Journal of Organometallic Chemistry 785 (2015) 32–43

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Carbosilane-supported (*p*-cymene) ruthenium ferrocenyl phosphines in the β-oxopropyl ester synthesis

Claus Schreiner, Janine Jeschke, Bianca Milde, Dieter Schaarschmidt, Heinrich Lang*

Technische Universität Chemnitz, Faculty of Sciences, Institute of Chemistry, Inorganic Chemistry, 09107 Chemnitz, Germany

ARTICLE INFO

Article history:
Received 24 November 2014
Received in revised form
17 February 2015
Accepted 23 February 2015
Available online 4 March 2015

Keywords:
Catalysis
Ferrocenyl phosphines
β-Oxopropyl benzoate
Ruthenium
X-ray structure determination

ABSTRACT

The synthesis and characterization of a series of carbosilane-supported ferrocenyl phosphine ruthenium complexes of type $SiMe_{4-n}(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)((\eta^5\text{-}C_5H_4PR_2)RuCl_2(\eta^6\text{-}p\text{-cymene})))_n$ (*p*-cymene = 1-*i*-Pr-4-Me-C_6H_4; $n = 2$: **10a**, R = Ph; **10b**, R = $^cC_6H_{11}$; **10c**, R = 2-(5-Me)C_4H_2O); $n = 4$: **11a**, R = Ph; **11b**, R = $^cC_6H_{11}$; **11c**, R = 2-(5-Me)C_4H_2O)) is described. For comparative reasons, the *non*-immobilized ferrocenyl phosphine ruthenium complexes $[FcPR_2(RuCl_2(\eta^6\text{-}p\text{-cymene}))]$ (Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$; **9a**, R = Ph; **9b**, R = $^cC_6H_{11}$; **9c**, R = 2-(5-Me)C_4H_2O) were prepared. The molecular structure of **9c** in the solid state is reported confirming the expected tetrahedral coordination sphere about the phosphorus atom and the "piano-stool" geometry about ruthenium. The ruthenium complexes **9**–**11** are catalytically active in the addition of benzoic acid to propargyl alcohol to form β-oxopropyl benzoate. The obtained activities and productivities show that a good solubility of the catalyst is necessary for a successful catalytic reaction. Furthermore, the rate of the reaction can be influenced by using less basic and electron-withdrawing phosphine ligands.

Introduction

β-Oxoalkyl esters are important intermediates in organic synthesis, since they can be transformed into heterocyclic furanones or imidazoles [1–3] and they can serve as activated esters for peptide synthesis [4], or as photolabile protecting groups for carboxylic acids [5]. Numerous synthetic methodologies for the preparation of β-oxoalkyl esters including the carboxylation of α-halo ketones [5], hydration/esterification of propargylic alcohols [6], or oxidation of ketones *via* metal acetate complexes [7] are known. On the other hand, the ruthenium-catalyzed addition of carboxylic acids to propargylic alcohols represents an elegant and atom-economic alternative to classical synthetic methodologies [8], since the starting materials are easily accessible, various functionalities at the carboxylic acid as well as at the alkyne are tolerated and the formation of side-products is limited [1,9,10]. The catalytic reaction proceeds under mild conditions (60 °C, 6 h) [1] and the best results were obtained by applying mononuclear half-sandwich complexes of type $[RuCl_2(\eta^6\text{-arene})(PR_3)]$ (arene = *p*-cymene, C_6Me_6; PR_3 = PMe_3, PPh_3, phosphoramidite, TPPMS, $P(C{\equiv}CFc)R'_2$; TPPMS = triphenyl phosphine-*m*-sulfonate; Fc = $Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)$; R′ = Ph, 2-Me$C_6H_4$, $^cC_4H_3O$, *t*-Bu, $^cC_6H_{11}$) [1,8–11] or dimeric ruthenium complexes $[Ru(\mu\text{-}O_2CH)(CO)_2(PPh_3)]_2$ [10] as catalysts. It was found that phosphines such as PMe_3 and PPh_3 achieve high conversions [1]. However, when electron-deficient phosphines (*e.g.*, $P(^cC_4H_3O)_3$) in combination with $[RuCl_2(\eta^6\text{-}p\text{-cymene})]$ are used in the related enol ester synthesis a better catalytic performance was obtained [12]. Another approach was reported by Štěpnička et al. who immobilized 1′-(diphenylphosphino)ferrocene carboxylic acid (=hdpf) on the mesoporous molecular sieve MCM-41, which was further reacted with $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ to give a $[RuCl_2(\eta^6\text{-}p\text{-cymene})(hdpf)]$-modified material [13]. However, in the reaction of benzoic acid with propargyl alcohol the immobilized catalysts showed lower activity and productivity, when compared to the homogenous catalysts $[RuCl_2(\eta^6\text{-}p\text{-cymene})(hdpf)]$, which is most probably caused by the formation of polymeric side products [13].

We here report on the synthesis and characterization of carbosilane-supported ferrocenyl phosphine ruthenium complexes and their application in the catalytic synthesis of β-oxopropyl benzoate. Thereby, the main focus was to clarify whether strong or weak σ donating phosphines accelerate the catalytic reaction and to study the effect of the degree of immobilization on the performance of the appropriate catalysts.

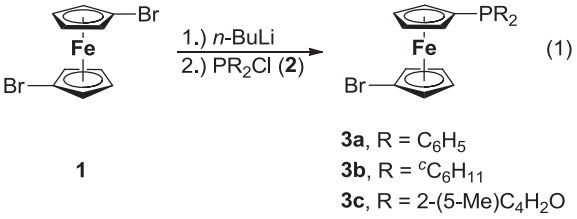
* Corresponding author. Tel.: +49 (0)371 531 21210; fax: +49 (0)371 531 21219.
E-mail address: heinrich.lang@chemie.tu-chemnitz.de (H. Lang).

http://dx.doi.org/10.1016/j.jorganchem.2015.02.036
0022-328X/

Results and discussion

Synthesis and characterization

As starting molecules Fe(η^5-$C_5H_4PR_2$)(η^5-C_5H_4Br) (**3a**, R = Ph; **3b**, R = $^cC_6H_{11}$; **3c**, R = 2-(5-Me)C_4H_2O) were chosen, which were synthesized by a modified reaction protocol firstly described by Dong and co-workers (Reaction 1) [14]. *Sub*-stoichiometric amounts of *n*-butyl lithium were used to prevent the formation of di-substituted phosphines, since it appeared that their separation using different methodologies is difficult.



Treatment of **3a**–**c** with *n*-BuLi and the respective chlorosilane $SiMe_{4-n}((CH_2)_3SiMe_2Cl)_n$ (**5a**, $n = 4$; **5b**, $n = 2$) gave the two- and fourfold substituted phosphanylferrocenyl carbosilanes **6a**–**c** and **7a**–**c** in good yields (Scheme 1, Table 1). Due to their sensitivity towards oxygen, **6a**–**c** and **7a**–**c** were converted into the corresponding sulfides **6a-S**–**6c-S** and **7a-S**–**7c-S** for analytical purposes (elemental analysis and IR spectroscopy) by their reaction with elemental sulfur.

Ruthenium complexes **10a**–**c** and **11a**–**c** were accessible by treatment of **6a**–**c** and **7a**–**c** with $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**8**) in dichloromethane at ambient temperature (Scheme 1, Table 1). After appropriate work-up, these complexes could be isolated as air and moisture stable red solids. In addition, the *non*-functionalized ferrocenyl phosphines **4a**–**c** were synthesized and converted into the respective ruthenium complexes **9a**–**c** for comparative purposes (Scheme 1, Experimental section).

Table 1
Synthesis of **6**, **7**, **10** and **11**.

Compd.	R	Yield/%[a]	Compd.	R	Yield/%[b]
6a	C_6H_5	71	**10a**	C_6H_5	98
6b	$^cC_6H_{11}$	80	**10b**	$^cC_6H_{11}$	95
6c	2-(5-Me)C_4H_2O	74	**10c**	2-(5-Me)C_4H_2O	96
7a	C_6H_5	62	**11a**	C_6H_5	97
7b	$^cC_6H_{11}$	58	**11b**	$^cC_6H_{11}$	96
7c	2-(5-Me)C_4H_2O	67	**11c**	2-(5-Me)C_4H_2O	95

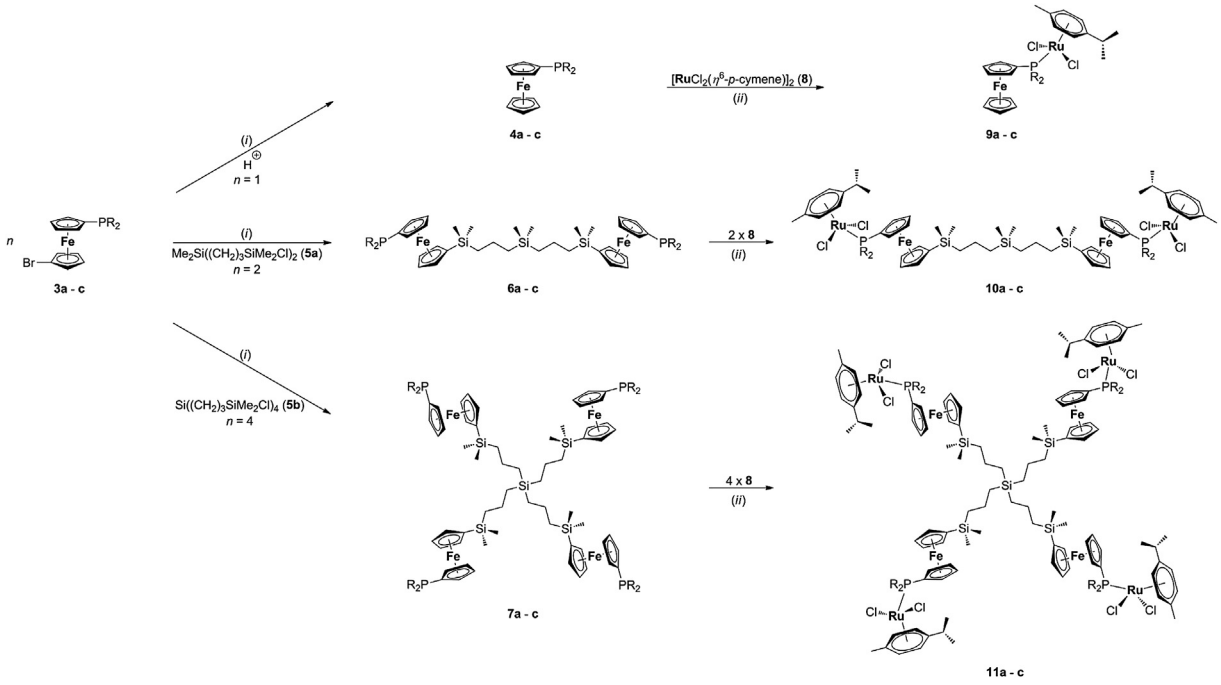
[a] Based on **5a** and **5b**, respectively.
[b] Based on **3a**–**c**.

All compounds were characterized by elemental analysis (except **6** and **7**, *vide supra*), IR and NMR (^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy. In addition, the structure of **9c** in the solid state was determined by single crystal X-ray structure analysis.

The IR spectra of the sulfides **6a-S**–**6c-S** and **7a-S**–**7c-S** and the ruthenium complexes **10a**–**c** and **11a**–**c** exhibit several characteristic absorptions for the carbosilane backbone, *e.g.* the Si–C deformation vibration ($\tilde{\nu} \approx 1250\ cm^{-1}$) as well as the Si–C and C–H stretching vibrations ($\tilde{\nu} \approx 830\ cm^{-1}$ and $\tilde{\nu} \approx 2850–2950\ cm^{-1}$, respectively). In addition, typical P=S absorptions can be observed for the respective sulfides **6a-S**–**6c-S** and **7a-S**–**7c-S**, which show a dependency on the electronic nature of the organic group at the phosphorus atom. With a decreasing –I effect, the P=S stretching frequencies decrease, *i.e.* **6a-S**, 656 cm^{-1}; **6c-S**, 694 cm^{-1}.

For the characterization of the newly prepared molecules **9**–**11** NMR spectroscopy is suitable at which 2D methods (HH-*gs*-COSY, HSi-*gs*-HMBC, HC-*gs*-HSQC, HC-*gs*-HMBC) are of importance to confirm the suggested molecular structures.

The ^1H NMR spectra of **3**, **6**, **7** and **9**–**11** consist of two signal sets for the α and β protons of the ferrocenyl cyclopentadienyl moieties between 3.6 and 4.7 ppm as typical for ferrocenes featuring C_5H_4 ligands [15]. Especially the signals for the α protons are highly dependent on the electronic nature of the phosphorus-bonded organic groups as they are shifted to lower field, when electron-withdrawing groups are attached (*e.g.*, H^{α}/C_5H_4P: **6b**, 4.12 ppm;



Scheme 1. Synthesis of **4**, **6**, **7** and **9**–**11** (**a**, R = C_6H_5; **b**, R = $^cC_6H_{11}$; **c**, R = 2-(5-Me)C_4H_2O). (*i*) *n*-BuLi, tetrahydrofuran, −50 °C, 1 h; (*ii*) dichloromethane, 25 °C, 2 h.

6c, 4.39 ppm). However, the resonance signals of the carbosilane backbone with their distinct splitting pattern are not influenced by the phosphine substituents R. Oxidation of the phosphorus atom, as given in compounds **6-S** and **7-S**, respectively, does not influence the chemical shift of the carbosilane backbone but results in a downfield shift of ca. 0.3 ppm of the C_5H_4 α proton signals (*e.g.*, H^{α}/C_5H_4P: **6a**, 4.07; **6a-S**, 4.42 ppm). The ^{1}H NMR spectra of the ruthenium complexes **10** and **11** show the expected signal patterns as typical for the ferrocenyl and carbosilane moieties with chemical shifts similar to those of the sulfides **6-S** and **7-S**. In contrast, the chemical shifts of the *p*-cymene protons depend on the nature of the phosphino units. More basic phosphines induce a shift of the respective protons to a higher magnetic field.

In the $^{13}C\{^1H\}$ NMR spectra of **6** and **7** a characteristic signal pattern for the carbosilane backbone can be found between 17 and 22 ppm, independent from the PR_2 building blocks. On the other hand, the internal silicon atom of the Si–CH_2 unit is by 2.5 ppm shifted to higher field, when going from **6** to **7**. The spectra of the ferrocenyl C_5H_4 rings show the expected resonance signals at ca. 70 ppm with typical J_{CP} coupling constants of which $^1J_{CP}$ shows a direct dependence on the electronic properties of the appropriate phosphine (*e.g.*, $^1J_{CP}$ = 17 (**6b**, **7b**), 7 (**6a**, **7a**), 5 (**6c**, **7c**) Hz). The oxidation of phosphorus, as given in compounds **6-S** and **7-S**, barely influences the shift of the resonance signals, though the $^1J_{CP}$ coupling constants are greatly enlarged (*e.g.*, $^1J_{CP}$ = 80 (**6b-S**, **7b-S**), 100 (**6a-S**, **7a-S**), 110 (**6c-S**, **7c-S**) Hz), which is a common phenomenon for phosphorus(V) compounds [16]. A similar behavior is found for ruthenium complexes **10** and **11**. Merely, the shifts of the *ipso*-carbon atoms to lower field and the $^1J_{CP}$ coupling constants are affected by the coordination of phosphorus to [$RuCl_2(\eta^6$-*p*-cymene)]. However, the magnitude of $^1J_{CP}$ is smaller, when compared to compounds **6-S** and **7-S**, respectively (*e.g.*, $^1J_{CP}$ = 5 (**6c**, **7c**), 110 (**6c-S**, **7c-S**), 55 (**10c**, **11c**) Hz) but is still a measure for the σ donor capability of the respective phosphine.

In addition, the newly prepared compounds have been identified by $^{29}Si\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. The $^{29}Si\{^1H\}$ spectra show two singlets of which the one at higher magnetic field can be assigned to the outer silicon atoms. Nevertheless, a shift upon oxidation or coordination of P to Ru cannot be observed. More expressive is $^{31}P\{^1H\}$ NMR spectroscopy. Upon coordination of the phosphorus atom to ruthenium a significant shift to lower field takes place, *i.e.* **6a**, −17.9 ppm; **10a**, 18.4 ppm. Oxidation of phosphorus also induces, as expected, a significant shift to lower field (*e.g.*, **6a**, −17.9 ppm; **6a-S**, 41.6 ppm). This allows controlling the reaction progress of **6** and **7** with sulfur or the ruthenium species. The nature of the organic group bound to the phosphorus atom also influences the chemical shift (*e.g.*, **6a**, −17.9 ppm; **6b**, −8.6 ppm) and hence the electronic properties of the phosphine. The σ donor capacity of phosphines can be quantified by the coupling constant $^1J_{31P-77Se}$ of the appropriate seleno phosphines [16,17]. Electron-withdrawing groups at the phosphorus atom increase $^1J_{31P-77Se}$ due to the increased *s* character of the phosphorus orbital involved in the P–Se bonding. To verify the basicity of the carbosilane-functionalized phosphines **6** and **7** the corresponding *non*-functionalized seleno phosphines **4a-Se**–**4c-Se** were prepared [16]. The $^{31}P\{^1H\}$ NMR data and the $^1J_{31P-77Se}$ coupling constants are summarized in Table 2.

Table 2
Chemical shifts and $^1J_{31P-77Se}$ data of **4a-Se**–**4c-Se**.

Compd.	δ/ppm	$^1J_{31P-77Se}$/Hz
4a-Se	30.8	733
4b-Se	48.8	699
4c-Se	−7.2	756

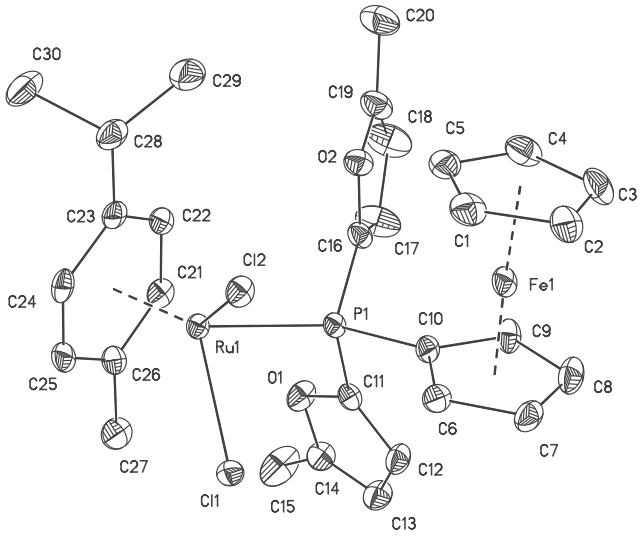


Fig. 1. ORTEP diagram (50% probability level) of the molecular structure of **9c** with the atom-numbering scheme. All hydrogen atoms and the packing solvents chloroform and pentane have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–P1 = 2.3326(10), Ru1–Cl1 = 2.3965(9), Ru1–Cl2 = 2.4110(10), P1–C10 = 1.808(4), P1–C11 = 1.799(4), P1–C16 = 1.795(4), D1–Fe1 = 1.641(3), D2–Fe1 = 1.641(3), D3–Ru1 = 1.697(2), Cl1–Ru1–Cl2 = 88.26(3), Cl1–Ru1–P1 = 81.95(3), Cl2–Ru1–P1 = 91.44(3), C16–P1–Ru1 = 113.78(14), C11–P1–Ru1 = 112.79(13), C10–P1–Ru1 = 124.38(14), C10–P1–C11 = 97.63(19), C10–P1–C16 = 104.19(19), C11–P1–C16 = 100.56(19), C11–O1–C14 = 106.9(3), C16–O2–C19 = 107.8(4), D1–Fe1–D2 = 176.87(5). (D1 denotes the centroid of C_5H_4 at Fe1, D2 denotes the centroid of C_5H_5 at Fe1, D3 denotes the centroid of C_6H_4 at Ru1).

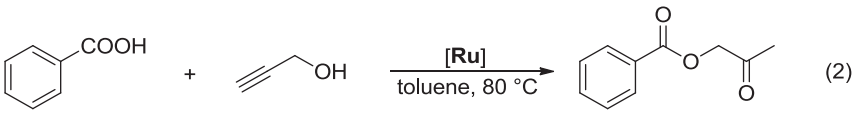
From Table 2 it can be seen that the most basic phosphine and hence the strongest σ donor is the cyclohexyl derivative **4b-Se**. In contrast, the methylfuryl-carrying seleno phosphine **4c-Se** with a significantly higher $^1J_{31P-77Se}$ magnitude is less basic. Based on the obtained data it is obvious that the electronic character of the phosphine can easily be modified by varying the attached groups.

The structure of **9c** in the solid state was determined by single crystal X-ray structure analysis (Fig. 1). Suitable crystals were obtained by slow diffusion of pentane into a saturated chloroform solution containing **9c** at ambient temperature. Selected bond distances (Å) and angles (°) are given in the caption of Fig. 1. The crystal and structure refinement data are presented in the Experimental section.

Complex **9c** crystallizes in the triclinic space group $P\bar{1}$ and is set-up by one ferrocenylphosphanyl unit, two 2-(5-methyl)furyl groups and a ruthenium dichloro *p*-cymene moiety at the phosphorus atom. The bond angles at P1 are between 97.63(19) and 104.19(19)° confirming the tetrahedral geometry. The ferrocenyl groups exhibit an almost eclipsed conformation (7.7(3)°) and the D1–Fe1 and D2–Fe1 separations are 1.641(3) and 1.641(3) Å (D1 denotes the centroid of C_5H_4 at Fe1, D2 denotes the centroid of C_5H_5 at Fe1). The bond angles at Ru1 are between 81.95(3) and 91.44(3) indicating the typical "piano-stool" geometry. All other structural parameters are unexceptional and correspond to those of related compounds [9,11,13].

Catalysis

As model reaction, to see if **9**–**11** can successfully be used as catalysts, the conversion of benzoic acid with propargyl alcohol to produce β-oxopropyl benzoate was chosen (Reaction 2).



(2)

The reaction conditions were optimized by varying the internal standard, the solvent and the ruthenium loading. The conversions were determined by ^{1}H NMR spectroscopy. In contrast to the reaction conditions reported by Dixneuf [1], initial experiments showed that the applied catalysts need higher reaction temperatures and hence the catalytic reactions were performed at 80 °C.

Internal standard

An ideal standard contains various beneficial properties such as inert behavior in the catalytic reaction, low vapor pressure and separated signals in the ^{1}H NMR spectra. Beletskaya et al. [18] suggested that acetyl ferrocene is a suitable standard for Suzuki–Miyaura and Buchwald–Hartwig cross-couplings. Preliminary tests applying acetyl ferrocene showed that the activities and productivities were lower, when compared to acenaphthene as internal standard (Table 3, Figure S1, Supporting information). This result can most probably be attributed to a competitive reaction of the acetyl group with the ruthenium center resulting in a hindering of the η^2-coordination of the acetylide group of the propargyl alcohol. However, after 24 h almost identical conversions (*e.g.*, **9c**, 94 and 95%, respectively; Table 3) were achieved, which suggests that the coordination of the acetyl ferrocene is a reversible reaction. Although, acenaphthene has a relatively low vapor pressure (0.3 Pa, 25 °C [19]) it is preferable over acetyl ferrocene as internal standard due to the aforementioned activity problems and its significantly lower toxicity.

Ruthenium loading

β-Oxoalkyl ester synthesis is usually performed using a ruthenium loading of 1.0 mol-% [1,10,11,20]. Since systematic studies concerning the influence of the catalyst concentration on the achieved conversions are not described so far, we decided to apply the well-known catalyst [$RuCl_2(PPh_3)(\eta^6$-*p*-cymene)] [1] in the formation of β-oxopropyl benzoate using ruthenium loadings in the range of 0.25–1.0 mol-% (Table 4, Figure S2, Supporting information). From Table 4 and Figure S2 it can be seen that the higher the catalyst loading, the higher the conversion is. Especially at low ruthenium loadings of 0.25 mol-% the reaction proceeds very slowly (*e.g.*, 24 h, 39%). In contrast, the differences of the conversions achieved with a higher ruthenium loading of 0.75 and 1.0 mol-%, respectively, are less significant (*e.g.*, 0.75 mol-%, 70%; 1.0 mol-%, 75% after 24 h). In further catalytic reactions catalyst loadings of 1.0 mol-% per ruthenium were applied.

Solvent

The success of a homogenous reaction is highly dependent on the solubility of the respective catalyst in the reaction medium. The most commonly used solvent in β-oxoalkyl ester synthesis is toluene [1,10,20]. Preliminary studies showed that the solubility of the carbosilane ruthenium complexes in toluene decreases in the order **9** > **10** > **11** and hence the catalytic activity and productivity decreases (Table 5, Figure S3, Supporting information). To clarify, whether the differences in activity and productivity are based on solubility issues, we compared the conversions for **9c** and the fourfold substituted carbosilane **11c** (Table 5, Figure S4, Supporting information) using catalyst loadings of 0.5 and 1.0 mol-%, respectively. As it can be seen from Table 5 and Figure S4 (Supporting information) the most significant differences in activity can be observed for *non*-supported **9c** which achieves conversions of 78 and 87%, when increasing the amount of ruthenium (*vide supra*). In contrast, complex **11c** shows virtually no dependency on the concentration (0.5 mol-%, 38%; 1.0 mol-%, 40%) which is attributed to its lower solubility in toluene.

Since the newly synthesized catalysts exhibit a divergent solubility behavior, which depends on the nature of the organic groups attached to the phosphorus atom as well as the degree of immobilization, we decided to use different reaction media to prevent

Table 3
Dependency of the productivity on the applied internal standard.

Compd.	Acetyl ferrocene		Acenaphthene	
	Conversion[a]/%	Conversion[b]/%	Conversion[a]/%	Conversion[b]/%
9a	24	82	23.5	79
9b	38	88	55	87
9c	30	95	40	94

Reaction conditions: 3.0 mmol benzoic acid, 4.5 mmol propargyl alcohol, 0.75 mmol acetyl ferrocene or 1.5 mmol acenaphthene, 15 mL toluene, 1.0 mol-% based on Ru, 80 °C.
[a] Reaction time 7.5 h.
[b] Reaction time 24 h.

Table 4
Dependency of the productivity on the Ru loading.

Ru loading/mol-%	Conversion/%			
	3 h	6 h	9 h	24 h
0.25	2	7	20	39
0.5	4	18	33	60
0.75	8	27	48	70
1.0	10	29	54	75

Reaction conditions: 3.0 mmol benzoic acid, 4.5 mmol propargyl alcohol, 1.5 mmol acenaphthene, 15 mL toluene, 1.0 mol-% [$RuCl_2(PPh_3)(\eta^6$-*p*-cymene)], 80 °C.

Table 5
Activity and productivity of **9b**, **10b** and **11b** after 9 h and of **9c** and **11c** with ruthenium loadings of 0.5 and 1.0 mol-%.

Compd.	TON	TOF/h^{-1}
9b	66[a]	7[a]
9c	94[a]	7[a,c]
	78[b]	4[b,c]
10b	39[b]	4[a]
11b	29[a]	3[a]
11c	40[a]	3[a,c]
	38[b]	2[b,c]

Reaction conditions: 3.0 mmol benzoic acid, 4.5 mmol propargyl alcohol, 1.5 mmol acenaphthene, 15 mL toluene, 80 °C.
[a] 1.0 mol-% based on Ru.
[b] 0.5 mol-% based on Ru.
[c] TOFs between 3 and 9 h.

Table 6
Influence of the solvent on the obtained conversions.

Solvent	Conversion/%		
	4 h	7 h	24 h
1,4-Dioxane	4	7	22
Toluene	7	16.5	78
Toluene/MeCN	26	47	82
Chlorobenzene	45	69	85

Reaction conditions: 3.0 mmol benzoic acid, 4.5 mmol propargyl alcohol, 1.5 mmol acenaphthene, 15 mL solvent, 1.0 mol-% **9c**, 80 °C.

solubility problems. We examined more polar solvents such as 1,4-dioxane, chlorobenzene and a mixture of toluene/acetonitrile (ratio 10:1, *v*/*v*). As catalyst, the *non*-supported complex [P(2-(5-Me)$C_4H_2O)_2$(Fc)$RuCl_2(\eta^6$-*p*-cymene)] (**9c**) was applied, which is soluble in all tested solvents and hence the obtained conversions should only dependent on the solvent itself. As it can be seen from Table 6 and Figure S5 (Supporting information), the catalytic reaction proceeds slowly in toluene and 1,4-dioxane with conversions below 20% after 7 h. The conversion obtained in toluene (78%) after 24 h is considerably higher, when compared to 1,4-dioxane (22%) (Table 6, Figure S5, Supporting information). Addition of 10 vol-% of acetonitrile barely increases the productivity (82%), whereas the rate of the reaction is significantly increased with conversions of 47% after 7 h (toluene: 16.5%). However, the highest activity and productivity is obtained, when chlorobenzene was used as solvent (70% conversion after 7 h). For this reason, this solvent was used in further catalytic reactions.

Catalyst screening

All ruthenium complexes **9**–**11** were studied under optimized reaction conditions in the addition of benzoic acid to propargyl alcohol to give β-oxopropyl benzoate (1.0 mol-% Ru loading, chlorobenzene as solvent and acenaphthene as internal standard). In Fig. 2 the reaction profiles obtained for cyclohexyl-substituted complexes **9b**, **10b** and **11b** are depicted. It can be seen that the degree of immobilization has virtually no influence on the catalytic performance due to the good solubility of the catalyst in the solvent chlorobenzene. Turnover frequencies of 7–8 h^{-1} and conversions ≥90% can be achieved for all catalysts **9**–**11** after 24 h. Furthermore, these results show that the influence of the basicity of the respective phosphine ligands on the productivity is negligible under these reaction conditions.

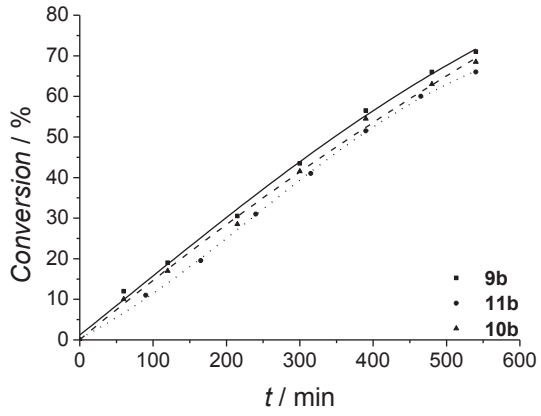


Fig. 2. Reaction profile for the coupling of benzoic acid (3.0 mmol) with propargyl alcohol (4.5 mmol) using 1.0 mol-% of **9b**, **10b** and **11b** (based on Ru) in chlorobenzene (15 mL) at 80 °C.

Table 7
Productivity of complexes **11a**–**c** after 24 h and a ruthenium loading of 0.1 mol-%.

Compd.	Conversion/%	TON
11a	39	390
11b	30	300
11c	48	480

Reaction conditions: 3.0 mmol benzoic acid, 4.5 mmol propargyl alcohol, 1.5 mmol acenaphthene, 15 mL chlorobenzene, 0.1 mol-% **11a** – **c** (based on Ru), 80 °C.

To investigate the influence of the basicity of the respective phosphine on the productivity of the catalyst, we reduced the catalyst loading to 0.1 mol-% (based on Ru). The conversions obtained for **11a**–**c** are shown in Table 7. The results indicate that phosphine complex **11c**, bearing electron-withdrawing methylfuryl groups, is the most productive system (48%, TON: 480). In contrast, electron-rich **11b** shows visibly lower conversions of 30% (TON: 300) attributing to its lower stability in solution, which is problematic when long reaction times and low catalyst loadings are required.

In contrast to the productivities, the activities show obvious tendencies concerning basicity even with higher catalyst loadings of 1.0 mol-% (Table 8, Figure S6, Supporting information). From Table 8 and Figure S6 it is obvious that the methylfuryl-substituted carbosilane-supported compounds **10c** and **11c** and the *non*-supported ruthenium complex **9c** with their electron-withdrawing methylfuryl groups are noticeably more active, when compared to strong (**9b**–**11b**) and moderate (**9a**–**11a**) σ donating ferrocenyl phosphines.

The obtained activities and conversions show that a good solubility of the applied catalyst is mandatory for the success of the β-oxopropyl ester synthesis. In case of incomplete solubility of the catalyst a great loss of activity is to be expected. Furthermore, we observed that the catalytic formation of β-oxopropyl esters is intolerant regarding immobilization unless the support is completely soluble in the reaction medium. In terms of basicity, the applied catalyst systems should carry electron-withdrawing and less basic groups to enhance the rate of the reaction which is in agreement with the results published earlier by Goossen and coworkers [12].

Conclusion

Within this study the synthesis and characterization of a series of carbosilane-supported ferrocenyl phosphine ruthenium complexes of type $SiMe_{4-n}((\eta^5$-$C_5H_4SiMe_2(CH_2)_3)Fe(\eta^5$-$C_5H_4PR_2)$ $RuCl_2(\eta^6$-*p*-cymene$))_n$ (*p*-cymene = 1-*i*-Pr-4-Me-C_6H_4; *n* = 2, 4: R = Ph, $^cC_6H_{11}$, 2-(5-Me)C_4H_2O) is reported. The carbosilane-supported ruthenium complexes were used as catalysts in the formation of β-oxopropyl benzoate by addition of benzoic acid to propargyl alcohol. The reaction conditions were optimized including the ruthenium loading (1.0 mol-%), the temperature (80 °C), the solvent (chlorobenzene) and the internal standard (acenaphthene). All complexes are suitable as catalysts although their performance is highly dependent on the solubility, due to the

Table 8
Activity of complexes **9**–**11** after 9 h.

Compd.	TOF/h^{-1}	Compd.	TOF/h^{-1}	Compd.	TOF/h^{-1}
9a	7	**10a**	6.5	**11a**	6
9b	8	**10b**	7	**11b**	7.5
9c	10	**10c**	9	**11c**	9

Reaction conditions: 3.0 mmol benzoic acid, 4.5 mmol propargyl alcohol, 1.5 mmol acenaphthene, 15 mL chlorobenzene, 1.0 mol-% **9**–**11** (based on Ru), 80 °C.

low tolerance of the reaction regarding immobilization. However, the degree of immobilization does not influence the activity or productivity. In accordance to the results published by Goossen et al. [12], catalysts featuring less basic electron-withdrawing groups enhance the rate of the reaction.

Experimental

General procedures

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

NMR spectra were recorded at 298 K with a Bruker Avance 250 or a Bruker Avance III 500 spectrometer. The ^{1}H NMR spectra were recorded at 250.13 or 500.3 MHz, the ^{13}C{^{1}H} at 125.7 MHz, the ^{29}Si{^{1}H} at 49.66 or 99.39 MHz and the ^{31}P{^{1}H} NMR spectra at 101.249 or 202.5 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^{1}H NMR: standard internal $CDCl_3$, δ 7.26; ^{13}C{^{1}H} NMR: standard internal $CDCl_3$, δ 77.16; ^{29}Si{^{1}H} NMR: standard external rel. $SiMe_4$, δ 0.0; ^{31}P{^{1}H} NMR: standard external rel. 85% H_3PO_4, δ 0.0; $P(OMe)_3$, δ 139.0). Elemental analyses were carried out with a Thermo Flashea 1112 series instrument. Melting points of analytical pure samples were determined with a Gallenkamp MFB 595 010 M melting point apparatus. FT IR spectra were recorded with a Thermo Nicolet IR 200 spectrometer using NaCl plates. All starting materials were obtained from commercial suppliers and used without further purification. 1,1′-Dibromo ferrocene (**1**) [14], $P(^{c}C_6H_{11})_2Cl$ (**2b**) [21], $P(2\text{-}(5\text{-Me})C_4H_2O)_2Cl$ (**2c**) [22], $Me_2Si(CH_2CH_2CH_2SiMe_2Cl)_2$ (**5a**) [23], $Si(CH_2CH_2CH_2SiMe_2Cl)_4$ (**5b**) [24], and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (**8**) [25] were prepared according to published procedures.

*Synthesis of 1-bromo-1′-di(2-(5-methylfuryl)phosphanyl)ferrocene (**3c**)*

To a solution of 1,1′-dibromo ferrocene (**1**, 2.58 g, 7.50 mmol, 1.0 equiv) dissolved in tetrahydrofuran (40 mL) a 2.5 M solution of *n*-butyl lithium in hexane (2.85 mL, 7.13 mmol, 0.95 equiv) was added dropwise at −70 °C. After stirring the reaction solution at this temperature for 1 h, chlorodi-2-(5-methyl)furyl phosphine (**2c**) (1.71 g, 7.50 mmol) was added in a single portion. The reaction mixture was stirred for 1 h at ambient temperature and was then concentrated in oil pump vacuum. The resulting residue was purified by column chromatography on alumina using a mixture of hexane–diethyl ether (ratio 5:1; *v*/*v*). After drying in oil pump vacuum the title compound was obtained as a pale yellow solid. Please, note that **3c** could not be completely separated from $P(Fc)(2\text{-}(5\text{-Me})C_4H_2O)_2$ formed as by-product and hence was used without additional purification in further reactions. Anal. Calcd. for $C_{20}H_{18}BrFeO_2P$ (457.08 g/mol): C, 52.55; H, 3.97. Found: C, 54.22*; H 3.92*. Mp.: 77 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 1019 (s, C–O–C), 1410/1446/1496/1593 (w, C=C), 2920/2951 (w, C–H), 3109 (w, =C–H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 2.36 (s, 6H, CH_3), 3.99 (pt, $^{3/4}J_{HH}$ = 1.9 Hz, 2H, H^{β}/C_5H_4Br), 4.31 (pt, $^{3/4}J_{HH}$ = 1.9 Hz, 2H, H^{α}/C_5H_4Br), 4.38 (dpt, $^{4}J_{PH}$ = 0.6 Hz, $^{3/4}J_{HH}$ = 2.0 Hz, 2H, H^{β}/C_5H_4P), 4.47 (dpt, $^{3}J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 2.0 Hz, 2H, H^{α}/C_5H_4P), 5.99 (ddq, $^{4}J_{PH}$ = 1.4 Hz, $^{3}J_{HH}$ = 3.1 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2H, H^{4}/5-MeC_4H_2O), 6.59 (ddq, $^{3}J_{PH}$ = 1.9 Hz, $^{3}J_{HH}$ = 3.1 Hz, $^{5}J_{HH}$ = 0.2 Hz, 2H, H^{3}/5-MeC_4H_2O). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 14.1 (s, CH_3), 68.5 (s, C^{β}/C_5H_4Br), 71.2 (s, C^{α}/C_5H_4Br), 74.0 (d, $^{3}J_{CP}$ = 5 Hz, C^{β}/C_5H_4P), 75.5 (d, $^{1}J_{CP}$ = 3 Hz, C^{i}/C_5H_4P), 75.8 (d, $^{2}J_{CP}$ = 18 Hz, C^{α}/C_5H_4P), 77.9 (s, C^{i}/C_5H_4Br), 107.0 (d, $^{3}J_{CP}$ = 6 Hz, C^{4}/5-MeC_4H_2O), 121.1 (d, $^{2}J_{CP}$ = 22 Hz, C^{3}/5-MeC_4H_2O), 150.2 (d, $^{1}J_{CP}$ = 4 Hz, C^{2}/5-MeC_4H_2O), 156.7 (d, $^{3}J_{CP}$ = 3 Hz, C^{5}/5-MeC_4H_2O). ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$, δ): −66.7 (s). *) The sample included 15% 1-di(2-(5-methylfuryl) phosphanyl)ferrocene (**4b**) which could not be separated from the title compound.

*Synthesis of Fe(η^5-C_5H_4P(2-(5-Me)$C_4H_2O)_2$Se)(η^5-C_5H_5) (**4c-Se**)*

To a toluene solution of **4c** (123 g, 0.27 mmol) selenium (43 mg, 0.55 mmol, 2.0 equiv) was added in a single portion. The reaction mixture was refluxed for 30 min and after cooling to ambient temperature the suspension was filtered through a pad of Celite. After removal of the solvent in oil pump vacuum, the title compound **4c-Se** was obtained as an orange solid. Yield: 125 mg (0.27 mmol, 100% based on **4c**). Anal. Calcd. for $C_{20}H_{19}FeO_2PSe$ (457.14 g/mol): C, 52.55; H, 4.19. Found: C, 52.38; H, 4.12; Mp.: 138 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 577 (m, P=Se), 1021 (s, C–O–C), 1590 (m, C=C), 2911/2956 (w, C–H), 3091 (w, =C–H). ^{1}H NMR (500.30 MHz, $CDCl_3$, δ): 2.32 (s, 6H, CH_3), 4.16 (s, 5H, C_5H_5), 4.45 (dpt, $^{4}J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H^{β}/C_5H_4), 4.67 (dpt, $^{3}J_{PH}$ = 2.7 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H^{α}/C_5H_4), 6.04 (ddq, $^{4}J_{PH}$ = 1.8 Hz, $^{3}J_{HH}$ = 3.2 Hz, $^{4}J_{HH}$ = 0.9 Hz, 2H, H^{4}/5-MeC_4H_2O), 6.88 (ddq, $^{3}J_{PH}$ = 3.2 Hz, $^{3}J_{HH}$ = 3.2 Hz, $^{5}J_{HH}$ = 0.4 Hz, 2H, H^{3}/5-MeC_4H_2O). ^{13}C{^{1}H} NMR (125.81 MHz, $CDCl_3$, δ): 14.0 (s, CH_3), 70.0 (s, C_5H_5), 71.6 (d, $^{3}J_{PC}$ = 11 Hz, C^{β}/C_5H_4), 71.9 (d, $^{1}J_{PC}$ = 101 Hz, C^{i}/C_5H_4), 72.8 (d, $^{2}J_{PC}$ = 14 Hz, C^{α}/C_5H_4), 107.5 (d, $^{3}J_{PC}$ = 9 Hz, C^{4}/5-MeC_4H_2O), 123.2 (d, $^{2}J_{PC}$ = 21 Hz, C^{3}/5-MeC_4H_2O), 144.8 (d, $^{1}J_{PC}$ = 117 Hz, C^{2}/5-MeC_4H_2O), 158.6 (d, $^{3}J_{PC}$ = 7 Hz, C^{5}/5-MeC_4H_2O). ^{31}P{^{1}H} NMR (101.25 MHz, $CDCl_3$, δ): −7.2 (s, $^{1}J_{77Se31P}$ = 756 Hz).

*General procedure for the synthesis of carbosilane-ferrocenyl phosphines **6a–c** and **7a–c***

To a solution of 2.5 or 5.0 equiv of **3a–c** dissolved in tetrahydrofuran (10 mL/mmol) 2.25 or 4.5 equiv of *n*-butyl lithium (2.5 M in hexane) were added dropwise at −50 °C. After stirring the reaction mixture for 1 h at −50 °C, a solution of **5** (1.0 equiv) in tetrahydrofuran (10 mL/mmol) was dropwise added. The reaction mixture was stirred for 1 h at ambient temperature and the solvent was removed in oil pump vacuum. The crude product was purified by column chromatography on alumina and dried in oil pump vacuum. For more details see below.

*Synthesis of $SiMe_2$(Fe(η^5-$C_5H_4SiMe_2(CH_2)_3$)(η^5-$C_5H_4PPh_2$))$_2$ (**6a**)*

Following the synthesis procedure described above, **3a** (1.1 g, 2.45 mmol) was reacted with *n*-butyl lithium (0.88 mL, 2.2 mmol) and $Me_2Si((CH_2)_3SiMe_2Cl)_2$ (**5a**, 323 mg, 0.98 mmol). The resulting residue was purified by column chromatography on alumina using a mixture of hexane–diethyl ether (ratio 10:1 to 1:1, *v*/*v*) as eluant. Product **6a** was obtained as a viscous yellow oil. Yield: 0.7 g (0.70 mmol, 71% based on **5a**). Anal. calcd. for $C_{56}H_{66}Fe_2P_2Si_3$ (997.02 g/mol): ^{1}H NMR (250.13 MHz, $CDCl_3$, δ): −0.07 (s, 6H, H^{1}/CH_3), 0.17 (s, 12H, H^{5}/CH_3), 0.52 (m, 4H, H^{2}/CH_2), 0.68 (m, 4H, H^{4}/CH_2), 1.33 (m, 4H, H^{3}/CH_2), 3.98 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4Si), 4.07 (dpt, $^{3}J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 4H, H^{α}/C_5H_4P), 4.17 (pt, $^{3/4}J_{HH}$ = 1.6 Hz, 4H, H^{β}/C_5H_4Si), 4.32 (pt, $^{3/4}J_{HH}$ = 1.8 Hz, 4H, H^{β}/C_5H_4P), 7.28–7.41 (m, 20H, C_6H_5). ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$, δ): −2.9 (s, C^{1}/CH_3), −1.9 (s, C^{5}/CH_3), 18.7 (s, C^{3}/CH_2), 20.1 (s, C^{2}/CH_2), 21.4 (s, C^{4}/CH_2), 71.1 (d, $^{3}J_{CP}$ = 3 Hz, C^{β}/C_5H_4P), 72.2 (s, C^{β}/C_5H_4Si),

72.4 (s, C^{i}/C_5H_4Si), 73.0 (d, $^{2}J_{CP}$ = 15 Hz, C^{α}/C_5H_4P), 74.1 (s, C^{α}/C_5H_4Si), 75.8 (d, $^{1}J_{CP}$ = 7 Hz, C^{i}/C_5H_4P), 128.2 (d, $^{3}J_{CP}$ = 7 Hz, C^{m}/C_6H_5), 128.5 (s, C^{p}/C_6H_5), 133.6 (d, $^{2}J_{CP}$ = 19 Hz, C^{o}/C_6H_5), 139.3 (d, $^{1}J_{CP}$ = 10 Hz, C^{i}/C_6H_5). $^{29}Si\{^{1}H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −2.9 (s, Si), 1.2 (s, Si_{core}). $^{31}P\{^{1}H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −17.9 (s).

*Synthesis of $SiMe_2(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4P(^{c}C_6H_{11})_2))_2$ (**6b**)*

Following the synthesis procedure described earlier, **3b** (0.82 g, 1.78 mmol) was reacted with *n*-butyl lithium (0.64 mL, 1.60 mmol) and $Me_2Si((CH_2)_3SiMe_2Cl)_2$ (**5a**, 234 mg, 0.71 mmol). The crude product was purified by column chromatography on alumina using a mixture of hexane–diethyl ether (ratio 15:1 to 1:1, *v*/*v*) as eluant. Product **6b** was obtained as viscous yellow oil. Yield: 0.58 g (0.57 mmol, 80% based on **5b**). Anal. calcd. for $C_{56}H_{90}Fe_2P_2Si_3$ (1021.21 g/mol): ^{1}H NMR (250.13 MHz, $CDCl_3$, δ): −0.06 (s, 6H, H^{1}/CH_3), 0.23 (s, 12H, H^{5}/CH_3), 0.55 (m, 4H, H^{2}/CH_2), 0.73 (m, 4H, H^{4}/CH_2), 0.95–1.35 (m, 22H, C_6H_{11}), 1.37 (m, 4H, H^{3}/CH_2), 1.59–1.98 (m, 22H, C_6H_{11}), 4.04 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4Si), 4.12 (dpt, $^{3}J_{PH}$ = 1.6 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4P), 4.23 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{β}/C_5H_4P), 4.28 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{β}/C_5H_4Si). $^{13}C\{^{1}H\}$ NMR (62.90 MHz, $CDCl_3$, δ): −3.0 (s, C^{1}/CH_3), −1.9 (s, C^{5}/CH_3), 18.7 (s, C^{3}/CH_2), 20.2 (s, C^{2}/CH_2), 21.5 (s, C^{4}/CH_2), 26.6 (d, $^{4}J_{CP}$ = 1 Hz, C^{11}/C_6H_{11}), 27.4 (d, $^{3}J_{CP}$ = 9 Hz, $C^{9/10}/C_6H_{11}$), 27.5 (d, $^{3}J_{CP}$ = 11 Hz, $C^{9/10}/C_6H_{11}$), 30.3 (d, $^{2}J_{CP}$ = 13 Hz, $C^{7/8}/C_6H_{11}$), 30.4 (d, $^{2}J_{CP}$ = 11 Hz, $C^{7/8}/C_6H_{11}$), 33.6 (d, $^{1}J_{CP}$ = 12 Hz, C^{6}/C_6H_{11}), 69.7 (d, $^{3}J_{CP}$ = 3 Hz, C^{β}/C_5H_4P), 71.6 (d, $^{2}J_{CP}$ = 11 Hz, C^{α}/C_5H_4P), 71.8 (s, C^{i}/C_5H_4Si), 72.8 (s, C^{β}/C_5H_4Si), 73.9 (s, C^{α}/C_5H_4Si), 76.5 (d, $^{1}J_{CP}$ = 17 Hz, C^{i}/C_5H_4P). $^{29}Si\{^{1}H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.0 (s, Si), 1.0 (s, Si_{core}). $^{31}P\{^{1}H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −8.6 (s).

*Synthesis of $SiMe_2(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4P(2\text{-}(5\text{-}Me)C_4H_2O)_2))_2$ (**6c**)*

Compound **3c** (0.87 g, 1.90 mmol) was reacted with *n*-butyl lithium (0.69 mL, 1.71 mmol) and $Me_2Si((CH_2)_3SiMe_2Cl)_2$ (**5a**, 250 mg, 0.76 mmol) as described above. The crude product was purified by column chromatography on alumina using a mixture of hexane–diethyl ether (ratio 7.5:1 to 1:1, *v*/*v*) as eluant. The title compound **6c** was obtained as a viscous dark yellow oil. Yield: 0.57 g (0.56 mmol, 74% based on **5a**). Anal. calcd. for $C_{52}H_{66}Fe_2O_4P_2Si_3$ (1012.97 g/mol): ^{1}H NMR (250.13 MHz, $CDCl_3$, δ): −0.06 (s, 6H, H^{1}/CH_3), 0.21 (s, 12H, H^{5}/CH_3), 0.54 (m, 4H, H^{2}/CH_2), 0.71 (m, 4H, H^{4}/CH_2), 1.35 (m, 4H, H^{3}/CH_2), 2.34 (s, 12H, H^{6}/CH_3), 3.95 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4Si), 4.16 (pt, $^{3/4}J_{HH}$ = 1.6 Hz, 4H, H^{β}/C_5H_4Si), 4.27 (pt, $^{3/4}J_{HH}$ = 1.8 Hz, 4H, H^{β}/C_5H_4P), 4.39 (dpt, $^{3}J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 4H, H^{α}/C_5H_4P), 5.97 (ddq, $^{4}J_{PH}$ = 1.3 Hz, $^{3}J_{HH}$ = 3.0 Hz, $^{4}J_{HH}$ = 1.0 Hz, 4H, H^{4}/5-MeC_4H_2O), 6.56 (ddq, $^{3}J_{PH}$ = 1.9 Hz, $^{3}J_{HH}$ = 3.0 Hz, $^{5}J_{HH}$ = 0.2 Hz, 4H, H^{3}/5-MeC_4H_2O) $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −3.0 (s, C^{1}/CH_3), −1.9 (s, C^{5}/CH_3), 14.1 (s, C^{6}/CH_3), 18.7 (s, C^{3}/CH_2), 20.1 (s, C^{2}/CH_2), 21.4 (s, C^{4}/CH_2), 71.0 (d, $^{3}J_{CP}$ = 5 Hz, C^{β}/C_5H_4P), 72.1 (s, C^{β}/C_5H_4Si), 72.4 (s, C^{i}/C_5H_4Si), 73.4 (d, $^{1}J_{CP}$ = 5 Hz, C^{i}/C_5H_4P), 73.6 (d, $^{2}J_{CP}$ = 18 Hz, C^{α}/C_5H_4P), 74.0 (s, C^{α}/C_5H_4Si), 107.0 (d, $^{3}J_{CP}$ = 6 Hz, C^{4}/5-MeC_4H_2O), 120.8 (d, $^{2}J_{CP}$ = 22 Hz, C^{3}/5-MeC_4H_2O), 150.7 (d, $^{1}J_{CP}$ = 5 Hz, C^{2}/5-MeC_4H_2O), 156.5 (d, $^{3}J_{CP}$ = 3 Hz, C^{5}/5-MeC_4H_2O). $^{29}Si\{^{1}H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.0 (s, Si), 1.1 (s, Si_{core}). $^{31}P\{^{1}H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −66.0 (s).

*Synthesis of $Si(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4PPh_2))_4$ (**7a**)*

Following the synthesis procedure described earlier, **3a** (1.45 g, 3.23 mmol) was reacted with *n*-butyl lithium (1.16 mL, 2.91 mmol) and $Si((CH_2)_3SiMe_2Cl)_4$ (**5b**, 369 mg, 0.65 mmol). The crude product was purified by column chromatography on alumina using first a mixture of hexane–diethyl ether (ratio 7.5:1, *v*/*v*) and then diethyl ether as eluant. Dendritic **7a** was obtained as a viscous dark orange oil. Yield: 0.88 g (0.45 mmol, 62% based on **5b**). Anal. calcd. for $C_{108}H_{120}Fe_4P_4Si_5$ (1905.81 g/mol): ^{1}H NMR (250.13 MHz, $CDCl_3$, δ): 0.20 (s, 24H, H^{4}/CH_3), 0.53 (m, 8H, H^{1}/CH_2), 0.70 (m, 8H, H^{3}/CH_2), 1.33 (m, 8H, H^{2}/CH_2), 4.01 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4Si), 4.10 (dpt, $^{3}J_{PH}$ = 1.9 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 8H, H^{α}/C_5H_4P), 4.20 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4Si), 4.35 (pt, $^{3/4}J_{HH}$ = 1.8 Hz, 8H, H^{β}/C_5H_4P), 7.28–7.44 (m, 40H, C_6H_5). $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −1.9 (s, C^{4}/CH_3), 17.6 (s, C^{1}/CH_2), 18.8 (s, C^{2}/CH_2), 21.9 (s, C^{3}/CH_2), 71.1 (d, $^{3}J_{CP}$ = 4 Hz, C^{β}/C_5H_4P), 72.3 (s, C^{β}/C_5H_4Si), 72.4 (s, C^{i}/C_5H_4Si), 73.0 (d, $^{2}J_{CP}$ = 15 Hz, C^{α}/C_5H_4P), 74.1 (s, C^{α}/C_5H_4Si), 75.9 (d, $^{1}J_{CP}$ = 7 Hz, C^{i}/C_5H_4P), 128.2 (d, $^{3}J_{CP}$ = 7 Hz, C^{m}/C_6H_5), 128.5 (s, C^{p}/C_6H_5), 133.6 (d, $^{2}J_{CP}$ = 19 Hz, C^{o}/C_6H_5), 139.3 (d, $^{1}J_{CP}$ = 10 Hz, C^{i}/C_6H_5). $^{29}Si\{^{1}H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.1 (s, Si), 0.7 (s, Si_{core}). $^{31}P\{^{1}H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −17.8 (s).

*Synthesis of $Si(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4P(^{c}C_6H_{11})_2))_4$ (**7b**)*

Compound **3b** (1.60 g, 3.47 mmol) was reacted with *n*-butyl lithium (1.25 mL, 3.12 mmol) and $Si((CH_2)_3SiMe_2Cl)_4$ (**5b**, 396 mg, 0.69 mmol) as described earlier. The crude product was purified by column chromatography on alumina using first a mixture of hexane–diethyl ether (ratio 10:1, *v*/*v*), followed by diethyl ether as eluant. Compound **7b** was obtained as a viscous dark yellow oil. Yield: 0.79 g (0.40 mmol, 58% based on **5b**). Anal. calcd. for $C_{108}H_{168}Fe_4P_4Si_5$ (1954.19 g/mol): ^{1}H NMR (250.13 MHz, $CDCl_3$, δ): 0.22 (s, 24H, H^{4}/CH_3), 0.53 (m, 8H, H^{1}/CH_2), 0.71 (m, 8H, H^{3}/CH_2), 0.95–1.30 (m, 44H, C_6H_{11}), 1.33 (m, 8H, H^{2}/CH_2), 1.59–1.98 (m, 44H, C_6H_{11}), 4.03 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4Si), 4.12 (dpt, $^{3}J_{PH}$ = 1.6 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4P), 4.22 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4P), 4.27 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4Si). $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −1.8 (s, C^{4}/CH_3), 17.7 (s, C^{1}/CH_2), 18.9 (s, C^{2}/CH_2), 21.9 (s, C^{3}/CH_2), 26.6 (d, $^{4}J_{CP}$ = 1 Hz, C^{10}/C_6H_{11}), 27.4 (d, $^{3}J_{CP}$ = 9 Hz, $C^{8/9}/C_6H_{11}$), 27.5 (d, $^{3}J_{CP}$ = 11 Hz, $C^{8/9}/C_6H_{11}$), 30.3 (d, $^{2}J_{CP}$ = 13 Hz, $C^{6/7}/C_6H_{11}$), 30.4 (d, $^{2}J_{CP}$ = 11 Hz, $C^{6/7}/C_6H_{11}$), 33.6 (d, $^{1}J_{CP}$ = 12 Hz, C^{5}/C_6H_{11}), 69.7 (d, $^{3}J_{CP}$ = 3 Hz, C^{β}/C_5H_4P), 71.5 (d, $^{2}J_{CP}$ = 11 Hz, C^{α}/C_5H_4P), 71.8 (s, C^{i}/C_5H_4Si), 72.8 (s, C^{β}/C_5H_4Si), 73.9 (s, C^{α}/C_5H_4Si), 76.5 (d, $^{1}J_{CP}$ = 17 Hz, C^{i}/C_5H_4P). $^{29}Si\{^{1}H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.1 (s, Si), 0.7 (s, Si_{core}). $^{31}P\{^{1}H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −8.8 (s).

*Synthesis of $Si(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4P(2\text{-}(5\text{-}Me)C_4H_2O)_2))_4$ (**7c**)*

Compound **3c** (1.55 g, 3.39 mmol) was treated with *n*-butyl lithium (1.22 mL, 3.05 mmol) and $Si((CH_2)_3SiMe_2Cl)_4$ (**5b**, 387 mg, 0.68 mmol) as described earlier. The resulting residue was purified by column chromatography on alumina using first a mixture of *n*-hexane–diethyl ether (ratio 5:1, *v*/*v*) followed by diethyl ether as eluant. The title compound **7c** was obtained as a viscous dark yellow oil. Yield: 0.88 g (0.45 mmol, 67% based on **5b**). Anal. calcd. for $C_{100}H_{120}Fe_4O_8P_4Si_5$ (1937.72 g/mol): ^{1}H NMR (250.13 MHz, $CDCl_3$, δ): 0.27 (s, 24H, H^{4}/CH_3), 0.53 (m, 8H, H^{1}/CH_2), 0.70 (m, 8H, H^{3}/CH_2), 1.32 (m, 8H, H^{2}/CH_2), 2.38 (d, $^{4}J_{HH}$ = 0.5 Hz, 24H, H^{9}/CH_3), 4.01 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4Si), 4.22 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4Si), 4.33 (dpt, $^{4}J_{PH}$ = 0.3 Hz, $^{3/4}J_{HH}$ = 1.9 Hz, 8H, H^{β}/C_5H_4P), 4.45 (dpt, $^{3}J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.9 Hz, 8H, H^{α}/C_5H_4P), 6.02 (ddq, $^{4}J_{PH}$ = 1.3 Hz, $^{3}J_{HH}$ = 3.1 Hz, $^{4}J_{HH}$ = 1.0 Hz, 8H, H^{7}/5-MeC_4H_2O), 6.61 (ddq, $^{3}J_{PH}$ = 2.0 Hz, $^{3}J_{HH}$ = 3.1 Hz, $^{5}J_{HH}$ = 0.3 Hz, 8H, H^{6}/5-MeC_4H_2O). $^{13}C\{^{1}H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −1.9 (s, C^{4}/CH_3), 14.0 (s, C^{9}/CH_3), 17.6 (s, C^{1}/CH_2), 18.8 (s, C^{2}/CH_2), 21.7 (s, C^{3}/CH_2), 70.9 (d, $^{3}J_{CP}$ = 5 Hz, C^{β}/C_5H_4P), 72.1 (s, C^{β}/C_5H_4Si), 72.3 (s, C^{i}/C_5H_4Si), 73.4 (d, $^{1}J_{CP}$ = 5 Hz, C^{i}/C_5H_4P), 73.6 (d, $^{2}J_{CP}$ = 18 Hz, C^{α}/C_5H_4P), 73.9 (s, $C^{\alpha}/$

C_5H_4Si), 106.9 (d, $^3J_{CP}$ = 6 Hz, C^7/5-MeC_4H_2O), 120.8 (d, $^2J_{CP}$ = 22 Hz, C^6/5-MeC_4H_2O), 150.7 (d, $^1J_{CP}$ = 5 Hz, C^5/5-MeC_4H_2O), 156.4 (d, $^3J_{CP}$ = 3 Hz, C^8/5-MeC_4H_2O). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.1 (s, Si), 0.7 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −66.0 (s).

*General procedure for the synthesis of carbosilane-ferrocenyl phosphine sulfides **6a-S**–**c-S** and **7a-S**–**c-S***

To a toluene solution (10 mL/mmol) of **6a**–**c** and **7a**–**c** (1.0 equiv), elemental sulfur (2.0 equiv) was added in a single portion and the mixture was stirred for 30 min under reflux. After cooling the reaction mixture to ambient temperature, all volatiles were removed in oil pump vacuum and the products were obtained as yellow to orange highly viscous oils in analytical pure form without the need of any further purification. For more details see below.

*Synthesis of $SiMe_2(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4PPh_2(S)))_2$ (**6a-S**)*

Based on the general procedure described above, **6a** (290 mg, 0.29 mmol) was reacted with sulfur (18.7 mg, 0.58 mmol). After appropriate work-up, **6a-S** was obtained as viscous pale orange oil. Yield: 305 mg (0.29 mmol, 100% based on **6a**). Anal. calcd. for $C_{56}H_{66}Fe_2P_2S_2Si_3$ (1061.15 g/mol): C, 63.38; H, 6.27. Found: C, 63.65; H, 6.38. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 656 (s, P═S), 813/832 (s, Si–C), 1248 (m, Si–Me), 1436/1481 (m, C═C), 2870/2911/2951 (m, C–H), 3055/3074 (m, ═C–H). ^{1}H NMR (500.3 MHz, $CDCl_3$, δ): −0.09 (s, 6H, H^1/CH_3), 0.13 (s, 12H, H^5/CH_3), 0.50 (m, 4H, H^2/CH_2), 0.64 (m, 4H, H^4/CH_2), 1.29 (m, 4H, H^3/CH_2), 4.01 (pt, $^{3/4}J_{HH}$ = 1.8 Hz, 4H, H^α/C_5H_4Si), 4.34 (pt, $^{3/4}J_{HH}$ = 1.8 Hz, 4H, H^β/C_5H_4Si), 4.42 (dpt, $^3J_{PH}$ = 2.1 Hz, $^{3/4}J_{HH}$ = 1.6 Hz, 4H, H^α/C_5H_4P), 4.45 (pt, $^{3/4}J_{HH}$ = 1.9 Hz, $^{3/4}J_{HH}$ = 1.6 Hz, 4H, H^β/C_5H_4P), 7.39–7.49 (m, 12H, $H^{m,p}$/C_6H_5), 7.68–7.75 (m, 8H, H^o/C_6H_5). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −2.9 (s, C^1/CH_3), −1.9 (s, C^5/CH_3), 18.7 (s, C^3/CH_2), 20.1 (s, C^2/CH_2), 21.4 (s, C^4/CH_2), 72.3 (d, $^3J_{CP}$ = 10 Hz, C^β/C_5H_4P), 72.9 (d, $^2J_{CP}$ = 13 Hz, C^α/C_5H_4P), 73.5 (s, C^β/C_5H_4Si), 73.6 (s, C^i/C_5H_4Si), 74.7 (s, C^α/C_5H_4Si), 74.8 (d, $^1J_{CP}$ = 98 Hz, C^i/C_5H_4P), 128.3 (d, $^3J_{CP}$ = 12 Hz, C^m/C_6H_5), 131.3 (d, $^4J_{CP}$ = 3 Hz, C^p/C_6H_5), 131.8 (d, $^2J_{CP}$ = 11 Hz, C^o/C_6H_5), 134.8 (d, $^1J_{CP}$ = 87 Hz, C^i/C_6H_5). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −2.9 (s, Si), 1.0 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 41.6 (s).

*Synthesis of $SiMe_2(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4P(^cC_6H_{11})_2(S)))_2$ (**6b-S**)*

Based on the general procedure described above, **6b** (320 mg, 0.31 mmol) was treated with sulfur (20.1 mg, 0.63 mmol). After appropriate work-up, **6b-S** was obtained as a viscous dark yellow oil. Yield: 335 mg (0.31 mmol, 100% based on **6b**). Anal. calcd. for $C_{56}H_{90}Fe_2P_2S_2Si_3$ (1085.34 g/mol): C, 61.97; H, 8.36. Found: C, 62.47; H, 8.83. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 621/641 (m, P═S), 819/831 (s, Si–C), 1248 (m, Si–Me), 2852/2929 (s, C–H), 3088(w, ═C–H). ^{1}H NMR (500.3 MHz, $CDCl_3$, δ): −0.09 (s, 6H, H^1/CH_3), 0.21 (s, 12H, H^5/CH_3), 0.52 (m, 4H, H^2/CH_2), 0.70 (m, 4H, H^4/CH_2), 1.09–1.44 (m, 22H, C_6H_{11}), 1.33 (m, 4H, H^3/CH_2), 1.63–2.05 (m, 22H, C_6H_{11}), 4.13 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^α/C_5H_4Si), 4.34 (pt, $^4J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^β/C_5H_4P), 4.35 (dpt,$^3J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^α/C_5H_4P), 4.58 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^β/C_5H_4Si). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −3.0 (s, C^1/CH_3), −2.0 (s, C^5/CH_3), 18.6 (s, C^3/CH_2), 20.1 (s, C^2/CH_2), 21.4 (s, C^4/CH_2), 25.8 (d, $^3J_{CP}$ = 3 Hz, $C^{9/10}$/C_6H_{11}), 25.9 (d, $^3J_{CP}$ = 2 Hz, $C^{9/10}$/C_6H_{11}), 26.7 (d, $^2J_{CP}$ = 14 Hz, $C^{7/8}$/C_6H_{11}), 26.7 (d, $^2J_{CP}$ = 13 Hz, $C^{7/8}$/C_6H_{11}), 26.8 (d, $^4J_{CP}$ = 3 Hz, C^{11}/C_6H_{11}), 38.0 (d, $^1J_{CP}$ = 52 Hz, C^6/C_6H_{11}), 70.9 (d, $^3J_{CP}$ = 9 Hz, C^β/C_5H_4P), 71.6 (d, $^2J_{CP}$ = 10 Hz, C^α/C_5H_4P), 73.1 (s, C^i/C_5H_4Si), 73.7 (d, $^1J_{CP}$ = 80 Hz, C^i/C_5H_4P), 74.1 (s, C^β/C_5H_4Si), 74.6 (s, C^α/C_5H_4Si). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −2.9 (s, Si), 1.0 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 57.1 (s).

*Synthesis of $SiMe_2(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4P(2\text{-}(5\text{-Me})C_4H_2O)_2(S)))_2$ (**6c-S**)*

Following the general procedure described above, **6c** (355 mg, 0.35 mmol) was reacted with sulfur (22.5 mg, 0.70 mmol). After appropriate work-up, **6c-S** was obtained as a viscous pale orange oil. Yield: 375 mg (0.35 mmol, 100% based on **6c**). Anal. calcd. for $C_{52}H_{66}Fe_2O_4P_2S_2Si_3$ (1077.10 g/mol): C, 57.98; H, 6.18. Found: C, 58.01; H, 6.46. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 694 (s, P═S), 798/834 (s, Si–C), 1020/1036 (s, C–O–C), 1248 (m, Si–Me), 1591 (m, C═C), 2874/2913/2953 (m, C–H), 3104 (w, ═C–H). ^{1}H NMR (500.3 MHz, $CDCl_3$, δ): −0.08 (s, 6H, H^1/CH_3), 0.18 (s, 12H, H^5/CH_3), 0.52 (m, 4H, H^2/CH_2), 0.68 (m, 4H, H^4/CH_2), 1.32 (m, 4H, H^3/CH_2), 2.36 (s, 12H, H^6/CH_3), 4.03 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^α/C_5H_4Si), 4.38 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^β/C_5H_4Si), 4.40 (pt, $^4J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.9 Hz, 4H, H^β/C_5H_4P), 4.66 (dpt, $^3J_{PH}$ = 2.7 Hz, $^{3/4}J_{HH}$ = 1.9 Hz, 4H, H^α/C_5H_4P), 6.06 (ddq, $^4J_{PH}$ = 1.8 Hz, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 1.0 Hz, 4H, H^4/5-MeC_4H_2O), 6.88 (ddq, $^3J_{PH}$ = 2.6 Hz, $^3J_{HH}$ = 3.3 Hz, $^5J_{HH}$ = 0.5 Hz, 4H, H^3/5-MeC_4H_2O). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −3.1 (s, C^1/CH_3), −2.0 (s, C^5/CH_3), 14.1 (s, C^6/CH_3), 18.6 (s, C^3/CH_2), 20.0 (s, C^2/CH_2), 21.3 (s, C^4/CH_2), 72.0 (d, $^3J_{CP}$ = 11 Hz, C^β/C_5H_4P), 72.3 (d, $^2J_{CP}$ = 14 Hz, C^α/C_5H_4P), 73.2 (d, $^1J_{CP}$ = 110 Hz, C^i/C_5H_4P), 73.4 (s, C^i/C_5H_4Si), 73.5 (s, C^β/C_5H_4Si), 74.6 (s, C^α/C_5H_4Si), 107.5 (d, $^3J_{CP}$ = 9 Hz, C^4/5-MeC_4H_2O), 122.8 (d, $^2J_{CP}$ = 21 Hz, C^3/5-MeC_4H_2O), 146.7 (d, $^1J_{CP}$ = 127 Hz, C^2/5-MeC_4H_2O), 158.5 (d, $^3J_{CP}$ = 7 Hz, C^5/5-MeC_4H_2O). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −2.9 (s, Si), 1.0 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (202.53 MHz, $CDCl_3$, δ): 10.2 (s).

*Synthesis of $Si(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4PPh_2(S)))_4$ (**7a-S**)*

Molecule **7a** (330 mg, 0.17 mmol) was reacted with sulfur (22.2 mg, 0.69 mmol) as described earlier. After appropriate work-up, **7a-S** was obtained as a viscous orange oil. Yield: 350 mg (0.17 mmol, 100% based on **7a**). Anal. calcd. for $C_{108}H_{120}Fe_4P_4S_4Si_5$ (2034.07 g/mol): C, 63.77; H, 5.95. Found: C, 64.37; H, 6.19. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 655 (s, P═S), 815/832(s, Si–C), 1248 (m, Si–Me), 1436/1481 (w, C═C), 2872/2914/2954 (m, C–H), 3056/3075 (m, ═C–H). ^{1}H NMR (500.3 MHz, $CDCl_3$, δ): 0.12 (s, 24H, H^4/CH_3), 0.49 (m, 8H, H^1/CH_2), 0.61 (m, 8H, H^3/CH_2), 1.23 (m, 8H, H^2/CH_2), 4.01 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^α/C_5H_4Si), 4.32 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^β/C_5H_4Si), 4.42 (dpt, $^3J_{PH}$ = 2.1 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^α/C_5H_4P), 4.44 (pt, $^4J_{PH}$ = 1.9 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^β/C_5H_4P), 7.88–7.49 (m, 24H, $H^{m,p}$/C_6H_5), 7.68–7.74 (m, 16H, H^o/C_6H_5). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −1.9 (s, C^4/CH_3), 17.6 (s, C^1/CH_2), 18.8 (s, C^2/CH_2), 21.7 (s, C^3/CH_2), 72.3 (d, $^3J_{CP}$ = 10 Hz, C^β/C_5H_4P), 73.0 (d, $^2J_{CP}$ = 13 Hz, C^α/C_5H_4P), 73.5 (s, C^β/C_5H_4Si), 73.6 (s, C^i/C_5H_4Si), 74.7 (s, C^α/C_5H_4Si), 74.9 (d, $^1J_{CP}$ = 98 Hz, C^i/C_5H_4P), 128.3 (d, $^3J_{CP}$ = 12 Hz, C^m/C_6H_5), 131.3 (d, $^4J_{CP}$ = 3 Hz, C^p/C_6H_5), 131.8 (d, $^2J_{CP}$ = 11 Hz, C^o/C_6H_5), 134.8 (d, $^1J_{CP}$ = 87 Hz, C^i/C_6H_5). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.0 (s, Si), 0.6 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 41.5 (s).

*Synthesis of $Si(Fe(\eta^5\text{-}C_5H_4SiMe_2(CH_2)_3)(\eta^5\text{-}C_5H_4P(^cC_6H_{11})_2(S)))_4$ (**7b-S**)*

Compound **7b** (295 mg, 0.15 mmol) was reacted with sulfur (19.4 mg, 0.60 mmol) as described above. After appropriate work-up, **7b-S** was obtained as a viscous pale orange oil. Yield: 310 mg (0.15 mmol, 100% based on **7b**). Anal. calcd. for $C_{108}H_{168}Fe_4P_4S_4Si_5$ (2082.45 g/mol): C, 62.29; H, 8.13. Found: C, 62.45; H, 8.50. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 621/641 (m, P═S), 818/831 (s, Si–C), 1247 (m, Si–Me), 2852/2928 (s, C–H), 3088 (w, ═C–H). ^{1}H NMR (500.3 MHz, $CDCl_3$,

δ): 0.19 (s, 24H, H^4/CH_3), 0.47 (m, 8H, H^1/CH_2), 0.66 (m, 8H, H^3/CH_2), 0.95–1.30 (m, 44H, C_6H_{11}), 1.30 (m, 8H, H^2/CH_2), 1.59–1.98 (m, 44H, C_6H_{11}), 4.11 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^α/C_5H_4Si), 4.33 (pt, $^4J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^β/C_5H_4P), 4.34 (dpt, $^3J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^α/C_5H_4P), 4.55 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^β/C_5H_4Si). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −2.0 (s, C^4/CH_3), 17.5 (s, C^1/CH_2), 18.7 (s, C^2/CH_2), 21.7 (s, C^3/CH_2), 25.8 (d, $^3J_{CP}$ = 2 Hz, $C^{8/9}/C_6H_{11}$), 25.9 (d, $^3J_{CP}$ = 1 Hz, $C^{8/9}/C_6H_{11}$), 26.7 (d, $^2J_{CP}$ = 13 Hz, $C^{6/7}/C_6H_{11}$), 26.7 (d, $^2J_{CP}$ = 13 Hz, $C^{6/7}/C_6H_{11}$), 26.8 (d, $^4J_{CP}$ = 3 Hz, C^{10}/C_6H_{11}), 38.0 (d, $^1J_{CP}$ = 53 Hz, C^5/C_6H_{11}), 70.9 (d, $^3J_{CP}$ = 9 Hz, C^β/C_5H_4P), 71.6 (d, $^2J_{CP}$ = 10 Hz, C^α/C_5H_4P), 73.0 (s, C^i/C_5H_4Si), 73.9 (d, $^1J_{CP}$ = 79 Hz, C^i/C_5H_4P), 73.9 (s, C^β/C_5H_4Si), 74.5 (s, C^α/C_5H_4Si). $^{29}Si\{^1H\}$ NMR (99.39 MHz, $CDCl_3$, δ): −3.1 (s, Si), 0.7 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 57.1 (s).

*Synthesis of Si(Fe(η^5-$C_5H_4SiMe_2(CH_2)_3$)(η^5-C_5H_4P(2-(5-Me)$C_4H_2O)_2$(S)))$_4$ (**7c-S**)*

Based on the general procedure described earlier, **7c** (310 mg, 0.16 mmol) was reacted with sulfur (20.5 mg, 0.64 mmol). After appropriate work-up, **7c-S** was obtained as a viscous pale orange oil. Yield: 330 mg (0.16 mmol, 100% based on **7c**). Anal. calcd. for $C_{100}H_{120}Fe_4O_8P_4S_4Si_5$ (2065.98 g/mol): C, 58.14; H, 5.85. Found: C, 58.14; H, 6.04. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 693 (s, P═S), 794/834 (s, Si–C), 1020/1036 (s, C–O–C), 1248 (m, Si–Me), 1590 (m, C═C), 2874/2915/2954 (m, C–H), 3104 (w, ═C–H). ^1H NMR (500.3 MHz, $CDCl_3$, δ): 0.18 (s, 24H, H^4/CH_3), 0.48 (m, 8H, H^1/CH_2), 0.66 (m, 8H, H^3/CH_2), 1.26 (m, 8H, H^2/CH_2), 2.35 (s, 24H, H^9/CH_3), 4.03 (pt, $^{3/4}J_{HH}$ = 1.8 Hz, 8H, H^α/C_5H_4Si), 4.36 (pt, $^{3/4}J_{HH}$ = 1.8 Hz, 8H, H^β/C_5H_4Si), 4.40 (dpt, $^4J_{PH}$ = 1.9 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 8H, H^β/C_5H_4P), 4.66 (dpt, $^3J_{PH}$ = 2.6 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 8H, H^α/C_5H_4P), 6.05 (ddq, $^4J_{PH}$ = 1.7 Hz, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 1.0 Hz, 8H, H^4/5-MeC_4H_2O), 6.87 (ddq, $^3J_{PH}$ = 2.5 Hz, $^3J_{HH}$ = 3.3 Hz, $^5J_{HH}$ = 0.4 Hz, 8H, H^3/5-MeC_4H_2O). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −2.0 (s, C^4/CH_3), 14.1 (s, C^9/CH_3), 17.5 (s, C^1/CH_2), 18.7 (s, C^2/CH_2), 21.6 (s, C^3/CH_2), 72.0 (d, $^3J_{CP}$ = 11 Hz, C^β/C_5H_4P), 72.3 (d, $^2J_{CP}$ = 15 Hz, C^α/C_5H_4P), 73.2 (d, $^1J_{CP}$ = 110 Hz, C^i/C_5H_4P), 73.4 (s, C^i/C_5H_4Si), 73.5 (s, C^β/C_5H_4Si), 74.5 (s, C^α/C_5H_4Si), 107.5 (d, $^3J_{CP}$ = 9 Hz, C^4/5-MeC_4H_2O), 122.8 (d, $^2J_{CP}$ = 21 Hz, C^3/5-MeC_4H_2O), 146.6 (d, $^1J_{CP}$ = 127 Hz, C^2/5-MeC_4H_2O), 158.5 (d, $^3J_{CP}$ = 7 Hz, C^5/5-MeC_4H_2O). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.0 (s, Si), 0.6 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 10.1 (s).

*General procedure for the synthesis of [$RuCl_2$(η^6-p-cymene)(PR_2Fc)] (**9a**–**c**)*

To a solution of **3a**–**c** (1.0 equiv) in tetrahydrofuran (10 mL/mmol) a 2.5 M solution of *n*-butyl lithium in hexane (1.1 equiv) was added dropwise at −40 °C. After stirring the reaction mixture for 45 min at this temperature, methanol (1.0 mL) was added dropwise. The reaction mixture was warmed to ambient temperature and all volatile materials were removed in oil pump vacuum. The residue was then dissolved in diethyl ether (30 mL) and filtered through a pad of Celite. After removal of the solvent, phosphines **4a**–**c** were dissolved in dichloromethane (10 mL/mmol), [$RuCl_2$(η^6-*p*-cymene)]$_2$ (**8**) (0.5 equiv) was added in a single portion and the reaction mixture was stirred for 2 h at ambient temperature. Afterward, all volatiles were removed in vacuum and the residue was washed thrice with 10 mL portions of pentane. After drying in oil pump vacuum, the appropriate complexes were obtained as orange to red solids. For more details see below.

*Synthesis of [$RuCl_2$(η^6-p-cymene)(PPh_2Fc)] (**9a**)*

Following the synthesis procedure described above, **3a** (580 mg, 1.29 mmol) was reacted with *n*-butyl lithium (0.57 mL, 1.42 mmol) and an excess of methanol (1.0 mL). Appropriate work-up, resulted in the formation of phosphine **4a**, which was then treated with [$RuCl_2$(η^6-*p*-cymene)]$_2$ (**8**) (395 mg, 0.64 mmol) to afford complex **9a** as a dark orange solid. Yield: 830 mg (1.23 mmol, 95% based on **3a**). Anal. calcd. for $C_{32}H_{33}Cl_2FePRu$ (676.40 g/mol): C, 56.82; H, 4.92. Found: C, 56.71; H, 5.15. Mp.: 205 °C (dec.). IR (NaCl, $\tilde{\nu}$/cm^{-1}): 1434/1482 (m, C═C), 2869/2924/2961 (m, C–H), 3050 (m, ═C–H). ^1H NMR (500.3 MHz, $CDCl_3$, δ): 0.97 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.80 (s, 3H, CH_3), 2.58 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), 3.77 (s, 5H, C_5H_5), 4.36 (dpt, $^4J_{PH}$ = 1.4 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H^β/C_5H_4), 4.49 (dpt, $^3J_{PH}$ = 2.0 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H^α/C_5H_4), 5.11 (m, 2H, C_6H_4), 5.14 (m, $^3J_{PH}$ = 1.5 Hz, 2H, C_6H_4), 7.35–7.47 (m, 6H, $H^{m,p}/C_6H_5$), 7.87–7.93 (m, 4H, H^o/C_6H_5). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 17.0 (s, CH_3), 21.6 (s, $CH(CH_3)_2$), 29.8 (s, $CH(CH_3)_2$), 69.8 (s, C_5H_5), 69.9 (d, $^3J_{CP}$ = 8 Hz, C^β/C_5H_4), 74.6 (d, $^2J_{CP}$ = 11 Hz, C^α/C_5H_4), 76.7 (d, $^1J_{CP}$ = 49 Hz, C^i/C_5H_4), 85.7 (d, $^2J_{CP}$ = 6 Hz, C_6H_4), 90.0 (d, $^2J_{CP}$ = 4 Hz, C_6H_4), 94.7 (s, C^i/C_6H_4), 108.8 (s, C^i/C_6H_4), 127.2 (d, $^3J_{CP}$ = 10 Hz, C^m/C_6H_5), 129.9 (d, $^4J_{CP}$ = 2 Hz, C^p/C_6H_5), 133.8 (d, $^2J_{CP}$ = 9 Hz, C^o/C_6H_5), 136.0 (d, $^1J_{CP}$ = 47 Hz, C^i/C_6H_5). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 18.4 (s).

*Synthesis of [$RuCl_2$(η^6-p-cymene)(P($^cC_6H_{11})_2$Fc)] (**9b**)*

Compound **3b** (605 mg, 1.31 mmol) was reacted with *n*-butyl lithium (0.58 mL, 1.44 mmol) and methanol (1.0 mL). After appropriate work-up, phosphine **4b** was then reacted with [$RuCl_2$(η^6-*p*-cymene)]$_2$ (**8**) (400 mg, 0.65 mmol) to afford complex **9b** as a pale red solid. Yield: 885 mg (1.28 mmol, 98% based on **3b**). Anal. calcd. for $C_{32}H_{45}Cl_2FePRu$ (688.49 g/mol): C, 55.82; H, 6.59. Found: C, 55.93; H, 6.76. Mp.: 195 °C (dec.). IR (NaCl, $\tilde{\nu}$/cm^{-1}): 1445 (m, C═C), 2849/2921 (s, C–H), 3046 (w, ═C–H). ^1H NMR (500.3 MHz, $CDCl_3$, δ): 1.14 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.19–1.42 (m, C_6H_{11}), 1.68–2.07 (m, C_6H_{11}), 1.89 (s, 3H, CH_3), 2.35–2.64 (m, C_6H_{11}), 2.68 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), 4.27 (s, 5H, C_5H_5), 4.49 (dpt, $^4J_{PH}$ = 0.9 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H^β/C_5H_4), 4.53 (dpt, $^3J_{PH}$ = 1.7 Hz, $^{3/4}J_{HH}$ = 1.8 Hz, 2H, H^α/C_5H_4), 4.84 (m, 2H, C_6H_4), 4.98 (m, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 17.7 (s, CH_3), 22.5 (s, $CH(CH_3)_2$), 26.3 (d, $^4J_{CP}$ = 1 Hz, C^6/C_6H_{11}), 27.8 (d, $^3J_{CP}$ = 11 Hz, $C^{4,5}/C_6H_{11}$), 28.1 (d, $^3J_{CP}$ = 11 Hz, $C^{4,5}/C_6H_{11}$), 29.4 (s, $C^{2,3}/C_6H_{11}$), 30.0 (s, $C^{2,3}/C_6H_{11}$), 30.4 (s, $CH(CH_3)_2$), 39.6 (d, $^1J_{PC}$ = 21 Hz, C^1/C_6H_{11}), 69.5 (d, $^3J_{CP}$ = 7 Hz, C^β/C_5H_4), 70.0 (s, C_5H_5), 72.5 (d, $^2J_{CP}$ = 8 Hz, C^α/C_5H_4), 82.0 (d, $^1J_{CP}$ = 30 Hz, C^i/C_5H_4), 85.4 (d, $^2J_{CP}$ = 5 Hz, C_6H_4), 89.8 (d, $^2J_{CP}$ = 4 Hz, C_6H_4), 93.8 (s, C^i/C_6H_4), 107.0 (s, C^i/C_6H_4). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 16.6 (s).

*Synthesis of [$RuCl_2$(η^6-p-cymene)(P(2-(5-Me)$C_4H_2O)_2$Fc)] (**9c**)*

Molecule **3c** (625 mg, 1.37 mmol) was treated with *n*-butyl lithium (0.60 mL, 1.50 mmol) and methanol (1.0 mL). After appropriate work-up, phosphine **4c** was reacted with [$RuCl_2$(η^6-*p*-cymene)]$_2$ (**8**) (419 mg, 0.68 mmol) to afford **9c** as a red solid. Yield: 900 mg (1.31 mmol, 96% based on **3c**). Anal. calcd. for $C_{30}H_{33}Cl_2FeO_2PRu$ (684.38 g/mol): C, 52.65; H, 4.86. Found: C, 52.64; H, 4.71. Mp.: 175 °C (dec.). IR (NaCl, $\tilde{\nu}$/cm^{-1}): 1024 (s, C–O–C), 1592 (m, C═C), 2855/2917/2958 (m, C–H), 3045 (w, ═C–H). ^1H NMR (500.3 MHz, $CDCl_3$, δ): 1.06 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.86 (s, 3H, CH_3), 2.44 (s, 6H, 5-$CH_3C_4H_2O$), 2.73 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), 4.06 (s, 5H, C_5H_5), 4.35 (dpt, $^4J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 2H, H^β/C_5H_4), 4.54 (dpt, $^3J_{PH}$ = 1.6 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 2H, H^α/C_5H_4), 5.26 (m, 2H, C_6H_4), 5.40 (m, $^3J_{PH}$ = 1.4 Hz, 2H, C_6H_4), 6.11 (ddq, $^4J_{PH}$ = 1.1 Hz, $^3J_{HH}$ = 3.4 Hz, $^4J_{HH}$ = 1.1 Hz, 8H, H^4/5-MeC_4H_2O), 6.87 (ddq, $^3J_{PH}$ = 1.4 Hz, $^3J_{HH}$ = 3.4 Hz, $^5J_{HH}$ = 0.4 Hz, 8H, H^3/5-MeC_4H_2O). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 14.1 (s, 5-$CH_3C_4H_2O$), 17.4 (s, CH_3), 21.8 (s, $CH(CH_3)_2$), 30.2 (s, $CH(CH_3)_2$), 70.1 (s, C_5H_5), 70.2 (d, $^3J_{CP}$ = 9 Hz, C^β/

C_5H_4), 73.4 (d, $^2J_{CP}$ = 12 Hz, C^{α}/C_5H_4), 74.3 (d, $^1J_{CP}$ = 56 Hz, C^{i}/C_5H_4), 85.6 (d, $^2J_{CP}$ = 6 Hz, C_6H_4), 90.9 (d, $^2J_{CP}$ = 5 Hz, C_6H_4), 94.6 (s, C^{i}/C_6H_4), 107.5 (d, $^3J_{CP}$ = 6 Hz, C^{4}/5-MeC_4H_2O), 108.8 (s, C^{i}/C_6H_4), 124.0 (d, $^2J_{CP}$ = 14 Hz, C^{3}/5-MeC_4H_2O), 145.1 (d, $^1J_{CP}$ = 74 Hz, C^{2}/5-MeC_4H_2O), 156.5 (d, $^3J_{CP}$ = 5 Hz, C^{5}/5-MeC_4H_2O). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −3.8 (s).

*General procedure for the synthesis of carbosilane-ferrocenyl phosphine $RuCl_2(\eta^6$-p-cymene) complexes **10a–c** and **11a–c***

To a dichloromethane solution (**10**, 25 mL/mmol; **11**, 50 mL/mmol) containing **3a–c** (1.0 equiv), $[RuCl_2(\eta^6$-*p*-cymene$)]_2$ (**8**) (**10**, 1.0 equiv; **11**, 2.0 equiv) was added in a single portion. This reaction solution was stirred for 2 h (**10**) or 5 h (**11**) at ambient temperature. Afterward, all volatiles were removed in vacuum and the crude product was washed thrice with 10 mL portions of a mixture of pentane–diethyl ether (**10**, ratio 1:1, *v*/*v*) or diethyl ether (**11**). After drying in oil pump vacuum, the products were obtained as red solids. For more details see below.

*Synthesis of $SiMe_2(Fe(\eta^5$-$C_5H_4SiMe_2(CH_2)_3)(\eta^5$-$C_5H_4PPh_2)RuCl_2(\eta^6$-p-cymene$))_2$ (**10a**)*

Following the synthesis procedure described above, **3a** (340 mg, 0.34 mmol) was reacted with **8** (209 mg, 0.34 mmol) to give, after appropriate work-up, complex **10a** as a red solid. Yield: 535 mg (0.33 mmol, 98% based on **3a**). Anal. calcd. for $C_{76}H_{94}Cl_4Fe_2P_2Ru_2Si_3$ (1609.41 g/mol): C, 56.72; H, 5.89. Found: C, 57.17; H, 6.11. Mp.: 120 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 802/831 (m, Si–C), 1248 (m, Si–Me), 1434/1482 (m, C=C), 2871/2911/2958 (m, C–H), 3053 (m, =C–H). ^1H NMR (500.3 MHz, $CDCl_3$, δ): −0.13 (s, 6H, H^1/CH_3), 0.08 (s, 12H, H^5/CH_3), 0.44 (m, 4H, H^2/CH_2), 0.57 (m, 4H, H^4/CH_2), 0.96 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.22 (m, 4H, H^3/CH_2), 1.79 (s, 6H, CH_3), 2.56 (sept, $^3J_{HH}$ = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 3.60 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4Si), 3.85 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{β}/C_5H_4Si), 4.31 (dpt, $^4J_{PH}$ = 1.3 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{β}/C_5H_4P), 4.48 (dpt, $^3J_{PH}$ = 1.9 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4), 5.10 (m, 4H, C_6H_4), 5.14 (m, $^3J_{PH}$ = 1.2 Hz, 4H, C_6H_4), 7.29–7.46 (m, 12H, $H^{m,p}$/C_6H_5), 7.85–7.92 (m, 8H, H^o/C_6H_5). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, δ): −3.4 (s, C^1/CH_3), −2.4 (s, C^5/CH_3), 16.9 (s, CH_3), 18.1 (s, C^3/CH_2), 19.5 (s, C^2/CH_2), 20.8 (s, C^4/CH_2), 21.5 (s, CH(CH_3)$_2$), 29.6 (s, CH(CH$_3$)$_2$), 71.1 (d, $^3J_{CP}$ = 8 Hz, C^{β}/C_5H_4P), 71.8 (s, C^{i}/C_5H_4Si), 73.6 (s, C^{α}/C_5H_4Si), 74.3 (s, C^{β}/C_5H_4Si), 74.5 (d, $^2J_{CP}$ = 11 Hz, C^{α}/C_5H_4P), 76.5 (d, $^1J_{CP}$ = 49 Hz, C^{i}/C_5H_4P), 85.6 (d, $^2J_{CP}$ = 6 Hz, C_6H_4), 90.0 (d, $^2J_{CP}$ = 4 Hz, C_6H_4), 94.7 (s, C^{i}/C_6H_4), 108.6 (s, C^{i}/C_6H_4), 128.2 (d, $^3J_{CP}$ = 10 Hz, C^{m}/C_6H_5), 129.7 (s, C^{p}/C_6H_5), 133.6 (d, $^2J_{CP}$ = 10 Hz, C^{o}/C_6H_5), 136.1 (d, $^1J_{CP}$ = 47 Hz, C^{i}/C_6H_5). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.1 (s, Si), 0.8 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 18.4 (s).

*Synthesis of $SiMe_2(Fe(\eta^5$-$C_5H_4SiMe_2(CH_2)_3)(\eta^5$-$C_5H_4P(^cC_6H_{11})_2)RuCl_2(\eta^6$-p-cymene$))_2$ (**10b**)*

Following the synthesis procedure described earlier, **3b** (225 mg, 0.22 mmol) was reacted with **8** (135 mg, 0.22 mmol) to give **10b** as a red solid. Yield: 340 mg (0.21 mmol, 95% based on **3b**). Anal. calcd. for $C_{76}H_{118}Cl_4Fe_2P_2Ru_2Si_3$ (1633.60 g/mol): C, 55.88; H, 7.28. Found: C, 56.43; H, 7.77. Mp.: 141 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 801/830 (s, Si–C), 1248 (m, Si–Me), 2851/2919 (s, C–H). ^1H NMR (500.3 MHz, $CDCl_3$, δ): −0.8 (s, 6H, H^1/CH_3), 0.23 (s, 12H, H^5/CH_3), 0.52 (m, 4H, H^2/CH_2), 0.71 (m, 4H, H^4/CH_2), 0.99–1.46 (m, H, C_6H_{11}), 1.11 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.36 (m, 4H, H^3/CH_2), 1.53–2.10 (m, C_6H_{11}), 1.86 (s, 6H, CH_3), 2.22–2.59 (m, C_6H_{11}), 2.62 (sept, $^3J_{HH}$ = 7.0 Hz, 2H, CH(CH$_3$)$_2$), 4.09 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4Si), 4.42 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{β}/C_5H_4Si), 4.45 (m, 8H, C_5H_4P), 4.83 (m, 4H, C_6H_4), 4.94 (m, $^3J_{PH}$ = 1.2 Hz, 4H, C_6H_4). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, δ): −3.2 (s, C^1/CH_3), −2.1 (s, C^5/CH_3), 17.6 (s, CH_3), 18.4 (s, C^3/CH_2), 19.9 (s, C^2/CH_2), 21.2 (s, C^4/CH_2), 22.4 (s, CH(CH_3)$_2$), 26.2 (s, C^6/C_6H_{11}), 27.8 (d, $^3J_{CP}$ = 12 Hz, $C^{4,5}$/C_6H_{11}), 28.1 (d, $^3J_{CP}$ = 12 Hz, $C^{4,5}$/C_6H_{11}), 29.4 (s, $C^{2,3}$/C_6H_{11}), 30.0 (s, $C^{2,3}$/C_6H_{11}), 30.3 (s, CH(CH$_3$)$_2$), 39.9 (d, $^1J_{CP}$ = 20 Hz, C^1/C_6H_{11}), 69.9 (d, $^3J_{CP}$ = 7 Hz, C^{β}/C_5H_4P), 72.1 (d, $^2J_{CP}$ = 9 Hz, C^{α}/C_5H_4P), 72.9 (s, C^{i}/C_5H_4Si), 73.5 (s, C^{β}/C_5H_4Si), 74.2 (s, C^{α}/C_5H_4Si), 82.1 (d, $^1J_{CP}$ = 30 Hz, C^{i}/C_5H_4P), 85.2 (d, $^2J_{CP}$ = 5 Hz, C_6H_4), 89.6 (d, $^2J_{CP}$ = 4 Hz, C_6H_4), 93.9 (s, C^{i}/C_6H_4), 106.8 (s, C^{i}/C_6H_4). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −2.8 (s, Si), 1.0 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 16.5 (s).

*Synthesis of $SiMe_2(Fe(\eta^5$-$C_5H_4SiMe_2(CH_2)_3)(\eta^5$-$C_5H_4P$(2-(5-Me)$C_4H_2O)_2)RuCl_2(\eta^6$-p-cymene$))_2$ (**10c**)*

Molecule **3c** (205 mg, 0.20 mmol) was reacted with **8** (124 mg, 0.20 mmol) as described earlier. After appropriate work-up, complex **10c** was obtained as a red solid. Yield: 315 mg (0.19 mmol, 96% based on **3c**). Anal. calcd. for $C_{72}H_{94}Cl_4Fe_2O_4P_2Ru_2Si_3$ (1625.36 g/mol): C, 53.20; H, 5.83. Found: C, 53.25; H, 5.96. Mp.: 95 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 800/830 (s, Si–C), 1024/1040 (s, C–O–C), 1246 (m, Si–Me), 1592 (m, C=C), 2871/2917/2955 (m, C–H), 3040 (w, =C–H). ^1H NMR (500.3 MHz, $CDCl_3$, δ): −0.10 (s, 6H, H^1/CH_3), 0.14 (s, 12H, H^5/CH_3), 0.49 (m, 4H, H^2/CH_2), 0.64 (m, 4H, H^4/CH_2), 1.06 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.29 (m, 4H, H^3/CH_2), 1.85 (s, 6H, CH_3), 2.45 (s, 12H, 5-$CH_3C_4H_2O$), 2.73 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, CH(CH$_3$)$_2$), 3.92 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4Si), 4.24 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{β}/C_5H_4Si), 4.30 (dpt, $^4J_{PH}$ = 1.9 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{β}/C_5H_4P), 4.53 (dpt, $^3J_{PH}$ = 1.9 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 4H, H^{α}/C_5H_4P), 5.25 (m, 4H, C_6H_4), 5.39 (m, $^3J_{PH}$ = 1.5 Hz, 4H, C_6H_4), 6.14 (ddq, $^4J_{PH}$ = 1.3 Hz, $^3J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 1.0 Hz, 4H, H^4/5-$CH_3C_4H_2O$), 6.94 (ddq, $^3J_{PH}$ = 1.5 Hz, $^3J_{HH}$ = 3.3 Hz, $^5J_{HH}$ = 0.4 Hz, 4, H, H^3/5-$CH_3C_4H_2O$). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, δ): −3.1 (s, C^1/CH_3), −2.1 (s, C^5/CH_3), 14.2 (s, 5-$CH_3C_4H_2O$), 17.4 (s, CH_3), 18.5 (s, C^3/CH_2), 20.0 (s, C^2/CH_2), 21.3 (s, C^4/CH_2), 21.9 (s, CH(CH_3)$_2$), 30.2 (s, CH(CH$_3$)$_2$), 70.8 (d, $^3J_{CP}$ = 9 Hz, C^{β}/C_5H_4P), 72.5 (s, C^{i}/C_5H_4Si), 73.0 (d, $^2J_{CP}$ = 12 Hz, C^{α}/C_5H_4P), 74.1 (s, C_5H_4Si), 74.1 (s, C_5H_4Si), 74.9 (d, $^1J_{CP}$ = 55 Hz, C^{i}/C_5H_4P), 85.6 (d, $^2J_{CP}$ = 7 Hz, C_6H_4), 90.9 (d, $^2J_{CP}$ = 5 Hz, C_6H_4), 94.6 (s, C^{i}/C_6H_4), 107.8 (d, $^3J_{CP}$ = 7 Hz, C^4/5-$CH_3C_4H_2O$), 108.9 (s, C^{i}/C_6H_4), 124.3(d, $^2J_{CP}$ = 14 Hz, C^3/5-$CH_3C_4H_2O$), 144.9 (d, $^1J_{CP}$ = 74 Hz, C^2/5-$CH_3C_4H_2O$), 156.5 (d, $^3J_{CP}$ = 5 Hz, C^5/5-$CH_3C_4H_2O$). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.2 (s, Si), 0.9 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −3.7 (s).

*Synthesis of $Si(Fe(\eta^5$-$C_5H_4SiMe_2(CH_2)_3)(\eta^5$-$C_5H_4PPh_2)RuCl_2(\eta^6$-p-cymene$))_4$ (**11a**)*

Following the synthesis procedure described above, **3a** (435 mg, 0.23 mmol) was reacted with **8** (280 mg, 0.46 mmol) to give complex **11a** as a red solid. Yield: 695 mg (0.22 mmol, 97% based on **3a**). Anal. calcd. for $C_{148}H_{176}Cl_8Fe_4P_4Ru_4Si_5$ (3130.59 g/mol): C, 56.78; H, 5.67. Found: C, 57.29; H, 5.79. Mp.: 165 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 813/831 (m, Si–C), 1246 (m, Si–Me), 1434/1482 (m, C=C), 2870/2914/2958 (m, C–H), 3052 (m, =C–H). ^1H NMR (500.3 MHz, $CDCl_3$, δ): 0.05 (s, 24H, H^4/CH_3), 0.35 (m, 8H, H^1/CH_2), 0.51 (m, 8H, H^3/CH_2), 0.96 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CH(CH_3)$_2$), 1.12 (m, 8H, H^2/CH_2), 1.79 (s, 12H, CH_3), 2.55 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, CH(CH$_3$)$_2$), 3.58 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4Si), 3.83 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4Si), 4.30 (pt, $^4J_{PH}$ = 1.5 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4P), 4.47 (dpt, $^3J_{PH}$ = 1.8 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4P), 5.09 (m, 8H, C_6H_4), 5.13 (m, $^3J_{PH}$ = 1.2 Hz, 8H, C_6H_4), 7.37–7.45 (m, 24H, $H^{m,p}$/C_6H_5), 7.85–7.91 (m, 16H, H^o/C_6H_5). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, δ): −2.0 (s, C^4/CH_3), 17.3 (s, CH_3), 17.5 (s, C^1/CH_2), 18.7 (s, C^2/CH_2), 21.7 (s, C^3/CH_2), 21.9 (s, CH(CH_3)$_2$), 30.1 (s, CH(CH$_3$)$_2$), 70.7 (d, $^3J_{CP}$ = 8 Hz, C^{β}/C_5H_4P), 72.4 (s, C^{i}/C_5H_4Si), 74.1 (s, C^{α}/C_5H_4Si), 74.9 (s,

C^{β}/C_5H_4Si), 75.0 (d, $^2J_{CP}$ = 10 Hz, C^{α}/C_5H_4P), 76.9 (d, $^1J_{CP}$ = 50 Hz, C^{i}/C_5H_4P), 86.0 (d, $^2J_{CP}$ = 6 Hz, C_6H_4), 90.3 (d, $^2J_{CP}$ = 4 Hz, C_6H_4), 95.2 (s, C^{i}/C_6H_4), 109.5 (s, C^{i}/C_6H_4), 127.6 (d, $^3J_{CP}$ = 10 Hz, C^{m}/C_6H_5), 130.2 (s, $^4J_{CP}$ = 2 Hz, C^{p}/C_6H_5), 134.2 (d, $^2J_{CP}$ = 9 Hz, C^{o}/C_6H_5), 136.6 (d, $^1J_{CP}$ = 47 Hz, C^{i}/C_6H_5). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.1 (s, Si), 0.5 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 18.1 (s).

*Synthesis of Si(Fe(η^5-$C_5H_4SiMe_2(CH_2)_3$)(η^5-$C_5H_4P(^cC_6H_{11})_2$) $RuCl_2(\eta^6$-p-cymene))$_4$ (**11b**)*

Compound **3b** (390 mg, 0.20 mmol) was reacted with **8** (245 mg, 0.40 mmol) as described earlier, whereby **11b** was obtained as red solid. Yield: 610 mg (0.19 mmol, 96% based on **3b**). Anal. calcd. for $C_{148}H_{224}Cl_8Fe_4P_4Ru_4Si_5$ (3178.97 g/mol): C, 55.92; H, 7.10. Found: C, 56.06; H, 7.30. Mp.: 148 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 802/830 (s, Si–C), 1248 (m, Si–Me), 2851/2919 (s, C–H), 3044 (w, =C–H). ^{1}H NMR (500.3 MHz, $CDCl_3$, δ): 0.26 (s, 24H, H^4/CH_3), 0.51 (m, 8H, H^1/CH_2), 0.71 (m, 8H, H^3/CH_2), 1.15 (d, $^3J_{HH}$ = 7.0 Hz, 24H, $CH(CH_3)_2$), 1.20–1.41 (m, 40H, $H^2/CH_2 + H^{4,5}/C_6H_{11} + H^6/C_6H_{11}$), 1.74–2.01 (m, 52H, $CH_3 + H^{2,3}/C_6H_{11} + H^{4,5}/C_6H_{11} + H^6/C_6H_{11}$), 2.41–2.58 (m, 16H, $H^1/C_6H_{11} + H^{2,3}/C_6H_{11}$), 2.65 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, $CH(CH_3)_2$), 4.11 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4Si), 4.44 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4Si), 4.47 (m, 16H, C_5H_4P), 4.82 (m, 8H, C_6H_4), 4.96 (m, 8H, C_6H_4). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −2.2 (s, C^4/CH_3), 17.3 (s, C^1/CH_2), 17.6 (s, CH_3), 18.5 (s, C^2/CH_2), 21.5 (s, C^3/CH_2), 22.3 (s, $CH(CH_3)_2$), 26.1 (s, C^6/C_6H_{11}), 27.8 (d, $^3J_{CP}$ = 10 Hz, $C^{4,5}/C_6H_{11}$), 28.0 (d, $^3J_{CP}$ = 11 Hz, $C^{4,5}/C_6H_{11}$), 29.3 (s, $C^{2,3}/C_6H_{11}$), 29.8 (s, $C^{2,3}/C_6H_{11}$), 30.3 ($CH(CH_3)_2$), 40.0 (d, $^1J_{CP}$ = 20 Hz, C^1/C_6H_{11}), 69.9 (d, $^3J_{CP}$ = 7 Hz, C^{β}/C_5H_4P), 72.1 (d, $^2J_{CP}$ = 9 Hz, C^{α}/C_5H_4P), 72.7 (s, C^{i}/C_5H_4Si), 73.4 (s, C_5H_4Si), 74.1 (s, C_5H_4Si), 82.1 (d, $^1J_{CP}$ = 30 Hz, C^{i}/C_5H_4P), 85.1 (s, C_6H_4), 89.6 (s, C_6H_4), 93.8 (s, C^{i}/C_6H_4), 106.7 (s, C^{i}/C_6H_4). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −2.8 (s, Si), 0.6 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): 16.3 (s).

*Synthesis of Si(Fe(η^5-$C_5H_4SiMe_2(CH_2)_3$)(η^5-C_5H_4P(2-(5-Me) $C_4H_2O)_2$)$RuCl_2(\eta^6$-p-cymene)$_2)_4$ (**11c**)*

Phosphine **3c** (490 mg, 0.25 mmol) was reacted with **8** (310 mg, 0.51 mmol) as described earlier. After appropriate work-up, complex **11c** was obtained as a red solid. Yield: 760 mg (0.24 mmol, 95% based on **3c**). Anal. calcd. for $C_{140}H_{176}Cl_8Fe_4O_8P_4Ru_4Si_5$ (3162.50 g/mol): C, 53.17; H, 5.61. Found: C, 53.09; H, 5.87. Mp.: 133 °C. IR (NaCl, $\tilde{\nu}$/cm^{-1}): 798/832 (m, Si–C), 1024 (s, C–O–C), 1248 (m, Si–Me), 1592 (m, C=C), 2917/2958 (m, C–H). ^{1}H NMR (500.3 MHz, $CDCl_3$, δ): 0.12 (s, 24H, H^4/CH_3), 0.45 (m, 8H, H^1/CH_2), 0.61 (m, 8H, H^3/CH_2), 1.07 (d, $^3J_{HH}$ = 7.0 Hz, 24H, $CH(CH_3)_2$), 1.23 (m, 8H, H^2/CH_2), 1.85 (s, 12H, CH_3), 2.45 (s, 24H, 5-$CH_3C_4H_2O$), 2.73 (sept, $^3J_{HH}$ = 7.0 Hz, $CH(CH_3)_2$), 3.91 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4Si), 4.23 (pt, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4Si), 4.29 (dpt, $^4J_{PH}$ = 1.7 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{β}/C_5H_4P), 4.53 (dpt, $^3J_{PH}$ = 1.9 Hz, $^{3/4}J_{HH}$ = 1.7 Hz, 8H, H^{α}/C_5H_4P), 5.26 (m, 16H, C_6H_4), 6.13 (ddq, $^4J_{PH}$ = 1.3 Hz, $^3J_{HH}$ = 3.2 Hz, $^4J_{HH}$ = 1.0 Hz, 8H, H^4/5-MeC_4H_2O), 6.92 (ddq, $^3J_{PH}$ = 1.5 Hz, $^3J_{HH}$ = 3.2 Hz, $^5J_{HH}$ = 0.4 Hz, 8H, H^3/5-MeC_4H_2O). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): −2.2 (s, C^4/CH_3), 14.1 (s, 5-$CH_3C_4H_2O$), 17.3 (s, C^1/CH_2), 17.3 (s, CH_3), 18.6 (s, C^2/CH_2), 21.5 (s, C^3/CH_2), 21.8 (s, $CH(CH_3)_2$), 30.1 (s, $CH(CH_3)_2$), 70.6 (d, $^3J_{CP}$ = 9 Hz, C^{β}/C_5H_4P), 72.4 (s, C^{i}/C_5H_4Si), 73.0 (d, $^2J_{CP}$ = 12 Hz, C^{α}/C_5H_4P), 74.0 (s, C^{α}/C_5H_4Si), 74.1 (s, C^{β}/C_5H_4Si), 74.6 (d, $^1J_{CP}$ = 55 Hz, C^{i}/C_5H_4P), 85.5 (d, $^2J_{CP}$ = 6 Hz, C_6H_4), 90.8 (d, $^2J_{CP}$ = 5 Hz, C_6H_4), 94.5 (s, C^{i}/C_6H_4), 106.9 (d, $^3J_{CP}$ = 7 Hz, C^4/5-MeC_4H_2O), 108.7 (s, C^{i}/C_6H_4), 124.1 (d, $^2J_{CP}$ = 15 Hz, C^3/5-MeC_4H_2O), 144.8 (d, $^1J_{CP}$ = 74 Hz, C^2/5-MeC_4H_2O), 156.4 (d, $^3J_{CP}$ = 4 Hz, C^5/5-MeC_4H_2O). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, δ): −3.2 (s, Si), 0.5 (s, Si_{core}). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, δ): −3.8 (s).

General procedure for the catalytic reactions

Benzoic acid (366 mg, 3.0 mmol, 1.0 equiv), acenaphthene (116 mg, 750 μmol, 0.25 equiv, internal standard) and the respective catalyst (**9**, **10** or **11**, 1.0 mol-% based on Ru) were dissolved in chlorobenzene (15 mL). After addition of propargyl alcohol (252 mg, 4.5 mmol, 1.5 equiv) the reaction mixture was stirred at 80 °C and samples (0.5 mL) were taken in different intervals (30–90 min). The samples were dried in vacuum and the conversions were determined by ^{1}H NMR spectroscopy.

*Crystal data for **9c***

Single crystals of **9c** were obtained from a saturated chloroform solution containing **9c** at 298 K. Data were collected with an Oxford Gemini S diffractometer, with graphite monochromatized Cu K_{α} radiation (λ = 1.54184 Å). The structure was solved by direct methods using *SHELXS-97* [26] and refined by full-matrix least square procedures on F^2 using *SHELXL-97* [27]. $C_{67}H_{80}Cl_{10}Fe_2O_4P_2Ru_2$, M_r = 1679.59 g mol^{-1}, triclinic, $P\bar{1}$, λ = 1.54184 Å, a = 11.6574(5) Å, b = 12.6942(5) Å, c = 13.7460(5) Å, α = 78.846(3)°, β = 85.974(4)°, γ = 67.643(4)°, V = 1845.70(14) Å^3, Z = 1, ρ_{calcd} = 1.511 mg m^{-3}, μ = 10.427 mm^{-1}, T = 100 K, Θ range = 4.10–62.00°, reflections collected: 12,705, independent: 5732 (R_{int} = 0.0299), R_1 = 0.0447, wR_2 = 0.1229 [$I > 2\sigma(I)$].

Acknowledgment

We are grateful to the Fonds der Chemischen Industrie for generous financial support. J.J. and D.S. thank the Fonds der Chemischen Industrie for Chemiefonds fellowships.

Appendix A. Supplementary material

CCDC 903832 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.

Appendix B. Supporting information

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.02.036.

References

[1] D. Devanne, C. Ruppin, P.H. Dixneuf, J. Org. Chem. 53 (1988) 925–926.
[2] D. Erdmann, K. Schührer, W. Koch, G. Schneider, DE 2 116 416, 1976.
[3] V. Stoeck, W. Schunack, Arch. Pharm. 309 (1976) 421–425.
[4] (a) M.M. Salunkhe, A.R. Sande, A.S. Kanade, P.P. Wadgaonkar, Synth. Commun. 27 (1997) 2885–2891;
(b) C. Bruneau, M. Neveux, Z. Kabouche, C. Ruppin, P.H. Dixneuf, Synlett 11 (1991) 755–763;
(c) R. Schwyzer, B. Iselin, M. Feurer, Helv. Chim. Acta 38 (1955) 69–79.
[5] (a) M. Arfan Ashraf, M.A. Jones, N.E. Kelly, A. Mullaney, J.S. Snaith, I. Williams, Tetrahedron Lett. 44 (2003) 3151–3154;
(b) M. Arfan Ashraf, A.G. Russell, C.W. Wharton, J.S. Snaith, Tetrahedron 63 (2007) 586–593.
[6] (a) P. Yates, R.S. Grewal, P.C. Hayes, J.F. Sawyer, Can. J. Chem. 66 (1988) 2805–2815;
(b) D.W. Hansen, R. Pappo, R.B. Garland, J. Org. Chem. 53 (1988) 4244–4253.
[7] (a) A.S. Demir, N. Camkerten, H. Akgun, C. Tanyeli, A.S. Mahasneh, D.S. Watt, Synth. Commun. 20 (1990) 2279–2289;
(b) G.W.K. Cavill, D.H. Solomon, J. Chem. Soc. (1955) 4426–4429.
[8] V. Cadierno, J. Francos, J. Gimeno, Green Chem. 12 (2010) 135–143.
[9] S. Costin, N.P. Rath, E.B. Bauer, Adv. Synth. Catal. 350 (2008) 2414–2424.
[10] (a) C. Bruneau, Z. Kabouche, M. Neveux, B. Seiller, P.H. Dixneuf, Inorg. Chim. Acta 222 (1994) 155–163;
(b) C. Darcel, C. Bruneau, P.H. Dixneuf, G. Neef, J. Chem. Soc. Chem. Commun.

(1994) 333–334;
(c) C. Bruneau, P.H. Dixneuf, Chem. Commun. (1997) 507–512.
[11] B. Milde, T. Rüffer, H. Lang, Inorg. Chim. Acta 387 (2012) 338–345.
[12] L.J. Goossen, J. Paetzold, D. Koley, Chem. Commun. (2003) 706–707.
[13] P. Štěpnička, J. Demel, J. Čejka, J. Mol. Catal. A Chem. 224 (2004) 161–169.
[14] T.-Y. Dong, L.-L. Lai, J. Organomet. Chem. 509 (1996) 131–134.
[15] S. Dietrich, A. Nicolai, H. Lang, J. Organomet. Chem. 696 (2011) 739–747.
[16] B. Milde, M. Lohan, C. Schreiner, T. Rüffer, H. Lang, Eur. J. Inorg. Chem. (2011) 5437–5449.
[17] For example: (a) D.W. Allen, B.F. Taylor, J. Chem. Soc. Dalton Trans. (1982) 51–54;
(b) R.P. Pinnell, C.A. Megerle, S.L. Manatt, P.A. Kroon, J. Am. Chem. Soc. 95 (1973) 977–978;
(c) D.W. Allen, I.W. Nowell, J. Chem. Soc. Dalton Trans. (1985) 2505–2508;
(d) S. Jeulin, S. Duprat de Paule, V. Ratovelomanana-Vidal, J.-P. Genet, N. Champion, P. Dellis, Angew. Chem. Int. Ed. 43 (2004) 320–325;
(e) D.J.M. Snelders, C. van der Burg, M. Lutz, A.L. Spek, G. van Koten, R.J.M. Klein Gebbink, Chem. Cat. Chem. 2 (2010) 1425–1437;
(f) A. Suarez, M.A. Mendez-Rojas, A. Pizzano, Organometallics 21 (2002) 4611–4621;
(g) B. Milde, D. Schaarschmidt, P. Ecorchard, H. Lang, J. Organomet. Chem. 706–707 (2012) 52–65.
[18] O.V. Gusev, T.A. Peganova, A.M. Kalsin, N.V. Vologdin, P.V. Petrovskii, K.A. Lyssenko, A.V. Tsvetkov, I.P. Beletskaya, Organometallics 25 (2006) 2750–2760.
[19] A. Delle Site, J. Phys. Chem. Ref. Data 26 (1997) 157–193.
[20] N.P. Hiett, J.M. Lynam, C.E. Welby, A.C. Whitwood, J. Organomet. Chem. 696 (2011) 378–387.
[21] H. Tomori, J.M. Fox, S.L. Buchwald, J. Org. Chem. 65 (2000) 5334–5341.
[22] S.-M. Lu, C. Bolm, Adv. Synth. Catal. 350 (2008) 1101–1105.
[23] R. Corriu, J. Masse, Bull. Soc. Chim. Fr. (1974) 3045–3048.
[24] A.W. van der Made, P.W.M.N. van Leeuwen, J.C. De Wilde, R.A.C. Brandes, Adv. Mater. 5 (1993) 466–468.
[25] S. Suravajjala, J.R. Polam, L.C. Porter, J. Organomet. Chem. 461 (1993) 201–205.
[26] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467–473.
[27] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.