, CH*Ph*), 7.59–7.66 (m, 2H, PPh). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): –6.1 ($SiCH_3$), –6.2 ($SiCH_3$), 16.7 (^{q}SiC), 26.1 ($C(CH_3)_3$), 68.1 (d, $^{3}J_{P,C}$ = 3.0 Hz, C_5H_3), 70.8 ($^{q}C_5H_4$), 71.1 (C_5H_3), 72.5 (d, $^{2}J_{P,C}$ = 3.2 Hz, C_5H_3), 73.2 (d, $J_{P,C}$ = 1.6 Hz, C_5H_4), 74.3 (C_5H_4), 75.3 (d, $J_{P,C}$ = 1.8 Hz, C_5H_4), 76.1 (d, $^{1}J_{P,C}$ = 9.1 Hz, $^{q}C_5H_3$), 77.1 (C_5H_4), 88.7 (d, $^{2}J_{P,C}$ = 21.0 Hz, $^{q}C_5H_3$), 125.9 (d, $^{3}J_{P,C}$ = 12.4 Hz, *C*HCHPh), 126.5 (CH*Ph*), 127.3 (CH*Ph*), 127.7 (d, $^{4}J_{P,C}$ = 1.2 Hz, *C*HPh), 128.2 (PPh), 128.6 (d, $^{3}J_{P,C}$ = 5.9 Hz, PPh), 128.7 (d, $^{3}J_{P,C}$ = 8.0 Hz, PPh), 129.0 (CH*Ph*), 129.8 (PPh), 132.5 (d, $^{2}J_{P,C}$ = 17.4 Hz, PPh), 135.9 (d, $^{2}J_{P,C}$ = 21.5 Hz, PPh), 137.7 (d, $^{1}J_{P,C}$ = 9.0 Hz, ^{q}PPh), 138.3 (^{q}CH*Ph*), 140.5 (d, ^{1}J(P,C) = 10.3 Hz, ^{q}PPh). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): –23.2 (s). HRMS: *m/z*: calcd. for $C_{36}H_{39}FePSi$: 586.1908, found 586.1904 $[M]^+$.

1′-Triphenylsilyl-1-(2-*(E)*-phenylvinyl)-2-(diphenyl-phosphino)-ferrocene (4d). Compound **4d** was synthesized according to the general procedure using diethyl benzylphosphonate (0.11 g, 0.47 mmol) and **3d** (0.10 g, 0.16 mmol). After evaporation of all volatiles **4d** was obtained as a dark orange solid.

Yield 94 mg (0.13 mmol, 82 % based on **3d**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 78.90; H, 5.38; found C, 78.58; H, 5.61. Mp. 93 °C. ^{1}H NMR ($CDCl_3$, δ): 3.58–3.61 (m, 1H, C_5H_3), 3.76 (ddd, $^3J_{H,H}$ = 2.1 Hz, $^4J_{H,H}$ = 1.0, 1.0 Hz, 1H, C_5H_4), 3.88 (dd, $^3J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 4.29 (ddd, $^3J_{H,H}$ = 2.3 Hz, $^4J_{H,H}$ = 1.1, 1.1 Hz, 1H, C_5H_4), 4.32 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.45 (ddd, $^3J_{H,H}$ = 2.4, 2.4 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.49–4.52 (m, 1H, C_5H_4), 6.63 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, C*H*Ph), 7.07–7.13 (m, 3H, PPh, C*H*CHPh), 7.16–7.23 (m, 4H, PPh, Ch*Ph*), 7.29 (t, $J_{H,H}$ = 7.4 Hz, 8H, CH*Ph*, SiPh), 7.35–7.43 (m, 8H, PPh, CH*Ph*, SiPh), 7.47–7.51 (m, 6H, SiPh), 7.53–7.58 (m, 2H, PPh). ^{13}C{^{1}H} NMR ($CDCl_3$, δ):= 67.4 ($^qC_5H_4$), 68.7 (d, $^3J_{P,C}$ = 3.2 Hz, C_5H_3), 72.3 (C_5H_3), 73.2 (d, $^2J_{P,C}$ = 3.4 Hz, C_5H_3), 74.4 (d, $J_{P,C}$ = 2.3 Hz, C_5H_4), 75.5 (C_5H_4), 76.3 (d, $^1J_{P,C}$ = 9.1 Hz, $^qC_5H_3$), 76.5 (d, $J_{P,C}$ = 1.6 Hz, C_5H_4), 78.0 (C_5H_4), 89.2 (d, $^2J_{P,C}$ = 21.0 Hz, $^qC_5H_3$), 125.4 (d, $^3J_{P,C}$ = 11.6 Hz, *C*HCHPh), 126.6 (CH*Ph*), 127.4 (CH*Ph*), 128.1 (*C*HPh, SiPh), 128.2 (PPh), 128.6 (d, $^3J_{P,C}$ = 5.7 Hz, PPh), 128.7 (d, $^3J_{P,C}$ = 8.0 Hz, PPh), 129.0 (CH*Ph*), 129.8 (PPh), 129.9 (SiPh), 132.5 (d, $^2J_{P,C}$ = 17.4 Hz, PPh), 135.8 (d, $^2J_{P,C}$ = 21.3 Hz, PPh), 135.9 (^{q}SiPh), 136.4 (SiPh), 137.6 (d, $^1J_{P,C}$ = 8.7 Hz, ^{q}PPh), 138.2 (^{q}CH*Ph*), 140.2 (d, $^1J_{P,C}$ = 10.1 Hz, ^{q}PPh). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –23.5 (s). HRMS: *m/z*: calcd. for $C_{48}H_{39}FePSi$: 730.1908, found 730.1835 $[M]^+$.

1′-Triisopropylsilyl-1-(2-*(E)*-phenylvinyl)-2-(diphenylphosphino)ferrocene (4e). Compound **4e** was synthesized according to the general procedure using diethyl benzylphosphonate (0.23 g, 0.99 mmol) and **3e** (0.21 g, 0.33 mmol). After evaporation of all volatiles **4e** was obtained as a dark orange solid.

Yield 198 mg (0.31 mmol, 94 % based on **3e**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 74.51; H, 7.21; found C, 74.32; H, 7.34. Mp. 60 °C. ^{1}H NMR ($CDCl_3$, δ): 1.00 (d, $^3J_{H,H}$ = 7.2 Hz, 9H, CH_3), 1.03 (d, $^3J_{H,H}$ = 7.2 Hz, 9H, CH_3), 1.06–1.16 (m, 3H, CH), 3.67 (ddd, $^3J_{H,H}$ = 2.2 Hz, $^4J_{H,H}$ = 1.0, 1.0 Hz, 1H, C_5H_4), 3.84 (ddd, $^3J_{H,H}$ = 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, $^3J_{P,H}$ = 1.1 Hz, 1H, C_5H_3), 4.19 (ddd, $^3J_{H,H}$ = 2.2 Hz, $^4J_{H,H}$ = 1.0, 1.0 Hz, 1H, C_5H_4), 4.31 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.36 (ddd, $^3J_{H,H}$ = 2.3, 2.3 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_5H_4), 4.41 (dd, $^3J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 4.83–4.86 (m, 1H, C_5H_3), 6.75 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, C*H*Ph), 7.13–7.24 (m, 7H, PPh, *CH*CH*Ph*), 7.29 (t, $^3J_{H,H}$ = 7.6 Hz, 2H, CH*Ph*), 7.36–7.44 (m, 5H, PPh, CH*Ph*), 7.58–7.65 (m, 2H, PPh). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 11.6 (CH), 18.6 (CH_3), 18.7 (CH_3), 68.2 (d, $^3J_{P,C}$ = 3.0 Hz, C_5H_3), 69.2 ($^qC_5H_4$), 72.2 (C_5H_3), 73.1 (d, $^2J_{P,C}$= 3.6 Hz, C_5H_3), 73.2 (d, $J_{P,C}$ = 3.0 Hz, C_5H_4), 75.3 (C_5H_4), 75.8 (d, $J_{P,C}$ = 1.2 Hz, C_5H_4), 75.9 (d, $^1J_{P,C}$ = 9.0 Hz, $^qC_5H_3$), 76.9 (C_5H_4), 88.7 (d, $^2J_{P,C}$ = 21.0 Hz, $^qC_5H_3$), 125.8 (d, $^3J_{P,C}$ = 12.0 Hz, *C*HCHPh), 126.5 (CH*Ph*), 127.3 (CH*Ph*), 127.9 (*C*HPh), 128.2 (PPh), 128.6 (d, $^3J_{P,C}$ = 5.9 Hz, PPh), 128.7 (d, $^3J_{P,C}$ = 8.0 Hz, PPh), 129.0 (CH*Ph*), 129.8 (PPh), 132.5 (d, $^2J_{P,C}$ = 17.4 Hz, PPh), 135.9 (d, $^2J_{P,C}$ = 21.4 Hz, PPh), 137.7 (d, $^1J_{P,C}$ = 8.4 Hz, ^{q}PPh), 138.3 (^{q}CH*Ph*), 140.4 (d, $^1J_{P,C}$ = Hz, ^{q}PPh). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –23.3 (s). HRMS: *m/z*: calcd. for $C_{39}H_{45}FePSi$: 628.2378, found 628.2322 $[M]^+$.

1′-*tert*-Butyldiphenylsilyl-1-(2-*(E)*-phenylvinyl)-2-(diphenyl-phosphino)ferrocene (4f). Compound **4f** was synthesized according to the general procedure using diethyl benzylphosphonate (0.10 g, 0.45 mmol) and **3f** (0.10 g, 0.15 mmol). After evaporation of all volatiles in vacuo **4f** was obtained as a dark orange oil.

Yield 75 mg (0.11 mmol, 71 % based on **3f**). ^{1}H NMR ($CDCl_3$, δ): 1.01 (s, 9H, CH_3), 3.54–3.57 (m, 1H, C_5H_3), 3.64–3.67 (m, 1H, C_5H_4), 3.87 (dd, $^3J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 4.24–4.27 (m, 1H, C_5H_4), 4.27–4.29 (m, 1H, C_5H_4), 4.42–4.45 (m, 1H, C_5H_4), 4.50–4.52 (m, 1H, C_5H_3), 6.61 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, C*H*Ph), 7.06–7.14 (m, 3H, C*H*CHPh, PPh), 7.16–7.24 (m, 4H, CH*Ph*, PPh), 7.27–7.35 (m, 4H, CH*Ph*, SiPh), 7.35–7.44 (m, 9H, PPh, CH*Ph*, SiPh), 7.56 (dt, $J_{H,H}$ = 1.5, 7.9 Hz, 2H, PPh), 7.60 (dd, $J_{H,H}$ = 1.2, 8.0 Hz, 2H, SiPh), 7.71 (dd, $J_{H,H}$ = 1.2, 7.9 Hz, 2H, SiPh). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 18.4 (^{q}C(CH_3)$_3$), 28.0 (CH_3), 67.8 ($^qC_5H_4$), 68.7 (d, $^3J_{P,C}$ = 3.0 Hz, C_5H_3), 72.5 (C_5H_3), 73.2 (d, $^2J_{P,C}$ = 3.6 Hz, C_5H_3), 73.9 (d, $J_{P,C}$ = 2.6 Hz, C_5H_4), 75.9 (d, $^1J_{P,C}$ = 8.9 Hz, $^qC_5H_3$), 76.0 (C_5H_4), 76.2 (d, $J_{P,C}$ = 1.6 Hz, C_5H_4), 78.0 (C_5H_4), 89.0 (d, $^2J_{P,C}$ = 21.3 Hz, $^qC_5H_3$), 125.5 (d, $^3J_{P,C}$ = 11.8 Hz, *C*HCHPh), 126.5 (CH*Ph*), 127.3 (CH*Ph*), 127.8 (SiPh), 127.9 (SiPh), 128.1 (d, $^4J_{P,C}$ = 1.7 Hz, *C*HPh), 128.2 (PPh), 128.5 (d, $^3J_{P,C}$ = 6.0 Hz, PPh), 128.6 (d, $^3J_{P,C}$ = 7.7 Hz, PPh), 129.0 (CH*Ph*), 129.5 (SiPh), 129.6 (SiPh), 129.8 (PPh), 132.5 (d, $^2J_{P,C}$ = 17.4 Hz, PPh), 135.8 (d, $^2J_{P,C}$ = 21.1 Hz, PPh), 136.0 (^{q}SiPh), 136.1 (^{q}SiPh), 136.8 (SiPh), 136.9 (SiPh), 137.6 (d, $^1J_{P,C}$ = 8.5 Hz, ^{q}PPh), 138.3 (^{q}CH*Ph*), 140.3 (d, $^1J_{P,C}$ = 10.1 Hz, ^{q}PPh). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –23.3 (s). HRMS: *m/z*: calcd. for $C_{46}H_{43}FePSi$: 710.2221, found 710.2164 $[M]^+$.

1′-(Tributyltin)-1-(2-*(E)*-phenylvinyl)-2-(diphenylphosphino)ferrocene (4g). Compound **4g** was synthesized according to the general procedure using diethyl benzylphosphonate (0.27 g, 1.20 mmol) and **3g** (0.27 g, 0.40 mmol). After evaporation of all volatiles in vacuo **4g** was obtained as an dark orange oil.

Yield 248 mg (0.33 mmol, 82 % based on **3g**). ^{1}H NMR ($CDCl_3$, δ): 0.87 (t, $^3J_{H,H}$ = 7.3 Hz, 9H, CH_3), 0.90–0.95 (m, 6H, $SnCH_2$), 1.29 (sext, $^3J_{H,H}$ = 7.3 Hz, 6H, CH_2CH_3), 1.44–1.51 (m, 6H, $CH_2CH_2CH_3$), 3.60–3.64 (m, 1H, C_5H_4), 3.80–3.82 (m, 1H, C_5H_3), 4.01–4.04 (m, 1H, C_5H_4), 4.23 (ddd, $^3J_{H,H}$ = 2.2, 2.2 Hz, $^4J_{H,H}$ = 0.9 Hz, 1H, C_5H_4), 4.33 (dd, $^3J_{H,H}$ = 2.5, Hz, 1H, C_5H_3), 4.33–4.36 (m, 1H, C_5H_4), 4.76–4.79 (m, 1H, C_5H_3), 6.75 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, C*H*Ph), 7.13–7.24 (m, 7H, *CH*CH*Ph*, PPh), 7.28 (t, $J_{H,H}$ = 7.8 Hz, 2H, CH*Ph*), 7.38 (d, $J_{H,H}$ = 7.4 Hz, 2H, CH*Ph*), 7.39–7.43 (m, 3H, PPh), 7.58–7.63 (m, 2H, PPh). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 10.3 ($SnCH_2$), 13.8 (CH_3), 27.5 ($^3J_{119Sn,13C}$ = 57.4 Hz, CH_2CH_3), 29.3 ($^2J_{119Sn,13C}$ = 19.9 Hz, $CH_2CH_2CH_3$), 67.7 (d, $^3J_{P,C}$ = 3.0 Hz, C_5H_3), 70.3 ($^qC_5H_4$), 70.9 (C_5H_3), 72.4 (d, $^2J_{P,C}$ = 3.4 Hz, C_5H_3), 73.0 (d, $J_{P,C}$ = 1.8 Hz, C_5H_4), 75.2 (d, $J_{P,C}$ = 1.3 Hz, C_5H_4), 75.3 (C_5H_4), 76.0 (d, $^1J_{P,C}$ = 9.0 Hz, $^qC_5H_3$), 77.7 (C_5H_4), 88.7 (d, $^2J_{P,C}$ = 21.0 Hz, $^qC_5H_3$), 125.7 (d, $^3J_{P,C}$ = 12.4 Hz, *C*HCHPh), 126.2 (CH*Ph*), 127.0 (CH*Ph*), 127.2 (d, $^4J_{P,C}$ = 1.4 Hz, *C*HPh), 127.9 (PPh), 128.3 (d, $^3J_{P,C}$ = 5.7 Hz, PPh), 128.4 (d, $^3J_{P,C}$ = 7.7 Hz, PPh), 128.7 (CH*Ph*), 129.4 (PPh), 132.2 (d, $^2J_{P,C}$ = 17.5 Hz, PPh), 135.5 (d, $^2J_{P,C}$ = 21.5 Hz, PPh), 137.4 (d, $^1J_{P,C}$ = 9.1 Hz, ^{q}PPh), 137.9 (^{q}CH*Ph*), 140.1 (d, $^1J_{P,C}$ = 10.2 Hz, ^{q}PPh). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –22.0 (s). ^{119}Sn{^{1}H} NMR ($CDCl_3$, δ): –19.4 (s). HRMS: *m/z*: calcd. for $C_{42}H_{52}FePSn$: 762.2100, found 762.2075 $[M]^+$.

1,1′-Bis(2-*(E)*-phenylvinyl)-2-(diphenylphosphino)ferrocene (4h). Compound **4h** was synthesized according to the general procedure using diethyl benzylphosphonate (1.17 g, 5.12 mmol) and **3h** (0.36 g, 0.85 mmol). After evaporation of all volatiles in vacuo **4h** was obtained as a dark orange solid.

Yield 187 mg (0.33 mmol, 38 % based on **3h**). Anal. calcd. for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 79.45; H, 5.44; found C, 78.59; H, 5.63 (best match). Mp. 151 °C. ^{1}H NMR ($CDCl_3$, δ): 3.83 (ddd, $^3J_{H,H}$ = 2.2 Hz, $^4J_{H,H}$ = 1.0 Hz, $^3J_{H,P}$ = 1.0 Hz, 1H, C_5H_3), 4.09–4.11 (m, 2H, C_5H_4), 4.30 (ddd, $^3J_{H,H}$ = 2.4, 2.4 Hz, $^4J_{H,H}$ = 1.4 Hz, 1H, C_5H_4), 4.42 (dd, $^3J_{H,H}$ = 2.5, 2.5 Hz, 1H, C_5H_3), 4.48 (ddd, $^3J_{H,H}$ = 2.6, 2.6 Hz, $^4J_{H,H}$ = 1.4 Hz, 1H, C_5H_4), 4.81 (ddd, $^3J_{H,H}$ = 2.5 Hz, $^4J_{H,H}$ = 1.4 Hz, $^4J_{H,P}$ = 1.4 Hz, 1H, C_5H_3), 6.58 (d, $^3J_{H,H}$ = 16.4 Hz, 1H, ′C*H*Ph), 6.61 (d, $^3J_{H,H}$ = 16.4 Hz, 1H, ′CH*CH*Ph), 6.69 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, C*H*Ph), 7.08 (dd, $^3J_{H,H}$ = 16.1 Hz, $^4J_{H,P}$ = 2.4 Hz, 1H, C*H*CHPh), 7.13–7.27 (m, 15H, PPh, CH*Ph*, ′CH*Ph*), 7.41–7.46 (m, 3H, PPh), 7.61–7.67 (m, 2H, PPh). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 68.1 (C_5H_4), 69.4 (d, $^3J_{C,P}$ = 3.0 Hz,

C_5H_3), 69.9 (d, $J_{C,P}$ = 1.3 Hz, C_5H_4), 70.9 (C_5H_4), 71.8 (C_5H_3), 71.9 (C_5H_4), 73.1 (d, $^2J_{C,P}$ = 3.6 Hz, C_5H_3), 76.8 (d, $^1J_{C,P}$ = 10.0 Hz, $^qC_5H_3$), 85.2 ($^qC_5H_4$), 89.7 (d, $^2J_{C,P}$ = 20.9 Hz, $^qC_5H_3$), 125.0 (d, $^3J_{C,P}$ = 12.0 Hz, *C*HCHPh), 125.9 (′*C*HCHPh), 126.4 (CH*Ph*), 126.5 (′CH*Ph*), 127.2 (′*C*HPh), 127.8 (CHPh, ′CHPh), 128.1 (d, $^4J_{C,P}$ = 1.5 Hz, *C*HPh), 128.2 (PPh), 128.6 (d, $^3J_{C,P}$ = 6.0 Hz, PPh), 128.8 (d, $^3J_{C,P}$ = 8.1 Hz, PPh), 128.9 (CH*Ph*), 129.0 (′CH*Ph*), 129.8 (PPh), 132.5 (d, $^2J_{C,P}$ = 17.8 Hz, PPh), 135.9 (d, $^2J_{C,P}$ = 21.6 Hz, PPh), 137.8 (d, $^1J_{C,P}$ = 9.0 Hz, ^{q}PPh), 138.1 (^{q}CH*Ph*), 138.2 (^{q}′CH*Ph*), 140.4 (d, $^1J_{C,P}$ = 10.7 Hz, ^{q}PPh). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –23.4 (s). HRMS: *m/z*: calcd. for $C_{38}H_{31}FeP$: 574.1513, found 574.1461 $[M]^+$.

Di(4-cyanophenyl)phosphino-(2-(*E*)-phenylvinyl)ferrocene (9e). In a Schlenk tube, (tributylstannyl)-(2-(*E*)-phenylvinyl)ferrocene ((*rac*)-**14**, 1.00 g, 1.73 mmol)[7] was dissolved in 15 mL of tetrahydrofuran and the solution was cooled to –78 °C. Afterwards, BuLi (0.8 mL, 1.9 mmol) was added dropwise over 10 min. The mixture was subsequently stirred for 1 h. In an additional Schlenk, chlorobis(*p*-cyanophenyl)phosphine (520 mg, 1.92 mmol) was dissolved in 15 mL of tetrahydrofuran and cooled to –78 °C. The latter solution was added dropwise to the solution of the lithiated ferrocene, by using a transfer cannula. The reaction mixture was warmed to ambient temperature and stirring was continued for 12 h. After removal of all volatiles in vacuo, purification was realized by column chromatography (silica, 4 × 12 cm column size) using a 7:1 hexane/dichloromethane (*v*/*v*) mixture as the eluent. The removal of all volatiles in vacuo gave *rac*-**9e** as an orange solid.

Yield: 430 mg (0.823 mmol; 48 % based on *rac*-**14**). Anal. calcd. for $C_{32}H_{23}FeN_2P$ (522.36 g/mol): C, 73.58; H, 4.44; N, 5.35; found C, 72.40; H, 4.44; N, 5.11 (best match). Mp. 230–232 °C. ^1H NMR ($CDCl_3$, δ): 3.72 (ddd, *J* = 2.4 Hz, *J* = 2.4 Hz, *J* = 1.1 Hz, 1H, C_5H_3), 4.06 (s, 5H, C_5H_5), 4.51 (pt, $^{3,4}J$(H,H) = 2.5 Hz, 1H, C_5H_3), 4.95 (dpt, *J*(H,H) = 2.0 Hz, *J*(H,P) = 1.5 Hz, *J*(H,H) = 1.5 Hz, 1H, C_5H_3), 6.80 (d, ^3J(H,H) = 16.1 Hz, 1H, CH=*CH*Ph), 7.08 (dd, $^3J_{H,H}$ = 16.1 Hz, $^4J_{H,P}$ = 2.3 Hz, 1H, *CH*=CHPh), 7.18–7.21 (m, 2H, *o*-C_6H_4), 7.23–7.24 (m, 1H, *p*-C_6H_5), 7.31 (t, $^3J_{H,H}$ = 7.6 Hz, 2H, *m*-C_6H_5), 7.39 (d, $^3J_{H,H}$ = 7.2 Hz, 2H, *o*-C_6H_5), 7.51 (dd, $^3J_{H,H}$ = 8.3 Hz, *J* = 7.3 Hz, 2H, *m*-C_6H_4), 7.66 (t, $^3J_{H,H}$ = 7.7 Hz, 2H, *o*-C_6H_4), 7.72 (dd, $^3J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 1.1 Hz, 2H, *m*-C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 68.4 (d, $J_{C,P}$ = 3.7 Hz, C_5H_3), 70.6 (s, C_5H_5), 71.5 (s, C_5H_3), 71.8 (d, $J_{C,P}$ = 3.8 Hz, C_5H_3), 72.8 (d, $^1J_{C,P}$ = 7.2 Hz, C_{C5H3}–P), 89.6 (d, $^2J_{C,P}$ = 22.8 Hz, C_{C5H3}–C), 112.1 (C–CN), 113.7 (C–CN), 118.4 (CN), 118.7 (CN), 124.2 (d, $^3J_{C,P}$ = 12.1 Hz, *C*H=CHPh), 126.2 (C_6H_5), 127.5 (*p*-C_6H_5), 128.4 (d, $^4J_{C,P}$ = 1.7 Hz, CH=*C*HPh), 128.8 (C_6H_5), 131.9–132.0 (m, *m*-C_6H_4), 132.5 (d, $^2J_{C,P}$ = 17.5 Hz, *o*-C_6H_4), 135.8 (d, $^2J_{C,P}$ = 21.5 Hz, *o*-C_6H_4), 137.4 ($^qC_6H_5$), 142.9 (d, $^1J_{C,P}$ = 13.6 Hz, C_{C6H4}–P), 145.8 (d, $^1J_{C,P}$ = 16.5 Hz, C_{C6H4}–P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –19.2 (s).

Crystal data: $C_{32}H_{23}FeN_2P$, *M* = 522.34 g mol^{-1}, crystal dimensions 0.40 × 0.04 × 0.02 mm, monoclinic, $P2_1/c$, λ = 0.71073 Å, *a* = 13.0467(9) Å, *b* = 17.1884(6) Å, *c* = 12.4981(9) Å, β = 118.424(9) °, *V* = 2464.9(3) Å^3, *Z* = 4, ρ_{calcd} = 1.408 Mg m^{-3}, μ = 0.701 mm^{-1}, *T* = 117.00(14) K, θ range 2.961–25.000°, 20334 reflections collected, 4277 independent reflections (R_{int} = 0.0728), R_1 = 0.0432, wR_2 = 0.0872 [$I > 2\sigma(I)$].

(S_p)-2-(Bis(diethylamino)phosphine)-(2-(*E*)-phenylvinyl)ferrocene ((S_p)-15). In a Schlenk tube, a solution of (S_p)-2-(tributylstannyl)-(2-(*E*)-phenylvinyl)ferrocene ((S_p)-**14**, 1.00 g, 1.73 mmol) in 18 mL of tetrahydrofuran was cooled to –80 °C. Over a period of 10 min, BuLi (0.77 mL, 1.91 mmol) was added dropwise and stirring of the reaction mixture was continued for 1 h. Afterwards, $ClP(NEt_2)_2$ (0.40 mL, 1.91 mmol) was added in a single portion at –80 °C and the solution was warmed to ambient temperature and stirred for additional 12 h. Diethyl ether (100 mL) was added and the crude mixture was washed with a K_2CO_3 solution (2 × 100 mL, *w* = 1 %). The organic phase was dried with $MgSO_4$ followed by the evaporation of all volatiles in vacuo. The obtained raw product was used without further purification, whereas one equivalent of $SnBu_4$ remains in the mixture as an innocent compound.

Yield: quantitative (1.73 mmol, 100 % based on **14**, calculated by NMR spectroscopy). ^1H NMR (C_6D_6, δ): 0.95 (t, $^3J_{H,H}$ = 7.3 Hz, 12H, CH_2–CH_3), 3.15–2.91 (m, 8H, CH_2-CH_3), 4.16 (s, 5H, C_5H_5), 4.27 (pt, $^{3,4}J_{H,H}$ = 2.5 Hz, 1H, C_5H_3), 4.36 (m, 1H, C_5H_3), 4.66 (m, 1H, C_5H_3), 6.79 (1H, d, $^3J_{H,H}$ = 16.4 Hz, HC=*CH*Ph), 7.09–7.04 (m, 1H, C_6H_5), 7.22–7.17 (m, 2H, C_6H_5), 7.48 (d, $^3J_{H,H}$ = 16.7 Hz, 1H, *HC*=CHPh), 7.53–7.49 (m, 2H, C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 15.0 (d, $^3J_{C,P}$ = 3.5 Hz, CH_2–CH_3), 15.1 (d, $^3J_{C,P}$ = 3.2 Hz, CH_2–CH_3), 43.3 (d, $^2J_{C,P}$ = 15.0 Hz, CH_2–CH_3), 43.6 (d, $^2J_{C,P}$ = 19.4 Hz, CH_2–CH_3), 67.1 (d, $J_{C,P}$ = 2.3 Hz, C_5H_3), 69.2 (s, C_5H_3), 71.1 (d, $J_{C,P}$ = 2.4 Hz, C_5H_5), 72.9 (s, C_5H_3), 82.1 (d, $^1J_{C,P}$ = 3.0 Hz, C_{C5H3}–P), 85.1 (d, $^2J_{C,P}$ = 14.8 Hz, C_{C5H3}–C), 125.6 (s, *C*H=CHPh), 126.2 (s, C_6H_5), 127.0 (s, C_6H_5), 127.5 (d, $^4J_{C,P}$ = 6.0 Hz, HC=*C*HPh, obtained from a $CDCl_3$ solution), 129.1 (s, C_6H_5), 138.9 (s, $^qC_6H_5$). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 103.5.

(S_p)-2-Dichlorophosphino-(2-(*E*)-phenylvinyl)ferrocene and (R_A,S_p)-2-(1,1′-Binaphthyl-2,2′-diylphosphonito)-(2-(*E*)-phenylvinyl)ferrocen ((R_A,S_p)-16). Compound (S_p)-15 (800 mg, 1.73 mmol) was dissolved in 40 mL of diethyl ether, cooled to –80 °C, and treated with a solution of HCl in diethyl ether (3.2 mL, 5.5 *M*, 17.3 mmol). Stirring was continued for 2 h at this temperature and subsequently warmed to ambient temperature. All volatiles were removed in vacuo. The raw material, which still contains one equivalent of $SnBu_4$ was used without further purification.

Yield: quantitative (1.73 mmol, 100 % based on **14**, calculated by NMR spectroscopy). ^1H NMR (C_6D_6, δ): 3.90 (s, 5H, C_5H_5), 4.18 (pt, $^{3,4}J_{H,H}$ = 2.3 Hz, 1H, C_5H_3), 4.43 (s, 1H, C_5H_3), 4.61 (s, 1H, C_5H_3), 6.83 (dd, $^3J_{H,H}$ = 16.0 Hz, $^4J_{H,P}$ = 2.6 Hz, 1H, *HC*=CHPh), 7.15–7.00 (m, 4H), 7.31 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 71.3 (d, $J_{C,P}$ = 0.9 Hz, C_5H_5), 71.3 (s, 1C, C_5H_3), 71.7 (s, 1C, C_5H_3), 73.1 (s, 1C, C_5H_3), 78.2 (d, $^1J_{C,P}$ = 57.3 Hz, C_{C5H3}–P), 89.5 (d, $^2J_{C,P}$ = 27.1 Hz, C_{C5H3}–C), 123.3 (d, $J_{C,P}$ = 9.6 Hz, HC=CHPh), 126.6 (s, C_6H_5), 127.9 (s, *p*-C_6H_5), 129.1 (s, C_6H_5), 130.5 (d, $J_{C,P}$ = 5.4 Hz, HC=CHPh), 137.4 (s, $^qC_6H_5$). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 175.8 (s).

The 2-dichlorophosphinovinylferrocene mixture (1.73 mmol) and (R_A)-BINOL (991 mg, 3.46 mmol), were dissolved in 70 mL of toluene, heated to 110 °C and stirred for 72 h. The volume of the mixture was subsequently reduced to ca. 15 mL and after cooling it to ambient temperature 80 mL of pentane were added, which let to the formation of an orange solid. The suspension was placed in a freezer (–30 °C) to complete precipitation. The solid was filtered off and washed with pentane to remove $SnBu_4$. The filtrate was concentrated and treated with pentane in the above mentioned procedure. Both fractions of solids were combined and filtered through a pad of silica (1.5 × 3 cm) using dichloromethane as solvent. After removal of all volatiles in vacuo (S_p)-**16** was obtained as an orange solid. Crystals suitable for single-crystal X-ray diffraction analysis were obtained by crystallization from dichloromethane at ambient temperature.

Yield: 610 mg (1.0 mmol, 59 % based on (S_p)-**14**). Anal. calcd. for $C_{38}H_{27}FePO_2$ (602.44 g/mol): C, 75.76; H, 4.52; found C, 75.44; H, 4.46. Mp. 216 °C (decomp.). ^1H NMR (CD_2Cl_2, δ): 3.81–3.82 (m, 1H, C_5H_3), 4.31 (s, 5H, C_5H_5), 4.33 (pt, $^{3,4}J_{H,H}$ = 2.5 Hz, 1H, C_5H_3), 4.84–4.86 (m, 1H, C_5H_3), 6.94 (d, $^3J_{H,H}$ = 8.8 Hz, 1H, HC=CHPh), 6.98 (d, $^3J_{H,H}$ = 16.1 Hz, 1H, HC=CHPh), 7.25–7.23 (m, 12H), 7.71 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 0.7 Hz, 1H), 7.77 (d, $^3J_{H,H}$ = 8.7 Hz, 1H), 7.92 (d, $^3J_{H,H}$ = 8.2 Hz, 1H), 8.02 (d, $^3J_{H,H}$ = 8.2 Hz, 1H), 8.11 (d, $^3J_{H,H}$ = 8.8 Hz, 1H).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 70.4 (d, $J_{C,P}$ = 3.3 Hz, C_5H_3), 71.0 (d, $J_{C,P}$ = 0.5 Hz, C_5H_5), 71.4 (C, s, C_5H_5), 72.0 (s, C_5H_3), 74.6 (d, $^1J_{C,P}$ = 38.9 Hz, C_{C5H3}–P), 89.8 (d, $^2J_{C,P}$ = 25.5 Hz, C_{C5H3}–C), 122.3 (CH), 123.0 (CH), 124.1 (d, $J_{C,P}$ = 2.4 Hz, ^{q}C), 125.2 (CH), 125.2 (CH), 125.3 (d, $J_{C,P}$ = 5.4 Hz, ^{q}C), 125.5 (CH), 126.5 (CH), 126.7 (CH), 126.9 (CH), 127.1 (CH), 127.3 (CH), 127.8 (CH), 128.96 (CH), 129.00 (CH), 129.05 (CH), 129.3 (CH), 129.8 (CH), 131.2 (CH), 131.7 (^{q}C), 132.2 (^{q}C), 133.2 (^{q}C), 133.5 (d, $J_{C,P}$ = 1.4 Hz, ^{q}C), 138.1 (^{q}C), 149.8 (d, $J_{C,P}$ = 4.5 Hz, ^{q}C), 150.9 (d, $J_{C,P}$ = 1.8 Hz, ^{q}C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 189.8 (s). IR (KBr, ν): 3108.2 (w), 3090.3 (w), 3060.3 (m), 3044.3 (m), 3030.6 (m), 2994.7 (w), 1617.2 (m), 1585.5 (m), 1497.6 (m), 1497.6 (m), 1461.8 (m), 1453.8 (m), 1430.0 (m), 1324.7 (m), 1229.3 (vs), 1201.0 (s), 1157.0 (s), 1105.8 (m), 1068.9 (s), 1034.3 (m), 1000.6 (m), 980.6 (m), 960.2 (m), 948.4 (vs), 863.6 (m), 819.5 (vs), 788.9 (s), 777.5 (s), 761.5 (s), 752.6 (s), 737.6 (s), 695.4 (s), 648.3 (s), 667.1 (m), 639.4 (s), 627.8 (s), 587.6 (m), 570.6 (m), 555.2 (s), 524.5 (s), 504.8 (m). HRMS (ESI-TOF, *m/z*): calcd. for $C_{38}H_{27}FePO_2$ 602.1098, found 602.1081 $[M]^+$.

Crystal data: $C_{38}H_{27}FeO_2P$, M = 602.41 g mol^{-1}, crystal dimensions 0.10 × 0.10 × 0.10 mm, orthorhombic, $P2_12_12_1$, λ = 0.71073 Å, a = 12.6618(4) Å, b = 14.4011(6) Å, c = 15.5222(4) Å, V = 2830.38(16) Å^3, Z = 4, ρ_{calcd} = 1.414 Mg m^{-3}, μ = 0.624 mm^{-1}, T = 110(2) K, θ range 2.982–28.448°, 14487 reflections collected, 6079 independent reflections (R_{int} = 0.0462), R_1 = 0.0438, wR_2 = 0.0692 [$I > 2\sigma(I)$], absolute structure parameter[33] = 0.005(11).

Chlorobis(*p*-cyanophenyl)phosphine. To a solution of *p*-bromobenzonitrile (1 g, 5.50 mmol) dissolved in 25 mL of tetrahydrofuran, BuLi (2.2 mL, 5.50 mmol) was added dropwise at –80 °C. The solution was stirred for 10 min at this temperature. The thus prepared mixture was added to a solution of 479 mg diisopropylamino-dichlorophosphine (2.75 mmol) in 10 mL of anhydrous tetrahydrofuran and the solution was stirred for 1 h at –80 °C followed by evaporation of all volatiles in vacuo. The obtained product could be used without further purification.

^1H NMR ($CDCl_3$, δ): 7.62–7.74 (m, 8H, $2C_6H_4$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 114.6 (^{q}CCN), 117.9 (^{q}CN), 132.0 (d, $J_{P,C}$ = 24.6 Hz, $2C_6H_4$), 132.3 (d, $J_{P,C}$ = 6.8 Hz, $2C_6H_4$), 143.5 ($^qC_6H_4$), 143.8 ($^qC_6H_4$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 73.6.

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Keywords: Biaryls · Ferrocenes · Phosphine ligands · Planar chirality · Cross-coupling

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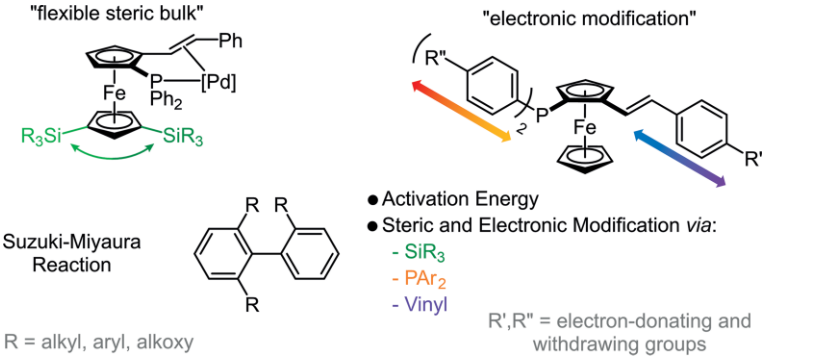
Planar Chiral Ferrocenes

*M. Korb, D. Schaarschmidt, M. Grumbt, M. König, H. Lang** 1–16

Evaluation of the Transferability of the "Flexible Steric Bulk" Concept from N-Heterocyclic Carbenes to Planar-Chiral Phosphinoferrocenes and their Electronic Modification



Planar-chiral vinyl-phosphino ferrocenes were modified electronically to evaluate the role of each donor functionality within Pd-catalyzed reactions. "Flexible steric bulk" was introduced to investigate its stabilization of the catalytically active species. The impact of additional asymmetry at the P-donor towards the atroposelective synthesis of sterically hindered biaryls is demonstrated.

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