DOI: 10.1002/ejic.201100842

(Metallocenylphosphane)palladium Dichlorides – Synthesis, Electrochemistry and Their Application in C–C Coupling Reactions

Bianca Milde,[a] Manja Lohan,[a] Claus Schreiner,[a] Tobias Rüffer,[a] and Heinrich Lang*[a]

Keywords: Ferrocene / Palladium / Phosphanes / C–C coupling / Electrochemistry

The synthesis and characterization of a series of metallocenylphosphanes of the type $PR_2Mc/Se{=}PR_2Mc$ [Mc = Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$, R = C_6H_5 (**3a/4a**), 2-MeC_6H_4 (**3b/4b**), *c*-C_4H_3O (**3c/4c**), *t*Bu (**3d/4d**), *c*-C_6H_{11} (**3e/4e**); Mc = Rc = $Ru(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$, R = C_6H_5 (**6a/7a**), 2-MeC_6H_4 (**6b/7b**), *c*-C_4H_3O (**6c/7c**), *c*-C_6H_{11} (**6d/7d**)] and their palladium complexes $[PdCl_2(PR_2Mc)_2]$ [Mc = Fc, R = C_6H_5 (**9a**), 2-MeC_6H_4 (**9b**), *c*-C_4H_3O (**9c**), *t*Bu (**9d**), *c*-C_6H_{11} (**9e**); Mc = Rc, R = C_6H_5 (**10a**), 2-MeC_6H_4 (**10b**), *c*-C_4H_3O (**10c**), *c*-C_6H_{11} (**10d**)] is reported. The solid-state structure of **4b** confirms the tetrahedrally distorted geometry at phosphorus with the *o*-tolyl groups indicating steric congestion, which is confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Phosphanes **3**, **4**, and **9** were characterized by cyclic voltammetry with $[N(nBu)_4][B(C_6F_5)_4]$ as the supporting electrolyte. In general, the first oxidation occurs at the phosphane metallocenyl unit(s), although the appropriate Pd complexes are oxidized at more positive potentials. Depending on the phosphane or selenophosphane, follow-up reactions occur, which are discussed. In contrast, the palladium complexes show reversible redox behavior. UV/Vis/NIR spectroelectrochemical studies carried out on **9b** indicate an electrostatic interaction between the two terminal ferrocenyl groups. All of the palladium complexes were examined as catalysts in Heck and Suzuki C–C cross-coupling and showed high catalytic activities. These results can be correlated to the electronic ($^1J_{^{31}P^{77}Se}$) parameters of the selenophosphanes.

Introduction

The development of new ligands for palladium-catalyzed C–C coupling reactions has accelerated over recent years because new ligand structures may effect the activation of aryl–chloro bonds under mild reaction conditions with high conversions and low catalyst loadings.[1] Hitherto, mono- and bidentate alkyl-, aryl-, and ferrocenyl-functionalized phosphanes, *N*-heterocyclic carbenes, and palladacycles have been successfully used in the synthesis of effective palladium catalysts.[1–4] Electron rich and/or bulky mono- and bidentate phosphanes are of particular interest,[4c,5] although it is still a challenge to predict their performance in homogeneous catalysis as small changes in their electronic and/or spatial structure may affect the activity of the catalyst.[4c] This prompted us to synthesize metallocenyl-based phosphanes of the type PR_2Fc [Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$] and PR_2Rc [Rc = $Ru(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$] because the metallocenyl entity achieves a significant increase in the stability of the respective phosphane towards air and moisture, and the ligands, R, are responsible for controlling the electronic and steric properties.

To quantify the σ donor ability of a phosphanyl group, the magnitude of the $^{31}P^{77}Se$ coupling constant of the corresponding selenophosphane should be measured. Allen and Taylor have reported that an increase in $^1J_{^{31}P^{77}Se}$ indicates an increase in the s character of the phosphorus lone-pair orbital and as result the basicity of the phosphane decreases.[6]

Herein we report the enrichment of the family of metallocenyl-functionalized phosphanes that feature electron-donating or -withdrawing groups by applying straightforward synthetic methodologies. The use of these phosphanes in palladium-catalyzed Heck and Suzuki reactions is discussed. A quantification of the electronic properties of the phosphanes towards the catalytic activities has been performed.

Results and Discussion

Ligand Synthesis and Properties

Metallocenyl-phosphanes **3a–e** and **6a–d**, the corresponding selenophosphanes **4a–e**, and **7a–d** as well as their palladium complexes **9a–e** and **10a–d** were prepared according to previously reported synthetic methodologies (Scheme 1, Reaction 1, Tables 1 and 2).[4b,6f,8]

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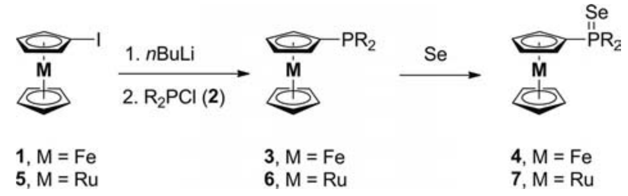
[a] Chemnitz University of Technology, Faculty of Science,
Institute of Chemistry, Department of Inorganic Chemistry,
Straße der Nationen 62, 09111 Chemnitz, Germany
Fax: +49-371-531-21219
E-mail: heinrich.lang@chemie.tu-chemnitz.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100842.



Scheme 1. Synthesis of **3**, **4**, **6**, and **7** from **1** or **5**.

Table 1. Synthesis of **3a**–**e**, **4a**–**e**, **6a**–**d**, and **7a**–**d**.

	M	R	% Yield[a]		M	R	% Yield[a]
3a	Fe	C_6H_5	57	**6a**	Ru	C_6H_5	35
3b	Fe	2-MeC_6H_4	69	**6b**	Ru	2-MeC_6H_4	36
3c	Fe	*c*-C_4H_3O	63	**6c**	Ru	*c*-C_4H_3O	46
3d	Fe	*t*Bu	48	**6d**	Ru	*c*-C_6H_{11}	42
3e	Fe	*c*-C_6H_{11}	31				
4a	Fe	C_6H_5	100	**7a**	Ru	C_6H_5	89
4b	Fe	2-MeC_6H_4	100	**7b**	Ru	2-MeC_6H_4	94
4c	Fe	*c*-C_4H_3O	100	**7c**	Ru	*c*-C_4H_3O	84
4d	Fe	*t*Bu	100	**7d**	Ru	*c*-C_6H_{11}	92
4e	Fe	*c*-C_6H_{11}	100				

[a] Based on **1** and **5** or **3** and **6**.

Table 2. Synthesis of **9a**–**e** and **10a**–**d**.

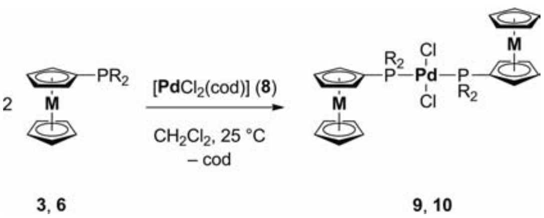
	M	R	% Yield[a]		M	R	% Yield[a]
9a	Fe	C_6H_5	90	**10a**	Ru	C_6H_5	83
9b	Fe	2-MeC_6H_4	84	**10b**	Ru	2-MeC_6H_4	84
9c	Fe	*c*-C_4H_3O	77	**10c**	Ru	*c*-C_4H_3O	86
9d	Fe	*t*Bu	74	**10d**	Ru	*c*-C_6H_{11}	70
9e	Fe	*c*-C_6H_{11}	81				

[a] Based on **8**.

The synthesis of the metallocenyl-phosphanes, PR_2Mc [Mc = Fc = Fe(η^5-C_5H_4)(η^5-C_5H_5), R = C_6H_5 (**3a**),[7] 2-MeC_6H_4 (**3b**), *c*-C_4H_3O (**3c**), *t*Bu (**3d**),[7] *c*-C_6H_{11} (**3e**);[7] Mc = Rc = Ru(η^5-C_5H_4)(η^5-C_5H_5), R = C_6H_5 (**6a**), 2-MeC_6H_4 (**6b**), *c*-C_4H_3O (**6c**), *c*-C_6H_{11} (**6d**)], and the appropriate selenophosphanes, Se=PR_2Mc [Mc = Fc (**4a**–**e**), Rc (**7a**–**d**)], was carried out by a consecutive reaction sequence (Scheme 1). Lithiation of M(η^5-C_5H_4I)(η^5-C_5H_5) [M = Fe (**1**), Ru (**5**)] and subsequent treatment with R_2PCl [R = C_6H_5 (**2a**), 2-MeC_6H_4 (**2b**), *c*-C_4H_3O (**2c**), *t*Bu (**2d**), *c*-C_6H_{11} (**2e**)] gave metallocenyl-phosphanes **3** and **6**, which further reacted with elemental selenium to produce the selenophosphanes **4** and **7**, respectively (Scheme 1, Table 1).

Complexation of **3** and **6** was performed by addition to [$PdCl_2$(cod)] (**8**, cod = cyclo-1,5-octadiene) at ambient temperature (Reaction 1). After work up, the orange to red colored ferrocenyl complexes **9** or pale yellow ruthenocenyl complexes **10** were isolated in 70–90% yield (Table 2).

Solid phosphanes **3** (yellow) and **6** (pale yellow) are stable in air, and no oxidation of the phosphorus(III) center is observed. However, it appeared that solutions containing these molecules slowly oxidized to give the corresponding phosphane oxides. As expected, **4**, **7**, **9**, and **10** are air- and moisture-stable. However, **7d** shows sensitivity towards light and slowly turns pale yellow.



(1)

All compounds were identified by elemental analysis, IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy, and ESI-TOF mass spectrometry (see Exp. Section). The electrochemical behavior of **3**, **4**, and **9** was determined.

Electrochemistry

The redox properties of **3**, **4**, and the corresponding complexes **9** were studied by cyclic voltammetry (CV), linear sweep voltammetry (LSV, **9**), square wave voltammetry (SWV, **9**), and spectroelectrochemistry (UV/Vis/NIR spectroscopy, **9b**) in dry dichloromethane with [N(nBu)$_4$][B(C_6F_5)$_4$] (0.1 mol L^{-1}) as the supporting electrolyte. This solvent/electrolyte combination was chosen because it was recently shown by Geiger et al.[9] that it provides almost optimal conditions for electrochemical experiments as it minimizes electrolyte–analyte interactions and, hence, follow-up reactions. The CV studies were carried out at scan rates of 100 mV s^{-1}, and the data are summarized in Table 3. All potentials are referenced to the FcH/FcH$^+$ redox couple as the internal standard as recommended by IUPAC.[10]

The electrochemically most studied member of the series of phosphanes reported in this work is ferrocenyl diphenylphosphane. Kotz and Nivert reported a reversible one-electron oxidation at E^0 = 0.48 V (vs. SCE) when measured to a maximum potential of 0.8 V, and irreversible oxidations

Table 3. Cyclovoltammetric data (potentials vs. FcH/FcH$^+$), scan rate 100 mV s^{-1} at a glassy-carbon electrode of 1.0 mmol L^{-1} solutions of **3** and **4** in dry dichloromethane containing 0.1 mol L^{-1} [N(nBu)$_4$][B(C_6F_5)$_4$] as the supporting electrolyte at 25 °C.[a]

	E^0 (ΔE_p) /V	$E_{ox-irrev}$ /V	$E_{red-irrev}$ /V		$E_{ox-irrev}$ /V	$E_{red-irrev}$ /V
3a	0.064 (0.082)		0.703	**4a**	0.288	–0.290
					0.934	0.021
					1.058	0.674
						0.838
3b	0.013 (0.090)			**4b**	0.241	–0.449
					0.895	0.713
3c	0.091 (0.108)			**4c**	0.326	–0.454
					1.122	0.238
						0.510
						0.802
3d		0.022	–0.046	**4d**	0.216	0.108
		0.188	0.158		0.858	0.360
		0.806	0.702			0.712
3e		0.023	–0.029	**4e**	0.270	–0.290
		0.207	0.175		0.706	0.176
		0.815	0.713			0.586

[a] E^0 = redox potential, ΔE_p = difference between oxidation and reduction potential, $E_{ox-irrev}$ = irreversible oxidation potential, $E_{red-irrev}$ = irreversible reduction potential.

occur at higher potentials (1.5 V).[11a,11b] The first oxidation process confirms the ferrocenyl oxidation, and the resulting ferrocenium ion participates in an intramolecular electron transfer from the PPh_2 group to iron.[11] Under our conditions, we observed a similar behavior for all the ferrocenylphosphanes (Table 3). Representative CVs of **3b** and **3e** are shown in Figure 1. As consequence of the nature of the alkyl or aryl substituent at phosphorus, a different electronic and, hence, electrochemical behavior is expected. The more electron-rich a compound is, the easier it is to oxidize. This meets the expected furyl < phenyl < *o*-tolyl trend for the aromatic phosphanes, whereas aliphatic **3d** and **3e** show a similar electronic character and completely irreversible behavior (Table 3).

All of the free phosphanes were converted into the corresponding selenophosphanes to investigate their electronic properties (vide infra). Ferrocenyl-phosphane chalcogenides are electrochemically less investigated than free phosphanes, of which phosphane sulfides and oxides are the best studied and show reversible behavior.[9,12a,12b] Although electrochemically-induced follow-up reactions are not expected because of the oxidation state of +5 at phosphorus, selenophosphanes show a different behavior. We examined the electrochemistry of **4a**–**e** under the same conditions described above (Figure 1). As expected, the selenophosphanes are more difficult to oxidize than the corresponding P^{III}-containing compounds **3a**–**e** (Table 3). In all of the CVs, almost irreversible oxidation events between 0.16 and

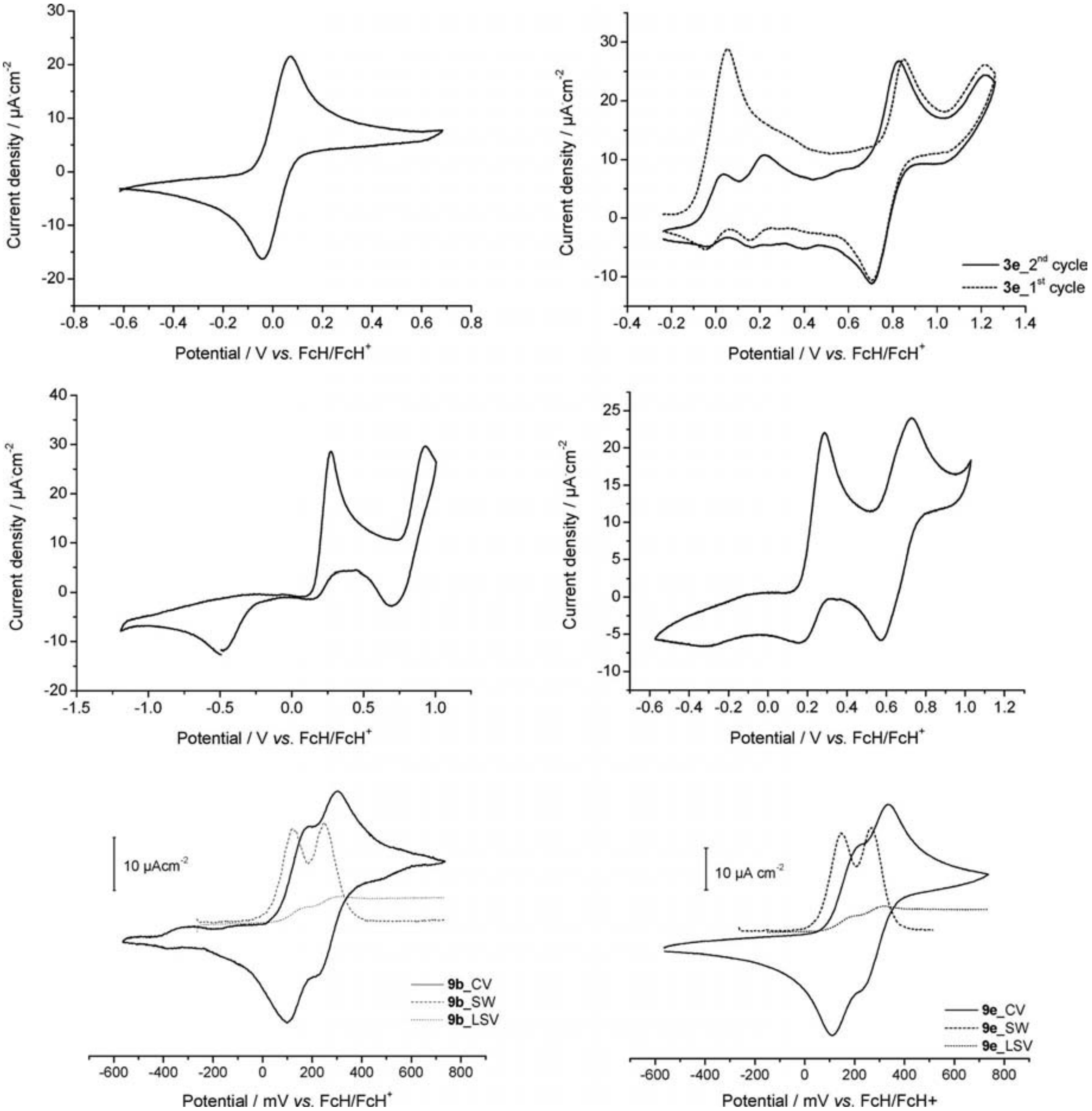


Figure 1. CVs of dichloromethane solutions containing 1.0 mmol L^{-1} of **3b** (top, left), **4b** (middle, left), and **9b** (bottom, left) and **3e** (top, right), **4e** (middle, right), and **9e** (bottom, right) at 25 °C with $[N(nBu)_4][B(C_6F_5)_4]$ as the supporting electrolyte at a scan rate of 100 mV s^{-1}.

0.33 V that give cathodic responses between –0.67 and –0.29 V are observed, which can be attributed to follow-up reactions. In addition, it is apparent that the more reversible the oxidation processes are, the lower the intensity of the cathodic response is. A similar behavior was recently described for diseleno-1,1′-bis(diphenylphosphanyl)ferrocene[12b] and seleno bi- and triferrocenyl-phenylphosphanes.[9] The corresponding follow-up products presumably result from intramolecular electron transfer from the selenium-centered radical. Therefore, contributions from either the iron, phosphorus, or selenium radicals are expected in the monocationic species of this series.

However, intramolecular oxidations are inhibited when the phosphorus atom in **3a**–**e** is datively-bonded to palladium as seen in **9a**–**e** (Figure 1, Table 4). Surprisingly, two reversible oxidation processes between E^0 = 0.11 and 0.27 V with ΔE^0 values of between 0.058 and 0.126 V were observed for these ferrocenyl-phosphane palladium complexes. This indicates that the two metallocenyls can be oxidized separately. The electrochemical data of these complexes are summarized in Table 4. No further redox events to indicate follow-up reactions were observed. Compared to the non-coordinated metallocenyl-phosphanes, the respective palladium complexes are more difficult to oxidize, which can be explained by the electron-withdrawing effect of the coordination of the phosphanes to palladium (Figure 1, Table 4). In addition to CV measurements, LSV and SWV studies were carried out (Figure 1), which confirm the one-electron processes.

Table 4. Cyclovoltammetric data (potentials vs. FcH/FcH$^+$), scan rate 100 mV s^{-1} at a glassy-carbon electrode of **9a**–**e** in dry dichloromethane solution (1.0 mmol L^{-1}) with 0.1 mol L^{-1} of [N(nBu)$_4$][B(C$_6$F$_5$)$_4$] as the supporting electrolyte at 25 °C.[a]

	$E_1{}^0$ (ΔE_p) /V	$E_2{}^0$ (ΔE_p) /V	ΔE^0 /V
9a	0.145 (0.097)	0.263 (0.099)	0.116
9b	0.118 (0.072)	0.244 (0.072)	0.126
9c	0.212 (0.082)	0.270 (0.080)	0.058
9d	0.118 (0.094)	0.203 (0.092)	0.085
9e	0.169 (0.090)	0.276 (0.088)	0.107

[a] $E_1{}^0$ = potential of the first redox process, $E_2{}^0$ = potential of the second redox process, ΔE_p = difference between oxidation and reduction potential, ΔE^0 = potential difference between two redox processes.

To investigate the electrochemically generated electronic absorptions in the visible and near infrared (NIR) regions, a spectroelectrochemical investigation was performed on **9b**, which was chosen as it shows the largest peak separation (ΔE^0 = 0.126 V) between the first and second oxidations. An absence of charge-transfer bands in the NIR would point to electron-localized mixed-valent complexes, whereas their presence would argue in favor of electron delocalization. The spectroelectrochemical studies were conducted by the stepwise increase of the potential from –0.2 to 1.2 V vs. Ag/AgCl in an optically transparent thin-layer electrode (OTTLE)[12f,12g] cell that contained dichloromethane solutions of **9b** (1.0 mmol L^{-1}) and [N(nBu)$_4$][B(C$_6$F$_5$)$_4$] (0.1 mol L^{-1}) as the supporting electrolyte. This procedure allowed the generation of **9b$^+$** from neutral **9b**. It can be seen from Figure 2 that **9b$^+$** does not exhibit any absorption in the NIR range, which confirms that the positive charges were localized on the Fc$^+$ groups in mixed-valent partially-oxidized intermediates (Figure 2). Nevertheless, during oxidation an absorption in the UV/Vis part of the spectrum at 524 nm occurs, which is assigned to a ligand-to-metal charge transfer transition from the ligand to the ferrocenium moiety.[12c–12e] The ΔE^0 value of 0.126 V indicates some electrostatic interaction between the two terminal ferrocenyl groups as the oxidation progresses.

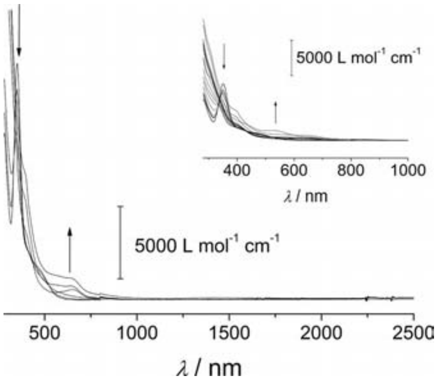


Figure 2. UV/Vis/NIR spectra of **9b** at rising potentials (–0.2 to 1.2 V vs. Ag/AgCl) at 25 °C in dichloromethane with [N(nBu)$_4$][B(C$_6$F$_5$)$_4$]. Arrows indicate increasing or decreasing of absorptions.

Single-Crystal X-ray Structure Determination

The molecular structure of **4b** was solved by single-crystal X-ray structure analysis. Suitable crystals were obtained from a saturated dichloromethane solution of **4b** at ambient temperature. The ORTEP diagram, selected bond lengths, bond angles, and torsion angles are shown in Figure 3. The crystal and structure refinement data are presented in the Exp. Section.

Compound **4b** crystallizes in the monoclinic space group $P2_1/n$. The structure of **4b** comprises one ferrocenyl unit, in which the two cyclopentadienyl rings are within 3° of parallel orientation to each other. Two o-tolyl groups, the Fe(η^5-C$_5$H$_4$)(η^5-C$_5$H$_5$) unit, and one selenium atom are bound to the phosphorus atom, which results in its tetrahedrally distorted geometry (Figure 3). The P–C bond lengths of 1.795(3) and 1.829(3) Å are representative for P–C$_{\text{aryl}}$ entities.[4b,6d,13,14] The P1–Se1 bond length of 2.1198(7) Å is characteristic of selenophosphanes (e.g. tri-o-tolylselenophosphane)[13,14] that contain electron-donating methyl substituents. As result, the s character of the p orbital involved in bonding to Se is decreased (vide infra). The C–P–C angles at P1 (Figure 3) are 103.74(12)–110.63(12)°, which is in the range typical for tertiary selenophosphanes.[4b,6d,13,14] Notably, the Se1–H12 distance of 2.830 Å is less than the sum of the van der Waals radii (3.10[15a]–3.35[15b]Å), which might be a reason for the broadened sig-

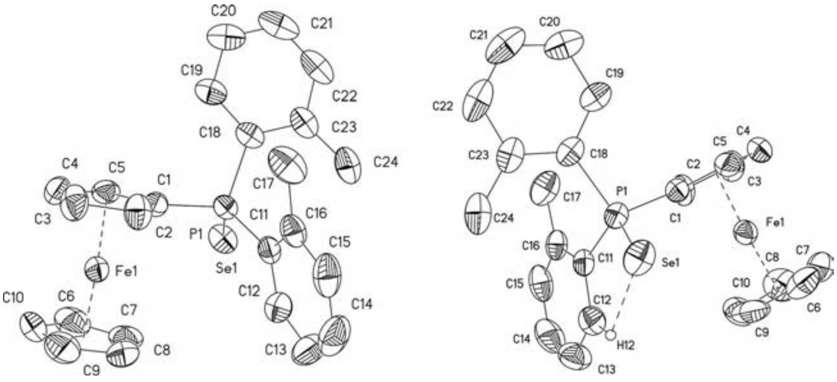


Figure 3. Left: ORTEP diagram (50% probability level) of the molecular structure of **4b** with the atom numbering scheme. Hydrogen atoms are omitted for clarity. Standard uncertainties of the last significant digit(s) are shown in parenthesis (D1 = the centroid of C_5H_4; D2 = the centroid of C_5H_5). Selected bond lengths [Å], bond angles [°], and torsion angles [°]: Fe–D1 1.673, Fe–D2 1.645, C1–P1 1.795(3), C11–P1 1.829(3), C18–P1 1.818(3), P1–Se1 2.1198(7); C1–P1–Se1 112.30(9), C11–P1–Se1 114.04(8), C18–P1–Se1 109.92(8), C1–P1–C11 103.74(12), C1–P1–C18 105.78(12), C18–P1–C11 110.63(12), D1–Fe–D2 176.8; C16–C11–P1–Se1 163.3(2), C12–C11–P1–Se1 –20.2(2), C23–C18–P1–Se1 –69.1(2), C5–C1–P1–Se1 –36.9(2), P1–C18–C23–C24 –6.3(4), P1–C11–C16–C17 –4.8(4). Right: Visualization of the short intramolecular Se1–H12 contact [*d*(Se1···H12) = 2.830 Å].

nals in the NMR spectra (vide infra). All other structural parameters are unexceptional and correspond to those of related compounds.[4b,6d,13,14] However, the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4b** and **6b** show very broad resonances for both the C_5H_4 and *o*-tolyl protons, which indicates dynamic behavior (Figure 4). Nevertheless, for both compounds it is typical that the $^{31}P\{^{1}H\}$ NMR signal of phosphorus(V) displays a sharp singlet at ambient temperature. The free rotation of the phosphanyl group was reduced by cooling the NMR sample of **4b** to –90 °C, which resulted in the appearance of four individual signals for the protons of the C_5H_4 moieties and eight aromatic signals of equal intensity for both *o*-tolyl units (Figure 4). This observation indicates that the *o*-tolyl units are not symmetrically equivalent, and a fast inversion of the configuration of phosphorus must occur at ambient temperature, which is frozen at –90 °C on the NMR timescale. Furthermore, the values of the $^{1}J_{^{31}P^{13}C}$ coupling constants of both *o*-tolyl moieties are almost equal, which indicates that the *o*-tolyl groups have no significant influence on the spatial orientation of the P–C configuration. Heteronuclear single quantum coherence and *H,H*-COSY measurements were performed to completely assign all of the peaks to the respective hydrogen and carbon atoms (see Supporting Information, Figure S1). The splitting pattern of the NMR signals reveals a C_2 symmetry for **4b** at low temperature in solution, which is in accordance with the XRD analysis. Moreover, the ^{1}H NMR signals assigned to the *ortho* protons of the tolyl moiety shift significantly upon cooling, which might be explained by their close proximity to the selenium atom (vide supra).

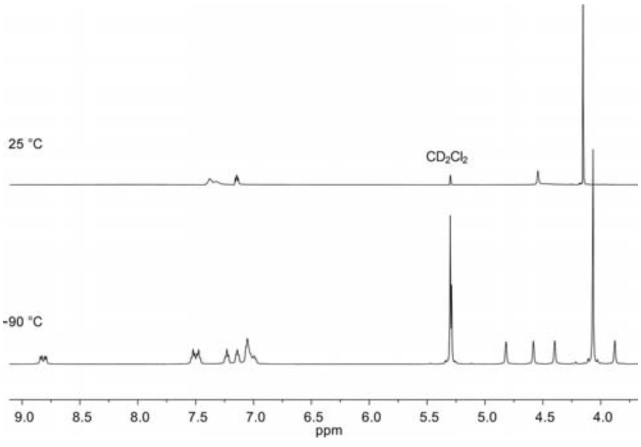


Figure 4. ^{1}H NMR spectra of **4b** between 3.5 and 9.5 ppm in CD_2Cl_2 at 25 °C (top) and at –90 °C (bottom).

The donor properties of PR_3 (R = alkyl, aryl, alkoxyl) towards selenium acceptors can be quantified by $^{1}J_{^{31}P^{77}Se}$ obtained from $^{31}P\{^{1}H\}$ NMR spectroscopy.[6] An electron-withdrawing group at phosphorus increases the value of $^{1}J_{^{31}P^{77}Se}$, which is explained by the increased s character of the phosphorus orbital involved in the P–Se bonding. Consequently, shorter bond lengths between the phosphorus and the acceptor carbon atoms are observed. This electronic impact has a direct influence on the phosphorus donor ability and, hence, on the electron density in the corresponding transition metal complex. The absolute value of $^{1}J_{^{31}P^{77}Se}$ is a decisive parameter for the specific design of compounds used as catalytically active species in homogeneous catalysis (vide infra). The $^{31}P\{^{1}H\}$ NMR spectroscopic data together with the values of $^{1}J_{^{31}P^{77}Se}$ for **4a–e** and **7a–d** are summarized in Table 5.

Table 5. Chemical shifts [ppm] and $^{1}J_{^{31}P^{77}Se}$ [Hz] values for **4a–e**, **7a–d**, and $Ph_3P{=}Se$[6a] for comparison.

	δ	$^{1}J_{^{31}P^{77}Se}$		δ	$^{1}J_{^{31}P^{77}Se}$
4a	31.8	733	**7a**	31.2	735
4b	29.4	716	**7b**	29.0	718
4c	–5.3	769	**7c**	–6.8	772
4d	74.7	702	**7d**	49.2	704
4e	49.8	700	$Ph_3P{=}Se$[6a]	35.9	732

From Table 5 it can be seen that **4c** and **7c**, which contain furyl ligands, are, as expected, the most electron-poor phosphanes as indicated by the absolute value of $J_{^{31}\text{P}^{77}\text{Se}}$. The most electron-donating systems are the aliphatic *t*-butyl (**4d**) and cyclohexyl (**4e**, **7d**) selenophosphanes with $^1J_{^{31}\text{P}^{77}\text{Se}} \approx 700$ Hz (Table 5). The ruthenocenyl-phosphanes have slightly higher coupling constants than the isostructural ferrocenyl derivatives, which emphasizes that the ferrocenyl-phosphanes are somewhat better σ donors. The data summarized in Table 5 indicate the suitability of the metallocenyl-phosphanes as ligands in, for example, Heck and Suzuki reactions. Furthermore, it is possible to compare the $J_{^{31}\text{P}^{77}\text{Se}}$ values of **4a**–**e** with the redox potentials E_1^0 of **9a**–**e**, which results in a linear correlation (Figure 5). It is obvious that only molecules that feature aromatic groups on the phosphorus atom fit this correlation, whereas the aliphatic phosphanes differ. This is most likely attributed to the different hybridization and, hence, geometry of the groups at the phosphorus atom. Therefore, it is necessary to exclusively compare structurally related molecules.

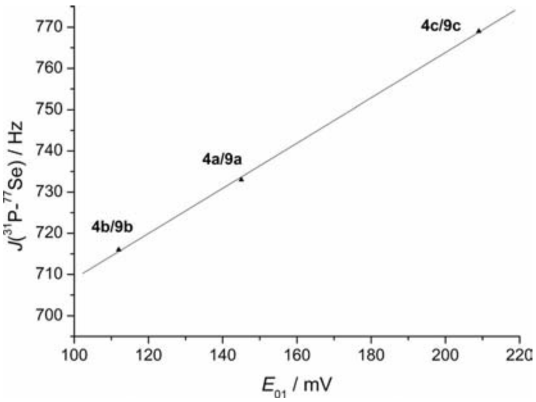
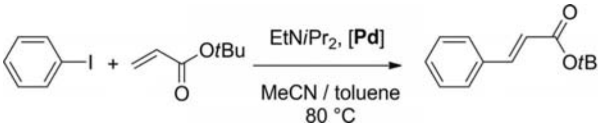


Figure 5. Correlation of E_1^0 and $^1J_{^{31}\text{P}^{77}\text{Se}}$ for **4a/9a**, **4b/9b**, and **4c/9c**.

Catalytic Investigations – Heck Catalysis

The reaction of iodobenzene with *tert*-butyl acrylate to give *E*-*tert*-butylcinnamate (Reaction 2) was used as the standard reaction to compare the catalytic activity of **9** and **10** with the known catalysts [$\text{PdCl}_2(\text{P}(iso\text{-C}_3\text{H}_7)_2\text{Fc})_2$] and [$\text{PdCl}_2$(disoppf)] [disoppf = 1,1′-bis(diisopropylphosphanyl)ferrocene].[4d] The reactions were performed in a mixture of toluene and acetonitrile (1:1, v/v) with a catalyst loading of 0.2 mol-% at 80 °C for 10 and 25 h. EtN(iso-C_3H_7)$_2$ was added as base and acetyl ferrocene as the internal standard (Table 6; reaction profiles are given in Figure S2). The conversions were determined by ^{1}H NMR spectroscopy (see Exp. Section).



(2)

It was found that **9d**, which has *tert*-butylphosphanyl ligands, was the most active catalyst (Entry 4, Table 6, Figure S2) within the series. Complexes **9b**, **9c**, and **9e** (Entries 2, 3, and 5; Table 6) are somewhat less active, which is explained by the more electron-rich phosphane **3d** providing a greater electronic stabilization to the active catalyst **9d**. The ruthenocenyl-based catalysts **10a**–**d** are less active than the ferrocenyl-based complexes with conversions of 76–84% after 25 h, which show no clear electronic dependency. However, catalysts **9** and **10** show some benefits in homogeneous catalysis compared with previously reported ferrocenyl mono- and diphosphanes[4d] (Entries 6 and 7, Table 6), which are (i) significantly lower catalyst loadings, (ii) no addition of a reductant (CuI) is necessary, and (iii) their high regioselectivity (only the *E* isomer was formed). The difference to the systems used by Butler and Boyes[4d] can be ascribed to electronic and steric factors, of which the bis(*tert*-butyl) ferrocenyl-phosphane has the optimum balance of both criteria. The fact that only one isomer was produced can be explained by the steric congestion of the *tert*-butyl groups (vide supra). This is in accordance with the observations made by Butler and Boyes, who used palladium(II) complexes of (diisopropylphosphanyl)ferrocenes, and associated their results with the lower flexibility and chelate effect of the sandwich compound. Nevertheless, the ferrocenyl and ruthenocenyl-phosphanes **3** and **6** are less active in the palladium-promoted Heck reaction than catalytic systems used to date.[2f,1,1m–1o]

Catalytic Investigations – Suzuki Catalysis

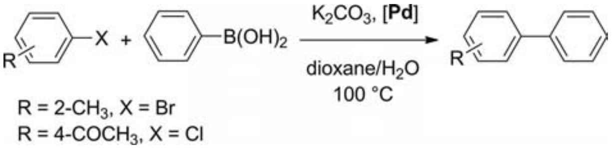
Complexes **9** and **10** were also applied to the Suzuki reaction of 2-bromotoluene or 4′-chloroacetophenone with phenylboronic acid in the presence of potassium carbonate

Table 6. Heck reaction of iodobenzene with *tert*-butyl acrylate catalyzed by **9** and **10** (0.2 mol-%), yields with [$\text{PdCl}_2(\text{P}(iso\text{-C}_3\text{H}_7)_2\text{Fc})_2$] and [$\text{PdCl}_2$(disoppf)] are given for comparison.[a]

Entry	Compound	% Conversion[b]	% Conversion[c]	Entry	Compound	% Conversion[b]	% Conversion[c]
1	**9a**	44.9	69.9	7	[PdCl_2(disoppf)]	–	100[c]
2	**9b**	76.4	94.7	8	**10a**	57.1	81.0
3	**9c**	65.2	89.5	9	**10b**	67.0	77.1
4	**9d**	100	100	10	**10c**	57.7	76.4
5	**9e**	59.8	90.0	11	**10d**	72.6	84.3
6	[$\text{PdCl}_2(\text{P}(iso\text{-C}_3\text{H}_7)_2\text{Fc})_2$]	–	96[a]				

[a] GLC yields after heating to reflux for 24 h with a catalyst loading of 1.0 mol-%.[4d] [b] Conversion after 10 h. [c] Conversion after 25 h.

as a base in a mixture of 1,4-dioxane and water (2:1, v/v) at 100 °C (Reaction 3). Acetyl ferrocene was added as the internal standard for conversion determinations by ^{1}H NMR spectroscopy.



(3)

As seen from Table 7 and the reaction profiles (Figures 6 and S3), all of the complexes are active in Pd-catalyzed Suzuki cross-couplings (vide supra), which reflects the electronic dependency of **3** and **6**, to give 2-methylbiphenyl and 4′-acetylbiphenyl as the only products (Figure S4). The most active catalysts for C–Br activation are the electron-rich ferrocenyl systems **9a**, **9b**, **9d**, and **9e**, and the ruthenocenyls **10b** and **10d**, whose reactions reached complete conversion after 2–20 min (Figure S3). The reaction of activated 4′-chloroacetophenone with phenyl boronic acid requires, as expected, longer conversion times and higher catalyst loadings (0.5 mol-%), in which only reactions with aliphatic **9d** and **9e** reached completion within 10 min and that of **10d** after 20 min. All of the other species were significantly less active and showed conversions below 60 % after 2 h (Entries 6–8 and 19–21, Table 7, Figure 6). Furthermore, it was found that the ruthenocenyl-phosphane palladium systems are somewhat less active than the isostructural ferrocenyls, which can be explained by the fact that the ferrocenyl species are more electron-rich. This also is reflected by the slightly higher $^{1}J_{^{31}P^{77}Se}$ coupling constants (vide supra, Table 5). These results are in accordance with the general statement that electron-rich, bulky phosphanes are suitable ligands for Suzuki C–C coupling reactions.[4c,5a,5b] However, **9** and **10** are somewhat less active than currently used catalytic systems.[2e–2h,2j–2l,4e,7e]

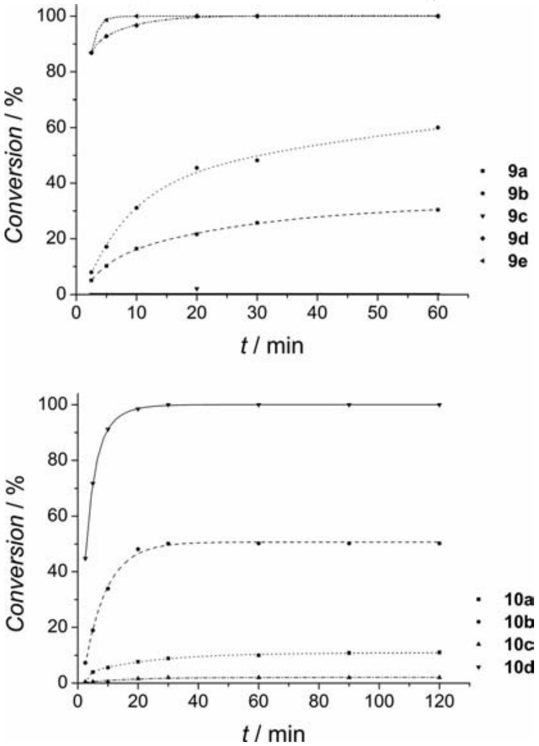


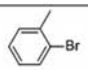
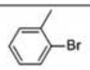
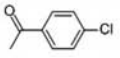
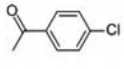
Figure 6. Reaction profiles for **9a**–**e** (top) and **10a**–**d** (bottom) for the reaction of 4′-chloroacetophenone with phenylboronic acid and a catalyst loading of 0.5 mol-%.

Because the Suzuki reaction strongly depends on the electronic nature of the phosphane, we could show that a relationship between phosphane basicity and catalytic activity exists. The lower the value of $^{1}J_{^{31}P^{77}Se}$ and, hence, the more basic the phosphane, the higher the catalytic activity.

Conclusions

The synthesis of a series of metallocenyl-phosphane palladium dichloride complexes of the type [$PdCl_2(PR_2Mc)_2$] is reported. These complexes were prepared by treatment of

Table 7. Reaction of 2-bromotoluene and 4′-chloroacetophenone with phenylboronic acid after 1 h with different catalyst loadings.

Entry		Aryl halide	Catalyst loading (mol-%)	Conversion (%)	Entry		Aryl halide	Catalyst loading (mol-%)	Conversion (%)
1	**9a**		0.1	100	11	**10a**		0.25	85.8
2	**9b**			100	12			0.1	26.7
3	**9c**			100	13	**10b**		0.25	100
4	**9d**			100	14			0.1	100
5	**9e**			100	15	**10c**		0.25	100
6	**9a**		0.5	30.4	16			0.1	4.0
7	**9b**			60.0	17	**10d**		0.25	100
8	**9c**			0	18			0.1	100
9	**9d**			100	19	**10a**		0.5	10.0
10	**9e**			100	20	**10b**			50.2
					21	**10c**			2.0
					22	**10d**			100

phosphanes R_2PMc with $[PdCl_2(cod)]$. CV measurements showed that the metallocenyl-functionalized aromatic phosphanes are first reversibly oxidized at the metallocenyl fragment when measuring to 0.8 V. The resulting ferrocenium ion participates in intramolecular electron transfer processes from the PR_2 groups to the transition metal ion. Irreversible oxidations occur on going to higher potentials (1.5 V). As expected, electron-rich phosphanes are easier to oxidize. This is verified in the series R = furyl < phenyl < *o*-tolyl, however, aliphatic phosphanes show a similar electronic character and completely irreversible behavior. Additionally, we investigated the electrochemical behavior of the selenophosphanes **4a**–**e** and the bis(phosphanyl)palladium(II) complexes **9a**–**e**, in which the lone pair of electrons at phosphorus atom is part of a phosphorus–selenium or phosphane–palladium bond. Nevertheless, as described earlier,[9,12b] the selenophosphanes also show follow-up products, which presumably result from an intramolecular electron transfer from the selenium-centered radical. Therefore, contributions from either the iron, phosphorus, or selenium radicals are expected in the monocationic species. Such oxidations are inhibited when the phosphorus atom is datively bonded to palladium, as in **9a**–**e**. As expected, the bis(phosphanyl) palladium complexes are more difficult to oxidize, which can be explained by their electron-withdrawing character upon coordination of the phosphane to Pd. UV/Vis/NIR spectroscopy revealed the absence of any NIR charge-transfer bands, which indicate electrostatic interactions. For classification of the σ donor ability of the phosphanes, the corresponding selenophosphanes, $Se{=}PR_2Mc$, were prepared by addition of elemental selenium.[6] High $J_{^{31}P^{77}Se}$ values indicate electron-poor phosphanes and hence, a lower donor capability. Furthermore, it is possible to correlate the $J_{^{31}P^{77}Se}$ values with the redox potential E_1^0 of the (ferrocenyl-phosphane)palladium complexes, which results in a linear correlation for the aromatic phosphanes. For the aliphatic *tert*-butyl and cyclohexyl derivatives a different behavior is observed, which is most probably because of the different hybridization. The bis(metallocenylphosphane) palladium(II) complexes were applied as catalysts in C–C cross-coupling reactions. In the Heck reaction, iodobenzene was treated with *tert*-butyl acrylate. All of the complexes were catalytically active, and the most efficient catalyst featured tBu_2PFc, which is explained by the fact that this ligand is bulky and electron rich. All of the palladium(II) complexes were active in the Suzuki coupling of aryl bromide and activated aryl chloride. A correlation was found between the basicity of the phosphanes and the catalytic activity of the corresponding complexes. The lower the ${}^1J_{^{31}P^{77}Se}$ coupling constant and, hence, the more basic the phosphane, the higher the catalytic activity. The catalysts reported here are less active than current catalytic systems,[2,4f,7e] but show higher activity under similar reaction conditions compared with other metallocenyl mono- and diphosphane palladium catalysts.[4b,4c] Moreover, they are active at lower catalyst loadings (Heck and Suzuki catalysis), require no additional reductant (CuI), and show high regioselectivity (Heck catalysis).

Experimental Section

General Methods: All reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Toluene and tetrahydrofuran were purified by distillation with sodium and sodium/benzophenone, respectively; dichloromethane was purified by distillation with calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel-de Haën) was used for filtrations. Alumina with a particle size of 90 µm (standard, Merck KGaA) or silica with a particle size of 40–60 µm [230–400 mesh (ASTM), Becker] was used for column chromatography.

Instrumentation: NMR spectra were recorded with a Bruker Avance III 500 spectrometer [500.3 MHz for ^1H, 125.7 MHz for $^{13}C(^1H)$, and 202.5 MHz for $^{31}P(^1H)$ NMR spectra]. Chemical shifts are reported in (parts per million) downfield from tetramethylsilane with the solvent as the reference signal [^1H NMR $\delta = 7.26$ for $CDCl_3$ and $\delta = 5.30$ for CD_2Cl_2; $^{13}C(^1H)$ NMR $\delta = 77.16$ for $CDCl_3$ and $\delta = 53.52$ for CD_2Cl_2]. HRMS were recorded with a Bruker Daltonik micrOTOF-QII spectrometer (ESI-TOF). Elemental analyses were measured with a Thermo FlashAE 1112 series instrument, and melting points of analytical pure samples were determined with a Gallenkamp MFB 595 010 M melting point apparatus. FTIR spectra were recorded with a Thermo Nicolet IR 200 spectrometer using KBr pellets or NaCl plates.

Electrochemistry: Measurements on 1.0 mmol L^{-1} solutions of **3**, **4**, and **9** in dry, degassed dichloromethane with 0.1 mol L^{-1} of $[N(nBu)_4][B(C_6F_5)_4]$ as the supporting electrolyte were carried out under argon at 25 °C with a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. A three electrode cell with a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.031 cm^2), and an Ag/Ag$^+$ (0.01 mmol L^{-1} $[AgNO_3]$) reference electrode fixed on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with 1 micron and then 1/4 micron diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of 0.01 mmol L^{-1} $[AgNO_3]$ and 0.1 mol L^{-1} $[N(nBu)_4][B(C_6F_5)_4]$ in acetonitrile, in a Luggin capillary with a vicor tip. This Luggin capillary was inserted into a second Luggin capillary with vicor tip filled with a 0.1 mmol L^{-1} $[N(nBu)_4][B(C_6F_5)_4]$ solution in dichloromethane. Experiments under the same experimental conditions showed that all reduction and oxidation potentials were reproducible within 15 mV. Experimental potentials were referenced against an Ag/Ag$^+$ reference electrode but the presented results are referenced against ferrocene as an internal standard as required by IUPAC.[10] Data were processed on a Microsoft Excel® worksheet to set the formal reduction potentials of the FcH/FcH$^+$ couple to 0.0 V. Under these conditions, the FcH/FcH$^+$ couple was at 260 mV vs. Ag/Ag$^+$, $\Delta E_p = 92$ mV.

Spectroelectrochemistry: Spectroelectrochemical UV/Vis/NIR measurements of a 1.0 mmol L^{-1} solution of **9b** in dry degassed dichloromethane containing 0.1 mol L^{-1} of $[N(nBu)_4][B(C_6F_5)_4]$ as the supporting electrolyte were carried in an OTTLE cell[12f,12g] with a Varian Cary 5000 spectrophotometer.

Materials: All starting materials were obtained from commercial suppliers and used without further purification. Iodoferrocene[16] (**1**), iodoruthenocene[16,17] (**5**), ferrocenyl-diphenylphosphane[18] (**3a**), ferrocenyl-di-*tert*-butylphosphane[19] (**3d**), ferrocenyl-dicyclohexylphosphane[20] (**3e**), $[PdCl_2(P(C_6H_5)_2Fc)_2]$[4e] (**9a**), $[PdCl_2(P(tBu)_2Fc)_2]$[21] (**9d**), chlorophosphanes (**2b**–**e**),[22–25] and $[PdCl_2(cod)]$[26] (**8**) were prepared according to published procedures.

General Procedure for the Synthesis of Phosphanes 3 and 6: To **1** or **5** dissolved in dry tetrahydrofuran (50 mL) was added one equivalent of a 2.5 M solution of *n*BuLi dropwise at –60 °C. After stirring the solution for 30 min at ambient temperature, it was cooled to –30 °C, and one equivalent of the appropriate chlorophosphane **2a**–**e** was added dropwise. The reaction mixture was stirred for 1 h at ambient temperature and then concentrated in vacuo. The resulting residue was purified by column chromatography and dried in vacuo.

$P(2\text{-}CH_3C_6H_4)_2Fc$ (3b): Using the general procedure described above, **1** (1.0 g, 3.21 mmol) was treated with *n*BuLi (1.30 mL, 3.21 mmol) and chlorodi-*o*-tolylphosphane (**2b**, 0.80 g, 3.21 mmol). The resulting residue was purified by column chromatography (column size: 3.5 × 15 cm on silica gel) using *n*-hexane as eluent to give **3b** as an orange solid; yield 0.88 g (2.21 mmol, 69% based on **1**). $C_{24}H_{23}FeP$ (398.26): calcd. C 72.38, H 5.82; found C 72.40, H 5.94; m.p. 168 °C. IR (KBr): $\tilde{\nu}$ = 752 (s, =C–H, *o*-disubst. benzene), 1465 (m, P–C), 1585/1623 (w, C=C), 2845/2908/2965 (w, C–H), 3003/3041 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 2.56 (s, 6 H, CH_3), 4.10 (s, 5 H, C_5H_5), 4.19 (dpt, $^3J_{HP}$ = 1.8, $^3J_{HH}$ = 1.8 Hz, 2 H, H^{α}/C_5H_4), 4.44 (pt, $^3J_{HH}$ = 1.8 Hz, 2 H, H^{β}/C_5H_4), 7.10 (m, 4 H, H^{o}/C_6H_4), 7.18–7.25 (m, 6 H, $H^{m,p}/C_6H_4$) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 21.4 (d, $^3J_{CP}$ = 21.8 Hz, CH_3), 69.1 (s, C_5H_5), 70.9 (d, $^3J_{CP}$ = 4.2 Hz, C^{β}/C_5H_4), 73.4 (d, $^2J_{CP}$ = 15.3 Hz, C^{α}/C_5H_4), 75.8 (d, $^1J_{CP}$ = 6.0 Hz, C^{i}/C_5H_4), 125.7 (s, C^{p}/C_6H_4), 128.5 (s, C^{m}/C_6H_4), 129.9 (d, $^3J_{CP}$ = 5.2 Hz, C^{m}/C_6H_4), 133.5 (s, C^{o}/C_6H_4), 137.9 (d, $^1J_{CP}$ = 10.8 Hz, C^{i}/C_6H_4), 141.7 (d, $^2J_{CP}$ = 26.3 Hz, C^{o}/C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = –36.4 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{24}H_{23}FeP$ $[M]^+$ 398.0882; found 398.0836.

$P(c\text{-}C_4H_3O)_2Fc$ (3c): Using the general procedure described above, **1** (1.0 g, 3.21 mmol) was treated with *n*BuLi (1.30 mL, 3.21 mmol) and chlorodifurylphosphane (**2c**, 0.64 g, 3.21 mmol). The resulting residue was purified by column chromatography on silica gel (column size: 3.5 × 15 cm) using *n*-hexane as eluent to give **3c** as an orange solid; yield 0.71 g (2.02 mmol, 63% based on **1**). $C_{18}H_{15}FeO_2P$ (350.13): calcd. C 61.75, H 4.32; found C 61.37, H 4.32; m.p. 115 °C. IR (KBr): $\tilde{\nu}$ = 1009 (s, C–O), 1459 (m, P–C), 1550/1560/1638/1654 (w, C=C), 3078/3125/3147 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 4.04 (s, 5 H, C_5H_5), 4.35 (pt, $^3J_{HH}$ = 1.5 Hz, H^{β}/C_5H_4), 4.44 (dpt, $^3J_{HP}$ = 1.9, $^3J_{HH}$ = 1.8 Hz, H^{α}/C_5H_4), 6.40 (dt, $^4J_{HP}$ = 1.6, $^3J_{HH}$ = 3.2, $^3J_{HH}$ = 1.6 Hz, 2 H, H^{4}/C_4H_3O), 6.69 (m, 2 H, H^{3}/C_4H_3O), 7.64 (m, 2 H, H^{5}/C_4H_3O) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 69.2 (s, C_5H_5), 70.9 (d, $^3J_{CP}$ = 5.4 Hz, C^{β}/C_5H_4), 72.5 (d, $^1J_{CP}$ = 5.1 Hz, C^{i}/C_5H_4), 73.7 (d, $^2J_{CP}$ = 18.3 Hz, C^{α}/C_5H_4), 110.6 (d, $^3J_{CP}$ = 6.2 Hz, C^{4}/C_4H_3O), 119.8 (d, $^2J_{CP}$ = 23.6 Hz, C^{3}/C_4H_3O), 146.7 (d, $^3J_{CP}$ = 2.4 Hz, C^{5}/C_4H_3O), 152.6 (d, $^1J_{CP}$ = 8.3 Hz, C^{2}/C_4H_3O) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = –64.4 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{18}H_{15}FeO_2P$ $[M]^+$ 350.0154; found 350.0116.

General Procedure for the Synthesis of Selenophosphanes 4 and 7: To a toluene solution (20 mL) of **3** or **6** (100 mg) was added 1.2 equivalents of elemental selenium in a single portion, and the reaction mixture was stirred for 1 h at 100 °C. After cooling to ambient temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was dried under vacuum.

$Se{=}P(C_6H_5)_2Fc$ (4a): The reaction of **3a** (100 mg, 0.27 mmol) with elemental selenium (26 mg, 0.33 mmol) gave **4a** as an orange solid; yield 120 mg (0.27 mmol, 100% based on **3a**). $C_{22}H_{19}FePSe$ (449.17): calcd. C 58.83, H 4.26; found C 58.90, H 4.28. IR (KBr): $\tilde{\nu}$ = 572 (s, P=Se), 1434 (m, P–C), 1638 (m, C=C), 3071 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 4.16 (s, 5 H, C_5H_5), 4.45 (dpt, $^3J_{HP}$ = 2.1, $^3J_{HH}$ = 1.9 Hz, 2 H, H^{α}/C_5H_4), 4.52 (dpt, $^4J_{HP}$ = 1.7, $^3J_{HH}$ = 1.8 Hz, 2 H, H^{β}/C_5H_4), 7.38–7.42 (m, 4 H, H^{m}/C_6H_5), 7.44–7.46 (m, 2 H, H^{p}/C_6H_5), 7.70–7.74 (m, 4 H, H^{o}/C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 70.2 (s, C_5H_5), 72.0 (d, $^3J_{CP}$ = 10.0 Hz, C^{β}/C_5H_4), 73.4 (d, $^2J_{CP}$ = 12.6 Hz, C^{α}/C_5H_4), 74.0 (d, $^1J_{CP}$ = 89.2 Hz, C^{i}/C_5H_4), 128.2 (d, $^2J_{CP}$ = 12.6 Hz, C^{o}/C_6H_5), 131.3 (d, ^4JCP = 2.9 Hz, C^{p}/C_6H_5), 132.1 (d, $^3J_{CP}$ = 10.9 Hz, C^{m}/C_6H_5), 133.6 (d, $^1J_{CP}$ = 78.4 Hz, C^{i}/C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = 31.8 ($^1J_{^{31}P^{77}Se}$ = 733.2 Hz) ppm. HRMS (ESI-TOF): calcd. for $C_{22}H_{19}FePSe$ $[M + nH]^+$ 450.9814; found 450.9757; $[M + nH + MeCN]^+$ 489.9923; found 489.9812.

$Se{=}P(2\text{-}CH_3C_6H_4)_2Fc$ (4b): Using the general procedure described above, **3b** (100 mg, 0.25 mmol) was treated with elemental selenium (24 mg, 0.30 mmol) to give **4b** as an orange solid; yield 119 mg (0.25 mmol, 100% based on **3b**). $C_{24}H_{23}FePSe$ (477.22): calcd. C 60.40, H 4.86; found C 60.49, H 5.34. IR (KBr): $\tilde{\nu}$ = 560/575 (s, P=Se), 761 (s, =C–H, *o*-disubst. benzene), 1449 (m, P–C), 1635 (m, C=C), 2857/2917/2965 (w, C–H), 3002/3034/3088 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, CD_2Cl_2, –90 °C): δ = 1.70 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 3.88 (m, 1 H, H^{β}/C_5H_4), 4.07 (s, 5 H, C_5H_5), 4.40 (m, 1 H, H^{α}/C_5H_4), 4.58 (m, 1 H, H^{β}/C_5H_4), 4.82 (m, 1 H, H^{α}/C_5H_4), 7.00 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, H^{o}/C_6H_4), 7.03 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, H^{m}/C_6H_4), 7.06 (t, $^3J_{HH}$ = 6.9 Hz, 1 H, H^{m}/C_6H_4), 7.14 (t, $^3J_{HH}$ = 6.1 Hz, 1 H, H^{m}/C_6H_4), 7.23 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, H^{p}/C_6H_4), 7.47 (t, $^3J_{HH}$ = 7.2 Hz, 1 H, H^{p}/C_6H_4), 7.52 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, H^{m}/C_6H_4), 8.82 (dd, $^3J_{HP}$ = 18.2, $^3J_{HH}$ = 7.5 Hz, 1 H, H^{o}/C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, CD_2Cl_2, –90 °C): δ = 19.9 (d, $^3J_{CP}$ = 6.1 Hz, CH_3), 22.0 (d, $^3J_{CP}$ = 3.5 Hz, CH_3), 69.6 (s, C_5H_5), 71.2 (d, $^2J_{CP}$ = 9.1 Hz, C^{α}/C_5H_4), 71.5 (d, $^3J_{CP}$ = 5.5 Hz, C^{β}/C_5H_4), 71.6 (d, $^3J_{CP}$ = 5.4 Hz, C^{β}/C_5H_4), 72.2 (d, $^1J_{CP}$ = 90.1 Hz, C^{i}/C_5H_4), 74.5 (d, $^2J_{CP}$ = 14.0 Hz, C^{α}/C_5H_4), 125.4 (d, $^3J_{CP}$ = 12.2 Hz, C^{m}/C_6H_4), 125.6 (d, $^1J_{CP}$ = 72.2 Hz, C^{i}/C_6H_4), 126.0 (d, $^3J_{CP}$ = 14.1 Hz, C^{m}/C_6H_4), 128.8 (d, $^2J_{CP}$ = 10.5 Hz, C^{o}/C_6H_4), 130.2 (d, $^4J_{CP}$ = 2.0 Hz, C^{p}/C_6H_4), 130.6 (d, $^3J_{CP}$ = 9.9 Hz, C^{m}/C_6H_4), 130.9 (d, $^3J_{CP}$ = 10.5 Hz, C^{m}/C_6H_4), 131.3 (d, $^4J_{CP}$ = 2.7 Hz, C^{p}/C_6H_4), 133.6 (d, $^1J_{CP}$ = 77.8 Hz, C^{i}/C_6H_4), 135.1 (d, $^2J_{CP}$ = 17.0 Hz, C^{o}/C_6H_4), 138.6 (d, $^2J_{CP}$ = 6.4 Hz, C^{o}/C_6H_4), 138.9 (d, $^2J_{CP}$ = 10.4 Hz, C^{o}/C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = 29.4 ($^1J_{^{31}P^{77}Se}$ = 715.5 Hz) ppm. HRMS (ESI-TOF): calcd. for $C_{24}H_{23}FePSe$ $[M]^+$ 478.0049; found 478.0004; $[M + nK]^+$ 516.9685; found 516.9624.

$Se{=}P(c\text{-}C_4H_3O)_2Fc$ (4c): Using the general procedure described above, **3c** (100 mg, 0.29 mmol) was treated with selenium (26 mg, 0.34 mmol) to give **4c** as an orange solid; yield 124 g (0.29 mmol, 100% based on **3c**). $C_{18}H_{15}FeO_2PSe$ (429.09): calcd. C 50.38, H 3.52; found C 50.53, H 3.48; m.p. 80 °C. IR (KBr): $\tilde{\nu}$ = 577 (m, P=Se), 1005 (m, C–O), 1458 (w, P–C), 3080/3105/3119 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 4.17 (s, 5 H, C_5H_5), 4.51 (dpt, $^4J_{HP}$ = 1.8, $^3J_{HH}$ = 1.8 Hz, 2 H, H^{β}/C_5H_4), 4.60 (pt, $^3J_{HP}$ = 2.3, $^3J_{HH}$ = 2.1 Hz, 2 H, H^{α}/C_5H_4), 6.49 (dpt, $^4J_{HP}$ = 1.7, $^3J_{HH}$ = 3.4, $^3J_{HH}$ = 1.6 Hz, 2 H, H^{4}/C_4H_3O), 7.11 (m, 2 H, H^{3}/C_4H_3O), 7.71 (m, 2 H, H^{5}/C_3H_4O) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 70.4 (s, C_5H_5), 72.1 (d, $^3J_{CP}$ = 11.1 Hz, C^{β}/C_5H_4), 73.1 (d, $^2J_{CP}$ = 14.5 Hz, C^{α}/C_5H_4), 111.2 (d, $^3J_{CP}$ = 9.1 Hz, C^{4}/C_4H_3O), 122.2 (d, $^2J_{CP}$ = 21.8 Hz, C^{3}/C_4H_3O), 147.4 (d, $^1J_{CP}$ = 114.3 Hz, C^{2}/C_4H_3O), 148.3 (d, $^4J_{CP}$ = 7.1 Hz, C^{5}/C_4H_3O) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = –5.3 ($^1J_{^{31}P^{77}Se}$ = 769.3 Hz) ppm. HRMS (ESI-TOF): calcd. for $C_{18}H_{15}FeO_2PSe$ $[M + nH]^+$ 430.9388; found 430.9399.

$Se{=}P(tBu)_2Fc$ (4d): Using the general procedure described above, **3d** (100 mg, 0.30 mmol) was treated with selenium (28 mg, 0.36 mmol) to give **4d** as an orange solid; yield 122 g (0.30 mmol, 100% based on **3d**). $C_{18}H_{27}FePSe$ (409.19): calcd. C 52.83, H 6.65; found C 52.81, H 6.81; m.p. 145 °C. IR (KBr): $\tilde{\nu}$ = 565 (m, P=Se), 1456 (P–C), 2867/2899/2968/2951/2988 (m, C–H), 3085 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 1.39 [d, $^{3}J_{HP}$ = 15.4 Hz, 18 H, $C(CH_3)_3$], 4.32 (s, 5 H, C_5H_5), 4.47 (dpt, $^{4}J_{HP}$ = 1.6, $^{3}J_{HH}$ = 1.5 Hz, 2 H, H^{β}/C_5H_4), 4.59 (dpt, $^{3}J_{HP}$ = 1.7, $^{3}J_{HH}$ = 1.5 Hz, 2 H, H^{α}/C_5H_4) ppm. $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 28.9 [d, $^{2}J_{CP}$ = 2.0 Hz, $C(CH_3)_3$], 38.3 [d, $^{1}J_{CP}$ = 36.2 Hz, $C(CH_3)_3$], 70.3 (d, $^{3}J_{CP}$ = 8.2 Hz, C^{β}/C_5H_4), 70.7 (s, C_5H_5), 73.8 (d, $^{2}J_{CP}$ = 9.1 Hz, C^{α}/C_5H_4), 74.6 (d, $^{1}J_{CP}$ = 64.1 Hz, C^{i}/C_5H_4) ppm. $^{31}P\{^{1}H\}$ NMR (202.53 MHz, $CDCl_3$): δ = 74.7 ($^{1}J_{^{31}P^{77}Se}$ = 701.7 Hz) ppm. HRMS (ESI-TOF): calcd. for $C_{18}H_{27}FePSe$ $[M]^+$ 410.0361; found 410.0312.

Se=P(c-C_6H_{11})$_2$Fc (4e): Using the general procedure described above, **3e** (100 mg, 0.26 mmol) was treated with selenium (24 mg, 0.31 mmol) to give **4e** as an orange solid; yield 119 mg (0.26 mmol, 100% based on **3e**). $C_{22}H_{31}FePSe$ (461.26): calcd. C 57.29, H 6.77; found C 57.40, H 6.99; m.p. 116 °C. IR (NaCl): $\tilde{\nu}$ = 531/551 (m, P=Se), 1453 (m, P–C), 2853/2930 (s, C–H), 3076/3097 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 1.14–1.21 (m, 2 H, C_6H_{11}), 1.23–1.31 (m, 6 H, C_6H_{11}), 1.33–1.40 (m, 2 H, C_6H_{11}), 1.66–1.69 (m, 2 H, C_6H_{11}), 1.81–1.86 (m, 4 H, C_6H_{11}), 1.97–2.03 (m, 6 H, C_6H_{11}), 4.32 (s, 5 H, C_5H_5), 4.41 (dpt, $^{3}J_{HP}$ = 1.8, $^{3}J_{HH}$ = 1.6 Hz, H^{α}/C_5H_4), 4.43 (dpt, $^{4}J_{HP}$ = 1.7, $^{3}J_{HH}$ = 1.6 Hz, H^{β}/C_5H_4) ppm. $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 26.0 (d, J_{CP} = 1.4 Hz, C_6H_{11}), 26.4 (d, J_{CP} = 1.6 Hz, C_6H_{11}), 26.6 (d, J_{CP} = 2.8 Hz, C_6H_{11}), 26.7 (d, J_{CP} = 1.8 Hz, C_6H_{11}), 27.4 (d, J_{CP} = 3.2 Hz, C_6H_{11}), 37.4 (d, $^{1}J_{CP}$ = 44.9 Hz, C_6H_{11}), 70.5 (d, $^{3}J_{CP}$ = 8.9 Hz, C^{β}/C_5H_4), 70.5 (s, C_5H_5), 72.2 (d, $^{2}J_{CP}$ = 10.0 Hz, C^{α}/C_5H_4), 72.6 (d, $^{1}J_{CP}$ = 71.0 Hz, C^{i}/C_5H_4) ppm. $^{31}P\{^{1}H\}$ NMR (202.53 MHz, $CDCl_3$): δ = 49.8 ($^{1}J_{^{31}P^{77}Se}$ = 699.9 Hz) ppm. HRMS (ESI-TOF): calcd. for $C_{22}H_{31}FePSe$ $[M + nH]^+$ 463.0743; found 463.0753; calcd. for $C_{22}H_{31}FePSeCH_3CN$ $[M + nH]^+$ 502.0843; found 502.0862.

P(C_6H_5)$_2$Rc (6a): Using the general procedure described above, **5** (2.0 g, 5.5 mmol) was treated with nBuLi (2.20 mL, 3.21 mmol) and chlorodiphenylphosphane (**2a**, 1.21 g, 5.5 mmol). The resulting residue was purified by column chromatography on ALOX (column size: 2.5 × 30 cm) using n-hexane/diethyl ether (5:1, v:v) as eluent. Phosphane **6a** was obtained as a pale yellow solid; yield 0.80 g (1.92 mmol, 35% based on **5**). $C_{22}H_{19}PRu$ (415.43): calcd. C 63.61, H 4.61; found C 63.55, H 4.62; m.p. 128 °C. IR (KBr): $\tilde{\nu}$ = 1432 (m, P–C), 1477/1652 (w, C=C), 3047/3067 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 4.45 (s, 5 H, C_5H_5), 4.49 (dpt, $^{3}J_{HP}$ = 1.7, $^{3}J_{HH}$ = 1.6 Hz, 2 H, H^{α}/C_5H_4), 4.71 (pt, $^{3}J_{HH}$ = 1.6 Hz, 2 H, H^{β}/C_5H_4), 7.30–7.33 (m, 6 H, $H^{m,p}/C_6H_5$), 7.36–7.39 (m, 4 H, H^{o}/C_6H_5) ppm. $^{13}C\{^{1}H\}$ NMR (125.81 MHz $CDCl_3$): δ = 71.5 (s, C_5H_5), 72.7 (d, $^{3}J_{CP}$ = 3.8 Hz, C^{β}/C_5H_4), 75.3 (d, $^{2}J_{CP}$ = 16.4 Hz, C^{α}/C_5H_4), 79.9 (d, $^{1}J_{CP}$ = 8.8 Hz, C^{i}/C_5H_4), 128.1 (d, $^{3}J_{CP}$ = 6.3 Hz, C^{m}/C_6H_5), 128.4 (s, C^{p}/C_6H_5), 133.4 (d, $^{2}J_{CP}$ = 18.9 Hz, C^{o}/C_6H_5), 139.4 (d, $^{1}J_{CP}$ = 8.8 Hz, C^{i}/C_6H_5) ppm. $^{31}P\{^{1}H\}$ NMR (202.53 MHz, $CDCl_3$): δ = –16.0 (s) ppm.

P(2-$CH_3C_6H_4$)$_2$Rc (6b): Using the general procedure described above, **5** (2.0 g, 5.5 mmol) was treated with nBuLi (2.2 mL, 3.21 mmol) and chlorodi-o-tolylphosphane (**2b**, 1.36 g, 5.5 mmol). The resulting residue was purified by column chromatography on ALOX (column size: 2.5 × 30 cm) using n-hexane/diethyl ether (5:1, v:v) as eluent. Compound **6a** was obtained as a pale yellow solid; yield 0.90 g (2.02 mmol, 36% based on **5**). $C_{24}H_{23}PRu$ (443.48): calcd. C 65.00, H 5.27; found C 64.71, H 5.32; m.p. 127 °C. IR (KBr): $\tilde{\nu}$ = 1432 (m, P–C), 1477 (w, C=C) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 2.43 (s, 6 H, CH_3), 4.44 (s, 5 H, C_5H_5), 4.53 (dpt, $^{3}J_{HP}$ = 1.6, $^{3}J_{HH}$ = 1.6 Hz, 2 H, H^{α}/C_5H_4), 4.74 (pt, $^{3}J_{HH}$ = 1.6 Hz, 2 H, H^{β}/C_5H_4), 7.06–7.2 (m, 8 H, C_6H_4) ppm. $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 21.4 (d, $^{2}J_{CP}$ = 21.9 Hz, CH_3), 71.4 (s, C_5H_5), 72.7 (d, $^{3}J_{CP}$ = 3.6 Hz, C^{β}/C_5H_4), 75.7 (d, $^{2}J_{CP}$ = 16.9 Hz, C^{α}/C_5H_4), 125.7 (s, C^{p}/C_6H_4), 128.5 (s, C^{m}/C_6H_4), 129.9 (d, $^{3}J_{CP}$ = 4.8 Hz, C^{m}/C_6H_4), 133.3 (s, C^{o}/C_6H_4), 138.0 (d, $^{1}J_{CP}$ = 10.8 Hz, C^{i}/C_6H_4), 141.8 (d, $^{2}J_{CP}$ = 26.4 Hz, C^{o}/C_6H_4) ppm. $^{31}P\{^{1}H\}$ NMR (202.53 MHz, $CDCl_3$): δ = –36.1 (s) ppm.

P(c-C_4H_3O)$_2$Rc (6c): Using the general procedure described above, **5** (2.0 g, 5.5 mmol) was treated with nBuLi (2.2 mL, 3.21 mmol) and chlorodifurylphosphane (**2c**, 1.10 g, 5.5 mmol). The resulting residue was purified by column chromatography on ALOX (column size: 2.5 × 30 cm) using n-hexane/diethyl ether (5:1, v:v) as eluent. Phosphane **6a** was obtained as a pale yellow solid; yield 1.0 g (2.53 mmol, 46% based on **5**). $C_{18}H_{15}O_2PRu$ (395.35): calcd. C 54.68, H 3.82; found C 54.33, H 3.84; m.p. 116 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1008 (m, C–O), 1458 (w, P–C), 3100 (m, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 4.41 (s, 5 H, C_5H_5), 4.69 (pt, $^{3}J_{HH}$ = 1.6 Hz, 2 H, H^{β}/C_5H_4), 4.85 (dpt, $^{3}J_{HP}$ = 1.7, $^{3}J_{HH}$ = 1.6 Hz, 2 H, H^{α}/C_5H_4), 6.38 (dt, $^{4}J_{HP}$ = 1.6, $^{3}J_{HH}$ = 3.2, $^{3}J_{HH}$ = 1.6 Hz, 2 H, H^{4}/C_4H_3O), 6.67 (m, 2 H, H^{3}/C_4H_3O), 7.61 (m, 2 H, H^{5}/C_4H_3O) ppm. $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 71.5 (s, C_5H_5), 72.8 (d, $^{3}J_{CP}$ = 5.0 Hz, C^{β}/C_5H_4), 76.0 (d, $^{2}J_{CP}$ = 19.9 Hz, C^{α}/C_5H_4), 110.6 (d, $^{3}J_{CP}$ = 6.2 Hz, C^{4}/C_4H_3O), 119.5 (d, $^{2}J_{CP}$ = 23.9 Hz, C^{3}/C_4H_3O), 146.5 (d, $^{4}J_{CP}$ = 1.9 Hz, C^{5}/C_4H_3O), 153.0 (d, $^{1}J_{CP}$ = 8.1 Hz, C^{2}/C_4H_3O) ppm. $^{31}P\{^{1}H\}$ NMR (202.53 MHz, $CDCl_3$): δ = –65.2 (s) ppm.

P(c-C_6H_{11})$_2$Rc (6d): Using the general procedure described above, **5** (2.0 g, 5.5 mmol) was treated with nBuLi (2.2 mL, 3.21 mmol) and chlorodicyclohexylphosphane (**2d**, 1.28 g, 5.5 mmol). The resulting residue was purified by column chromatography on ALOX (column size: 2.5 × 30 cm) using n-hexane/diethyl ether (5:1, v:v) as eluent. Please note that **6d** could not be completely separated from free ruthenocene and was used without additional purification in further reactions. $C_{22}H_{31}PRu$ (427.53): C 61.81, H 7.31. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 1.18–1.27 (m, 10 H, C_6H_{11}), 1.62–1.88 (m, 10 H, C_6H_{11}), 1.81–1.84 (m, 2 H, C_6H_{11}), 4.45 (s, 5 H, C_5H_5), 4.48 (m, 2 H, C_5H_4), 4.56 (pt, $^{3}J_{HH}$ = 1.5 Hz, 2 H, C_5H_4) ppm. $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 26.6 (s, C_6H_{11}), 27.4 (d, J_{CP} = 8.3 Hz, C_6H_{11}), 27.5 (d, J_{CP} = 11.2 Hz, C_6H_{11}), 30.3 (d, J_{CP} = 2.5 Hz, C_6H_{11}), 30.4 (d, J_{CP} = 7.5 Hz, C_6H_{11}), 33.8 (d, $^{1}J_{CP}$ = 11.2 Hz, C^{1}/C_6H_{11}), 70.2 [s, Ru(η^5-C_5H_5)$_2$], 71.4 (d, $^{3}J_{CP}$ = 2.6 Hz, C^{β}/C_5H_4), 71.6 (s, C_5H_5), 74.4 (d, $^{2}J_{CP}$ = 12.7 Hz, C^{α}/C_5H_4), 77.3 (C^{i}/C_5H_4*) ppm. $^{31}P\{^{1}H\}$ NMR (202.53 MHz, $CDCl_3$): δ = –7.1 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{22}H_{21}PRu$ $[M + nH]^+$ 429.1278; found 429.1286, calcd. for $C_{10}H_{10}Ru$ $[M + nH]^+$ 232.9897; found 232.9901. * signal concealed by $CDCl_3$.

Se=P(C_6H_5)$_2$Rc (7a): Using the general procedure described above, the reaction of **5a** (100 mg, 0.22 mmol) with selenium (22 mg, 0.28 mmol) gave **7a** as a pale red solid; yield 105 mg (0.21 mmol, 89% based on **5a**). $C_{22}H_{19}PRuSe\cdot 0.25Et_2O$ (494.39): calcd. C 53.85, H 4.22; found C 53.87, H 4.15; m.p. 179 °C. IR (KBr): $\tilde{\nu}$ = 534/545 (m, P=Se), 1449 (m, P–C), 1476 (m, C=C) cm^{-1}. ^{1}H NMR (500.30 MHz, $CDCl_3$): δ = 1.21 [t, $^{3}J_{HH}$ = 7.0 Hz, $(CH_3CH_2)_2O$], 3.43 [q, $^{3}J_{HH}$ = 7.0 Hz, $(CH_3CH_2)_2O$], 4.45 (s, 5 H, C_5H_5), 4.68 (dpt, $^{3}J_{HP}$ = 1.9, $^{3}J_{HH}$ = 1.7 Hz, 2 H, H^{α}/C_5H_4), 4.74 (dpt, $^{4}J_{HP}$ = 1.6, $^{3}J_{HH}$ = 1.7 Hz, 2 H, H^{β}/C_5H_4), 7.32–7.4 (m, 6 H, $H^{m,p}/C_6H_5$), 7.64–7.69 (m, 4 H, H^{o}/C_6H_5) ppm. $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 15.2 [s, $(CH_3CH_2)_2O$], 65.9 [$(CH_3CH_2)_2O$], 73.0 (s, C_5H_5), 73.7 (d, $^{3}J_{CP}$ = 9.2 Hz, C^{β}/C_5H_4), 75.4 (d, $^{2}J_{CP}$ = 13.3 Hz, C^{α}/C_5H_4), 79.2 (d, $^{1}J_{CP}$ = 86.1 Hz, C^{i}/C_5H_4), 128.2 (d, $^{2}J_{CP}$ = 12.5 Hz, C^{o}/C_6H_5), 131.4 (d, $^{4}J_{CP}$ = 2.8 Hz, C^{p}/C_6H_5), 132.3 (d,

$^3J_{CP}$ = 10.9 Hz, C^m/C_6H_5), 133.7 (d, $^1J_{CP}$ = 78.8 Hz, C^i/C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = 31.2 ($^1J_{^{31}P^{77}Se}$ = 735.2 Hz) ppm.

$Se{=}P(2\text{-}CH_3C_6H_4)_2Rc$ (7b): According to the general procedure described earlier, **5b** (100 mg, 0.23 mmol) was treated with selenium (21 mg, 0.27 mmol) to give **7b** as a colorless solid; yield 110 mg (0.21 mmol, 94% based on **5b**). $C_{24}H_{23}PRuSe\cdot 0.5Et_2O$ (522.44): calcd. C 55.81, H 5.04; found C 55.91, H 4.94; m.p. 200 °C (dec.). IR (KBr): $\tilde{\nu}$ = 571 (m, P=Se), 1453 (m, P–C), 1559 (m, C=C) cm^{-1}. ^1H NMR (500.30 MHz, $CDCl_3$): δ = 1.21 [t, $^3J_{HH}$ = 7.0 Hz, $(CH_3CH_2)_2O$], 2.05 (s, 6 H, CH_3), 3.43 [q, $^3J_{HH}$ = 7.0 Hz, $(CH_3CH_2)_2O$], 4.52 (s, 5 H, C_5H_5), 4.84 (m, 4 H, $H^{\alpha,\beta}/C_5H_4$), 7.10–7.13 (m, 2 H, C_6H_4), 7.35–7.37 (m, 4 H, C_6H_4), 7.9–8.4 (m, 2 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 15.2 [s, $(CH_3CH_2)_2O$], 22.0 (d, $3J_{CP}$ = 3.9 Hz, CH_3), 65.9 [s, $(CH_3CH_2)_2O$], 73.2 (s, C_5H_5), 73.6 (d, $^2J_{CP}$ = 9.1 Hz, C^α/C_5H_4), 74.7 (m, C^β/C_5H_4), 80.3 (d, $^1J_{CP}$ = 85.4 Hz, C^i/C_5H_4), 126.4 (d, $^2J_{CP}$ = 13.4 Hz, C^o/C_6H_4), 131.5 (d, $^4J_{CP}$ = 2.4 Hz, C^p/C_6H_4), 131.7 (d, $^3J_{CP}$ = 10.3 Hz, C^m/C_6H_4), 140.1 (d, $^1J_{CP}$ = 9.2 Hz, C^i/C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = 29.0 ($^1J_{^{31}P^{77}Se}$ = 717.5 Hz) ppm.

$Se{=}P(c\text{-}C_4H_3O)_2Rc$ (7c): Using the general procedure described above, the reaction of **5c** (100 mg, 0.25 mmol) with selenium (24 mg, 0.30 mmol) gave **7c** as a pale red solid; yield 100 mg (0.21 mmol, 84% based on **5c**). $C_{18}H_{15}O_2PRuSe$ (474.30): calcd. C 45.58, H 3.19; found C 45.45, H 3.20; m.p. 242 °C. IR (KBr): $\tilde{\nu}$ = 549/570 (m, P=Se), 1013 (m, C–O), 1457 (w, P–C), 1556 (m, C=C), 3097 (m, =C–H) cm^{-1}. ^1H NMR (500.30 MHz, $CDCl_3$): δ = 4.51 (s, 5 H, C_5H_5), 4.81 (dpt, $^3J_{HP}$ = 1.6, $^3J_{HH}$ = 1.5 Hz, 2 H, H^β/C_5H_4), 5.06 (dpt, $^3J_{HP}$ = 2.0, $^3J_{HH}$ = 1.8 Hz, 2 H, H^α/C_4H_5), 6.48 (dpt, $^4J_{HP}$ = 1.7, $^3J_{HH}$ = 3.4, $^3J_{HH}$ = 1.7 Hz, 2 H, H^4/C_4H_3O), 7.12 (m, 2 H, H^3/C_4H_3O), 7.68 (m, 2 H, H^5/C_3H_4O) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 72.9 (s, C_5H_5), 73.7 (d, $^3J_{CP}$ = 10.7 Hz, C^β/C_5H_4), 74.8 (d, $^2J_{CP}$ = 15.5 Hz, C^α/C_5H_4), 75.9 (d, $^1J_{CP}$ = 98.0 Hz, C^i/C_5H_4), 111.1 (d, $^3J_{CP}$ = 9.2 Hz, C^4/C_4H_3O), 122.0 (d, $^2J_{CP}$ = 21.9 Hz, C^3/C_4H_3O), 147.3 (d, $^1J_{CP}$ = 114.7 Hz, C^2/C_4H_3O), 148.2 (d, $^4J_{CP}$ = 7.1 Hz, C^5/C_4H_3O) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = –6.8 ($^1J_{^{31}P^{77}Se}$ = 772 Hz) ppm.

$Se{=}P(c\text{-}C_6H_{11})_2Rc$ (7d): According to the general procedure described above, **5d** (100 mg, 0.26 mmol) was treated with selenium (22 mg, 0.28 mmol) to give **7d** as a colorless solid. $C_{22}H_{31}PRuSe$ (506.49): calcd. C 52.17, H 6.17; found C 53.33, H 6.29. Please note that the results of the elemental analysis deviate from the calculated values due to the light sensitivity and, therefore, decomposition of this compound. IR (KBr): $\tilde{\nu}$ = 549 (m, P=Se), 1453 (w, P–C), 1556 (m, C=C), 3097 (m, =C–H) cm^{-1}. ^1H NMR (500.30 MHz, $CDCl_3$): δ = 1.15–1.41 (m, 10 H, C_6H_{11}), 1.66–1.69 (m, 2 H, C_6H_{11}), 1.79–1.86 (m, 4 H, C_6H_{11}), 1.96–2.02 (m, 6 H, C_6H_{11}), 4.63 (s, 5 H, C_5H_5), 4.74 (m, 2 H, C_5H_4), 4.76 (dpt, J_{HP} = 1.6, J_{HH} = 1.5 Hz, 2 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$): δ = 26.0 (d, J_{CP} = 1.4 Hz, C_6H_{11}), 26.4 (d, J_{CP} = 1.6 Hz, C_6H_{11}), 26.6 (d, J_{CP} = 4.5 Hz, C_6H_{11}), 26.7 (d, J_{CP} = 3.7 Hz, C_6H_{11}), 27.6 (d, J_{CP} = 3.3 Hz, C_6H_{11}), 37.3 (d, $^1J_{CP}$ = 44.7 Hz, C^1/C_6H_{11}), 72.4 (d, $^3J_{CP}$ = 8.0 Hz, C^β/C_5H_4), 73.1 (s, C_5H_5), 74.3 (d, $^2J_{CP}$ = 10.8 Hz, C^α/C_5H_4), 76.7 (d, $^1J_{CP}$ = 68.0 Hz, C^i/C_5H_4) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = 49.2 ($^1J_{^{31}P^{77}Se}$ = 704 Hz) ppm. HRMS (ESI-TOF): calcd. for $C_{22}H_{31}PRuSe$ $[M + nH]^+$ 509.0455; found 509.0378.

General Procedure for the Synthesis of Palladium Complexes 9a–e and 10a–d: Phosphane **3** or **6** (0.5 g) and $[PdCl_2(cod)]$ (**8**, 0.5 equiv.) were dissolved in dry dichloromethane (40 mL). This solution was stirred for 2 h at ambient temperature. All of the volatile materials were removed under vacuum, and the residue was washed with diethyl ether (5×5 mL). After drying the residue under vacuum, the complexes were obtained as yellow or red solids.

$[PdCl_2(P(2\text{-}CH_3C_6H_4)_2Fc)_2]$ (9b): Following the general procedure described above, **3b** (0.5 g, 1.26 mmol) was treated with **8** (0.18 g, 0.63 mmol) to give **9b** as an air-stable red solid; yield 0.52 g (0.53 mmol, 84% based on **8**). $C_{48}H_{46}Cl_2Fe_2P_2Pd\cdot 2/3CH_2Cl_2$ (1030.46): calcd. C 56.72, H 4.63; found C 56.23, H 4.64; m.p. 210 °C (dec.). IR (KBr): $\tilde{\nu}$ = 754 (s, =C–H, *o*-disubst. benzene), 1449 (m, P–C), 1561/1638/1655 (m, C=C), 2928/2969 (w, C–H), 3053 (w, =C–H) cm^{-1}. ^1H NMR (500.30 MHz, CD_2Cl_2): δ = 2.39 (s, 12 H, CH_3), 4.23 (s, 10 H, C_5H_5), 4.51 (pt, $^3J_{HH}$ = 1.7 Hz, 4 H, C_5H_4), 4.68 (m, 4 H, C_5H_4), 5.29 (s, CH_2Cl_2), 7.16–7.19 (m, 8 H, C_6H_4), 7.32–7.35 (m, 4 H, C_6H_4), 7.85–7.89 (m, 4 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, CD_2Cl_2): δ = 23.9 (pt, $^3J_{CP}$ = 3.4 Hz, CH_3), 53.5 (s, CH_2Cl_2), 70.9 (s, C_5H_5), 71.1 (pt, $^3J_{CP}$ = 4.0 Hz, C^β/C_5H_4), 77.4 (pt, $^2J_{CP}$ = 6.4 Hz, C^α/C_5H_4), 125.0 (pt, J_{CP} = 5.0 Hz, C_6H_4), 130.4 (s, C^p/C_6H_4), 131.1 (pt, J_{CP} = 4.2 Hz, C_6H_4), 134.9 (pt, J_{CP} = 5.7 Hz, C_6H_4), 142.7 (pt, J_{CP} = 5.3 Hz, C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, CD_2Cl_2): δ = 13.9 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{48}H_{46}Fe_2P_2PdCl_2$ $[M - Cl]^+$ 937.0510; found 937.0464; $[M + nH - 2Cl]^+$ 901.0746; found 901.0699.

$[PdCl_2(P(c\text{-}C_4H_3O)_2Fc)_2]$ (9c): Following the general procedure described above, **3c** (0.5 g, 1.43 mmol) was treated with **8** (0.20 g, 0.70 mmol) to give **9c** as an air-stable red solid; yield 0.47 g (0.54 mmol, 77% based on **8**). $C_{36}H_{30}Cl_2Fe_2O_4P_2Pd\cdot 1/3\ CH_2Cl_2$ (905.90): calcd. C 48.17, H 3.41; found C 48.65, H 3.45; m.p. 242 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1005/1010 (s, C–O), 1457 (w, P–C), 1654 (w, C=C), 3047/3127/3152 (w, =C–H) cm^{-1}. ^1H NMR (500.30 MHz, CD_2Cl_2): δ = 4.43 (s, 10 H, C_5H_5), 4.50 (pt, $^3J_{HH}$ = 1.8 Hz, 4 H, C_5H_4), 4.74 (m, 4 H, C_5H_4), 5.30 (s, CH_2Cl_2), 6.50 (m, 4 H, H^4/C_4H_3O), 7.00 (m, 4 H, H^3/C_4H_3O), 7.75 (m, 4 H, H^5/C_4H_3O) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, CD_2Cl_2): δ = 53.5 (s, CH_2Cl_2), 70.5 (s, C_5H_5), 71.9 (pt, $^3J_{CP}$ = 4.5 Hz, C^β/C_5H_4), 74.7 (pt, $^2J_{CP}$ = 7.4 Hz, C^α/C_5H_4), 110.9 (pt, $^3J_{CP}$ = 3.4 Hz, C^4/C_4H_3O), 123.3 (m, C^3/C_4H_3O), 147.8 (pt, $^4J_{CP}$ = 3.1 Hz, C^5/C_4H_3O) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, CD_2Cl_2): δ = –14.0 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{36}H_{30}Cl_2Fe_2O_4P_2Pd$ $[M - Cl]^+$ 840.9051; found 840.9041, $[M - C_{18}H_{15}FeO_2P - Cl]^+$ 492.8880; found 492.8847.

$[PdCl_2(P(c\text{-}C_6H_{11})_2Fc)_2]$ (9e): According to the general procedure described earlier, **3e** (0.5 g, 1.31 mmol) was treated with **8** (0.18 g, 0.63 mmol) to give **9e** as an air-stable red solid; yield 0.48 g (0.51 mmol, 81% based on **8**). $C_{44}H_{62}Cl_2Fe_2P_2Pd\cdot 1/2\ Et_2O$ (978.68): C 56.44; H 6.90; found C 56.70; H 6.78; m.p. 253 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1433/1436 (m, P–C), 2857/2926/2979 (w, C–H), 3038/3050/3088 (w, =C–H) cm^{-1}. ^1H NMR (500.30 MHz, CD_2Cl_2): δ = 1.27–1.31 [m, 12 H, C_6H_{11} + $(CH_3CH_2)_2O$], 1.69–1.78 (m, 20 H, C_6H_{11}), 2.08–2.10 (m, 4 H, C_6H_{11}), 2.33–2.55 (m, 4 H, C_6H_{11}), 2.56–2.61 (m, 4 H, H^1/C_6H_{11}), 3.48 [q, $^3J_{HH}$ = 7.0 Hz, $(CH_3CH_2)_2O$], 4.36 (s, 10 H, C_5H_5), 4.41 (m, 4 H, C_5H_4), 4.71 (m, 4 H, C_5H_4) ppm. $^{13}C\{^1H\}$ NMR (125.81 MHz, CD_2Cl_2): δ = 15.4 [s, $(CH_3CH_2)_2O$], 26.5 (s, C^6/C_6H_{11}), 27.6 (pt, $^2J_{CP}$ = 5.5 Hz, $C^{2/3}/C_6H_{11}$), 27.8 (pt, $^2J_{CP}$ = 6.3 Hz, $C^{2/3}/C_6H_{11}$), 28.9 (s, $C^{4/5}/C_6H_{11}$), 30.2 (s, $C^{4/5}/C_6H_{11}$), 36.9 (pt, $^1J_{CP}$ = 11.7 Hz, C^1/C_6H_{11}), 65.9 [s, $(CH_3CH_2)_2O$], 70.1 (pt, $^3J_{CP}$ = 3.4 Hz, C^β/C_5H_4), 70.2 (s, C_5H_5), 72.1 (pt, $^1J_{CP}$ = 20.0 Hz, C^i/C_5H_4), 75.0 (pt, $^2J_{CP}$ = 5.3 Hz, C^α/C_5H_4) ppm. $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$): δ = 18.0 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{44}H_{62}Cl_2Fe_2P_2Pd$ $[M + nH - C_{22}H_{31}FePCl_2]^+$ 487.0475; found 487.0413.

$[PdCl_2(P(C_6H_5)_2Rc)_2]$ (10a): Following the synthetic methodology described above, **6a** (0.5 g, 1.20 mmol) was treated with **8** (0.17 g, 0.60 mmol) to give **10a** as an air-stable yellow solid; yield 0.50 g (0.50 mmol, 83% based on **8**). $C_{44}H_{38}Cl_2P_2PdRu_2\cdot 1/3\ CH_2Cl_2$

(1008.19): C 51.37, H 3.76; found C 51.41, H 3.83; m.p. 164 °C (dec.). IR (KBr): ṽ = 1437 (w, P–C), 1481 (m, C=C) cm^{-1}. ^{1}H NMR (500.30 MHz, CDCl$_3$): δ = 4.81 (m, 4 H, C_5H_4), 4.84 (m, 10 H, C_5H_5), 4.95 (m, 4 H, C_5H_4), 5.30 (s, CH_2Cl_2), 7.36–7.47 (m, 12 H, $H^{m,p}/C_6H_5$), 7.63–7.67 (m, 8 H, H^o/C_6H_5) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CDCl$_3$): δ = 53.5 (s, CH_2Cl_2), 72.9 (s, C_5H_5), 73.3 (m, C_5H_4), 77.5 (m, C_5H_4), 127.7 (pt, $^3J_{CP}$ = 4.9 Hz, C^m/C_6H_5), 130.4 [s, $C^p/(C_6H_5)$], 131.5 (pt, $^1J_{CP}$ = 25.3 Hz, C^i/C_6H_5), 134.3 (pt, $^2J_{CP}$ = 5.9 Hz, C^o/C_6H_5) ppm. ^{31}P{^{1}H} NMR (202.53 MHz, CDCl$_3$): δ = 14.8 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{44}H_{38}ClP_2PdRu_2$ [M]$^+$ 972.9278; found 972.9249, calcd. for $C_{22}H_{19}ClPRu$ [M]$^+$ 450.9954; found 450.9926.

[PdCl$_2$(P(2-CH$_3$C$_6$H$_4$)$_2$Rc)$_2$] (10b): Following the synthetic procedure described above, **6b** (0.5 g, 1.13 mmol) was treated with **8** (0.16 g, 0.56 mmol) to give **10b** as an air-stable yellow solid; yield 0.50 mg (0.47 mmol, 84% based on **8**). $C_{48}H_{46}Cl_2P_2PdRu_2\cdot 1/2CH_2Cl_2$ (1064.29): C 52.58, H 4.36; found C 52.36, H 4.39; m.p. 250 °C (dec.). IR (KBr): ṽ = 1448 (w, P–C), 1559 (m, C=C) cm^{-1}. ^{1}H NMR (500.30 MHz, CDCl$_3$): δ = 2.69 (s, 12 H, CH_3), 4.66 (s, 10 H, C_5H_5), 4.79 (m, 4 H, C_5H_4), 5.00 (pt, $^3J_{HH}$ = 1.6 Hz, 4 H, C_5H_4), 5.30 (s, CH_2Cl_2), 7.12–7.15 (m, 4 H, C_6H_4), 7.21–7.23 (m, 4 H, C_6H_4), 7.34–7.37 (m, 4 H, C_6H_4), 7.57–7.61 (m, 4 H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CDCl$_3$): δ = 24.3 (pt, $^3J_{CP}$ = 3.3 Hz, CH_3), 53.5 (CH_2Cl_2), 72.9 (pt, $^3J_{CP}$ = 3.6 Hz, C^β/C_5H_4), 73.5 (s, C_5H_5), 77.8 (pt, $^1J_{CP}$ = 25.5 Hz, C^i/C_5H_4), 79.3 (pt, $^2J_{CP}$ = 6.8 Hz, C^α/C_5H_4), 125.0 (pt, J_{CP} = 5.2 Hz, C_6H_4), 130.4 (s, C_6H_4), 130.6 (pt, $^1J_{CP}$ = 24.0 Hz, C^i/C_6H_4), 131.1 (pt, J_{CP} = 3.8 Hz, C_6H_4), 135.2 (pt, J_{CP} = 5.7 Hz, C_6H_4), 142.6 (pt, J_{CP} = 5.3 Hz, C_6H_4) ppm. ^{31}P{^{1}H} NMR (202.53 MHz, CDCl$_3$): δ = 16.2 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{48}H_{46}ClP_2PdRu_2$ [M]$^+$ 1028.9906; found 1028.9891, calcd. for $C_{48}H_{46}P_2PdRu_2$ [M]$^+$ 994.02; found 994.0216, calcd. for $C_{24}H_{23}PPdClRu$ [M]$^+$ 584.9309; found 584.9286, calcd. for $C_{24}H_{23}PPdRu$ [M + *n*H]$^+$ 548.9547; found 548.9517.

[PdCl$_2$(P(*c*-C$_4$H$_3$O)$_2$Rc)$_2$] (10c): Following the synthetic procedure described above, the reaction of **6c** (0.5 g, 1.26 mmol) with **8** (0.18 g, 0.63 mmol) gave **10c** as an air-stable yellow solid; yield 0.52 g (0.54 mmol, 86% based on **8**). $C_{36}H_{30}Cl_2O_4P_2PdRu_2$ (968.03): C 44.67, H 3.12; found C 44.63, H 3.13; m.p. 242 °C. IR (KBr): ṽ = 1024 (w, C–O), 1454 (w, P–C), 1536 (m, C=C) cm^{-1}. ^{1}H NMR (500.30 MHz, CDCl$_3$): δ = 4.75 (s, 10 H, C_5H_5), 4.79 (pt, $^3J_{HH}$ = 1.7 Hz, 4 H, C_5H_4), 5.13 (m, 4 H, C_5H_4), 6.45 (m, 4 H, H^4/C_4H_3O), 7.08 (m, 4 H, H^3/C_4H_3O), 7.67 (m, 4 H, H^5/C_4H_3O) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CDCl$_3$): δ = 73.0 (s, C_5H_5), 73.5 (pt, $^3J_{CP}$ = 4.2 Hz, C^β/C_5H_4), 76.5 (pt, $^2J_{CP}$ = 7.5 Hz, C^α/C_5H_4), 110.9 (pt, $^3J_{CP}$ = 3.5 Hz, C^4/C_4H_3O), 123.4 (pt, $^2J_{CP}$ = 9.2 Hz, C^3/C_4H_3O), 144.59 (pt, $^1J_{CP}$ = 39.2 Hz, C^2/C_4H_3O), 147.6 (pt, $^4J_{CP}$ = 2.8 Hz, C^5/C_4H_3O) ppm. ^{31}P{^{1}H} NMR (202.53 MHz, CDCl$_3$): δ = –15.0 (s) ppm.

[PdCl$_2$(P(*c*-C$_6$H$_{11}$)$_2$Rc)$_2$] (10d): Following the synthetic procedure described earlier, **6d** (0.5 g, 1.17 mmol) was treated with **8** (0.16 g, 0.56 mmol) to give **10d** as an air-stable red solid; yield 0.40 g (0.39 mmol, 70% based on **8**). $C_{44}H_{62}Cl_2P_2PdRu_2$ (1032.38): C 51.19, H 6.05; found C 51.19, H 5.92; m.p. 180 °C (dec.). IR (KBr): ṽ = 1448 (m, P–C), 1655 (w, C=C), 2847/2927 (s, C–H), 3108 (w, =C–H) cm^{-1}. ^{1}H NMR (500.30 MHz, CDCl$_3$): δ = 1.23–1.27 (m, 12 H, C_6H_{11}), 1.70–1.79 (m, 20 H, C_6H_{11}), 2.09–2.11 (m, 4 H, C_6H_{11}), 2.25–2.27 (m. 4 H, C_6H_{11}), 2.49–2.54 (m, 4 H, H^1/C_6H_{11}), 4.68 (s, 10 H, C_5H_5), 4.70 (m, 4 H, C_5H_4), 5.00 (m, 4 H, C_5H_4) ppm. ^{13}C{^{1}H} NMR (125.81 MHz, CDCl$_3$): δ = 26.5 (s, C^6/C_6H_{11}), 27.7 (pt, $^2J_{CP}$ = 5.7 Hz, $C^{2/3}/C_6H_{11}$), 27.8 (pt, $^2J_{CP}$ = 6.3 Hz, $C^{2/3}/C_6H_{11}$), 28.9 (s, $C^{4/5}/C_6H_{11}$), 30.3 (s, $C^{4/5}/C_6H_{11}$), 37.1 (pt, $^1J_{CP}$ = 11.8 Hz, C^1/C_6H_{11}), 72.0 (pt, $^3J_{CP}$ = 3.0 Hz, C^β/C_5H_4), 72.6 (s, C_5H_5), 75.2 (pt, $^1J_{CP}$ = 19.0 Hz, C^i/C_5H_4), 77.0 (pt, $^2J_{CP}$ = 5.6 Hz, C^α/C_5H_4) ppm. ^{31}P{^{1}H} NMR (202.53 MHz, CDCl$_3$): δ = 16.4 (s) ppm. HRMS (ESI-TOF): calcd. for $C_{44}H_{62}ClP_2PdRu_2$ [M]$^+$ 977.1156; found 997.1156.

General Procedure for the Heck Reaction: Iodobenzene (612 mg, 3.0 mmol), *t*-butyl acrylate (397 mg, 3.1 mmol), EtN(*iso*-C$_3$H$_7$)$_2$ (452 mg, 3.5 mmol), and acetyl ferrocene (114 mg, 0.5 mmol) were dissolved in toluene/acetonitrile (15 mL, 1:1, v:v) with 0.2 mol-% of the catalyst (**9a**–**e** or **10a**–**d**). The reaction mixture was stirred at 80 °C and samples (1 mL) were taken every hour. The samples were chomatographed on silica gel with diethyl ether as eluent. All volatiles were evaporated, and the conversions were determined by ^{1}H NMR spectroscopy.

General Procedure for the Suzuki Reaction: 2-Bromotoluene (500 mg, 2.92 mmol) or 4′-chloroacetophenone (464 mg, 3.00 mmol), phenylboronic acid (470 mg, 3.85 mmol), potassium carbonate (1.21 g, 8.76 mmol), and acetyl ferrocene (114 mg, 0.50 mmol) were dissolved in 1,4-dioxane/water (12 mL, 2:1, v:v). After addition of 0.1 mol-%, 0.25 mol-% (reaction of 2-bromotoluene) or 0.5 mol-% (reaction of 4′-chloroacetophenone) of the catalyst (**9a**–**e** or **10a**–**d**), the reaction mixture was stirred for 1 h at 100 °C. Samples of 1 mL were taken after 2.5, 5, 10, 20, 30, and 60 min and chromatographed on silica gel with diethyl ether as eluent. All volatiles were evaporated under reduced pressure, and the conversions were determined by ^{1}H NMR spectroscopy.

Crystal Data for 4b: $C_{24}H_{23}FePSe$, M$_r$ = 477.20 g mol^{-1}, monoclinic, $P2_1/n$, λ = 0.71073 Å, a = 15.7844(4) Å, b = 7.4393(2) Å, c = 17.6781(5) Å, β = 90.127(2)°, V = 2075.84(10) Å^3, Z = 4, ρ_{calcd} = 1.527 mg m^{-3}, μ = 2.563 mm^{-1}, T = 298(2) K, Θ range = 3.03–26.00°, reflections collected: 10904, independent: 4054 (R_{int} = 0.0321), R_1 = 0.0297, wR_2 = 0.0647 [$I > 2\sigma(I)$]. Single crystals of **4b** were obtained from a saturated dichloromethane solution of **4b** at 298 K. Data were collected with an Oxford Gemini S diffractometer, with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares procedures on F^2.[27]

CCDC-834561 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR spectra and reaction profiles are given.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie (FCI) for generous financial support.

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Received: August 11, 2011