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Highly enantioselective palladium-catalyzed hydrosilylation of norbornene with trichlorosilane using ferrocenyl ligands

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Abstract

The Pd-catalyzed hydrosilylation of norbornene with trichlorosilane using different chiral ferrocenyl ligands containing a phosphine and a pyrazole as donors was studied. Both steric and electronic factors affect stereoselectivity in this system. The combination of a sterically bulky pyrazole substituent with a π-acidic phosphine leads to an enantioselectivity of >99.5% ee. Important substrate electronic effects on stereoselectivity were observed using *para*-substituted styrenes.

1. Introduction

We previously reported studies aimed at developing a ferrocene-based ligand system characterized by a modular synthetic approach.[1] Thus, e.g., diphosphine derivatives affording high enantioselectivities in hydrogenation, hydroboration, and allylic substitution reactions were found.[2] More recently, we described the synthesis of mixed phosphorus/nitrogen donors, prepared by following the same strategy.[3] These are excellent auxiliaries in, e.g., Pd-catalyzed allylic amination.[4] We have now extended the use of such ligands to the asymmetric hydrosilylation of olefins.[5]

Hydrosilylation with trichlorosilane[6] offers a powerful tool for the one-pot conversion of an olefin into an alcohol, via the oxidation of the alkyltrichlorosilane formed as the product of the catalytic reaction, e.g., by the method developed by Tamao.[7,8] In fact, complete retention of configuration in the oxidation step allows the stereoselective synthesis of alcohols.[9] Hayashi, Kumada, and Ito first reported the Pd-catalyzed hydrosilylation of olefins utilizing chiral ferrocenyl phosphineamine ligands, bearing, among others, perfluoroalkyl substituents enhancing catalyst solubility in the reactants mixture.[10–13] In more recent years Hayashi and co-workers were able to achieve both high chemoselectivities (linear to branched product ratios up to 1:100) and enantioselectivities (up to 97% ee) for many different olefins, including terminal ones, using Pd catalysts containing MOP and related ligands.[6,14–17]

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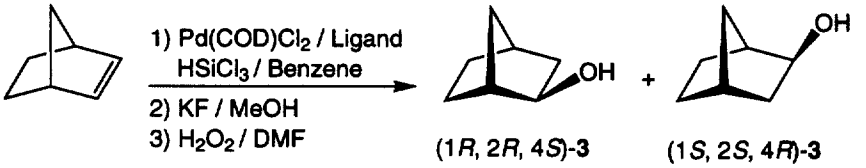
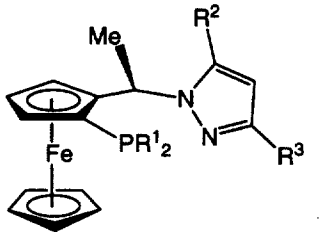
2. Results and discussion

2.1. Hydrosilylation of norbornene

In order to assess the steric and electronic requirements of the ligands in the Pd-catalyzed hydrosilylation, we studied the reaction of norbornene **1** with trichlorosilane **2**, producing after oxidative workup, *exo*-norborneol **3** (Scheme 1). The reactions have been carried out at different temperatures, depending on the observed activity of the corresponding catalyst. The latter was used in a concentration of 0.1 mol% in all experiments and was either generated in situ from equimolar amounts of $Pd(COD)Cl_2$ and the ferrocenyl P,N-ligand or from the preformed dichloropalladium complex (see Experimental). Table 1 collects the results obtained using ligands bearing different substituents at the phosphorus atom and at positions 3 and 5 of the pyrazole, respectively. It is apparent that for diphenylphosphino derivatives **4–9**, the activity of the catalyst shows a pronounced dependence on the steric bulk of the substituent R^3 of the nitrogen donor fragment (position 3). With the catalyst containing ligand **4** (methyl substituent), the reaction has to be run at 70°C in order to obtain a reasonable conversion within 15 h. Correspondingly, the enantioselectivity is very low (10% ee). On the other hand, the two bulky 2,4,6-trisubstituted phenyl groups (2,4,6-trimethoxy- and 2,4,6-trimethylphenyl, ligands **7** and **8**, respectively), give catalysts of much higher activity with which comparable or higher yields are obtained operating at 0°C for an equal reaction time. This also leads to much higher enantioselectivities of 82% and 91% ee, respectively. That the stereoselectivity of the reaction is influenced by the electronic nature of the phosphorus donor is demonstrated by ligand **9**, containing the electron-withdrawing 3,5-bis(trifluoromethyl)phenyl groups. In this case, an ee of >99.5% is obtained. This is the highest value reported for this particular reaction so far.





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Scheme 1. The Pd-catalyzed hydrosilylation of norbornene using various ferrocenyl P,N-ligands

2.2. Hydrosilylation of para-substituted styrenes

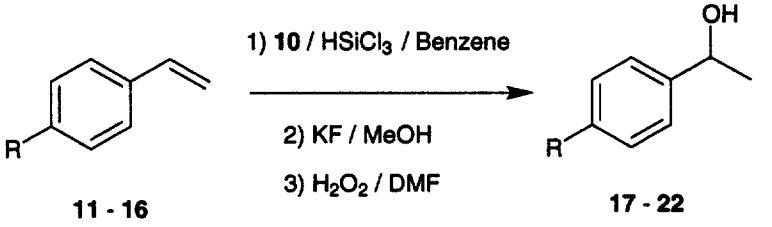
The electronic effects on stereoselectivity due to the substrate were analyzed by performing the hydrosilylation of a series of *para*-substituted styrenes, utilizing complex **10** as a catalyst precursor at room temperature (Scheme 2). As the results in Table 2 indicate, the electron-withdrawing or releasing

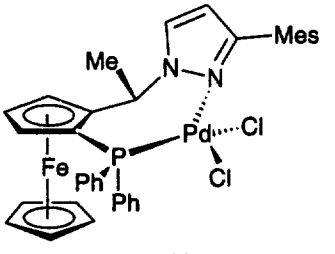
Table 1
Hydrosilylation of norbornene using different ferrocenyl ligands.

Ligand	R1 a	R2 a	R3 a	T / °C	%ee b	%yield
4	Ph	Me	Me	70	10	54
5	Ph	Me	Ph	50	39	47
6	Ph	H	9-Anthryl	25	81	54
7	Ph	H	2,4,6-$(OMe)_3$Ph	0	82	30
8	Ph	H	2,4,6-$(Me)_3$Ph	0	91	56
9	3,5-$(F_3C)_2$Ph	H	2,4,6-$(Me)_3$Ph	0	>99.5	59

[a] See general structure in Scheme 1. [b] The ee (preferred enantiomer (1*R*, 2*R*, 4*S*)-**3**) was determined by gas chromatography on a Supelco β-DEX (0.25 mm x 30 m, 0.25 μm film) column (temperature program: 65 min at 80°C, 1°C/min rate up to 100°C. Gas flow: 1.4 mL/min, He). The absolute configuration was determined by comparision of the specific rotation for the product of the catalysis with ligand **8** with the value reported for the optically pure product. See: ref. 13.

nature of the *para*-substituent plays a crucial role in determining both the level and the sense of chiral induction. Highest *R*-selectivity of 64% ee was obtained with 4-dimethylaminostyrene, whereas the corresponding chloro derivative afforded the *S*-product in 67.2% ee. Thus, this is a rare example of enantioselectivity reversal due to a remote substituent in the substrate.





Scheme 2. The Pd-catalyzed hydrosilylation of *para*-substituted styrenes

A clear demonstration that one is dealing with electronic effects is given by the linear correlations of

Table 2
Results of the hydrosilylation of styrene and its derivatives with trichlorosilane, with **10** as catalyst precursor.

Substrate	R	%Yield	$[\alpha]_D^{20}$ [a]	%ee Product [b]	log(er)[c]	σ_p [d]	σ_p^+ [d]
11	H	63	-33.5 (c=1.37)	63.4 ((*S*)-**17**)	0.650	0	0
12	Me	71	-26.1 (c=1.32)	46.9 ((*S*)-**18**)	0.442	-0.14	-0.31
13	OMe	59	+3.2 (c=1.26)	6.4 ((*R*)-**19**)	-0.056	-0.27	-0.78
14	Nme_2	49	+31.1 (c=1.02)	64 ((*R*)-**20**)	-0.659	-0.83	-1.7
15	Cl	61	-29.7 (c=1.45)	67.2 ((*S*)-**21**)	0.707	0.24	0.11
16	CF_3	39	-19.5 (c=1.08)	58.7 ((*S*)-**22**)	0.586	0.54	0.61

[a] Measured in $CHCl_3$. [b] The enantiomeric excess for **17-21** were determined by HPLC-analysis of the product on a Chiracel OB-H (4.6 x 250mm, 5μm mesh) column. For each case the eluent proportions (hexane/isopropanol) was optimized. For **22** the enantiomeric excess was determined by gas chromatography on a Supelco β-DEX (0.25 mm x 30 m, 0.25 μm film) column. The absolute configurations were determined by comparision of the specific rotations with those reported for optically pure products: for (*S*)-**17**, (*S*)-**18**, (*S*)-**19**, (*S*)-**21**, (*S*)-**22** see: Mathre, D. J.; Thompson, A.S.; Douglas, A.W.; Hoogsteen, K.; Caroll, J.D. *J. Org. Chem.* **1993**, *58*, 2880-2888; for (*S*)-**20** see: Hashiguchi S.; Fujii, A.; Haack, K.-J.; Matsumura, K.; Ikariya, T.; Noyori, R. *Angew. Chem. Int. Engl. Ed.* **1997**, *36*, 288. [c] er=Enantiomer ratio ([*R*]/[*S*]). [d] Parameters taken from ref. 14.

log(er) (er=enantiomer ratio) presented as Hammett plots in Fig. 1 (linear free-energy relationship).[18] The best correlation is obtained utilizing the parameter σ_p^+ and not with the more commonly used σ_p. However, the results for trifluoromethylstyrene **16** significantly deviate in both cases from the linear correlation. In other words, the obtained 58.7% ee is much lower than expected, based upon the linear free-energy relationship (range of 84–87% ee (*S*)). Furthermore, **16** reacts significantly slower than the other substrates of the series. The exact reason for the deviating behavior of this substrate is unknown.

The correlation with σ_p^+, as originally introduced by Brown for reactions involving, e.g., arenium or cationic benzyl species,[19,20] in our case is indicative of the development of positive charge in the transition state of the enantioselectivity-determining step of the catalytic reaction. From this observation, a possible mechanistic implication may be derived. In the course of the olefin insertion process (the likely enantioselectivity-determining step) a significant build-up of positive charge occurs at the benzylic center as a consequence of the ensuing η^3-coordination mode preferred in the product, as illustrated in Scheme 3. This means that the benzylic center becomes more electrophilic, by virtue of its π-allylic nature. An analogous situation is encountered in the Ni-catalyzed hydrocyanation of vinylarenes, studied in detail by Rajanbabu and co-workers.[21] However, for this particular reaction, no data regarding substrate electronic effects were reported. It is important to note that both olefin coordination and the η^3-coordination mode in the insertion product are likely to require a ligand dissociation reaction. The

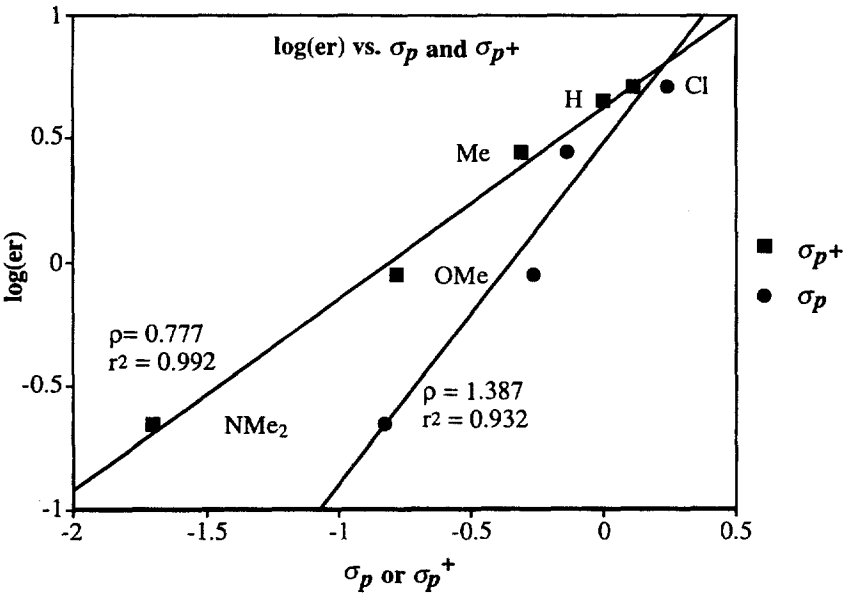
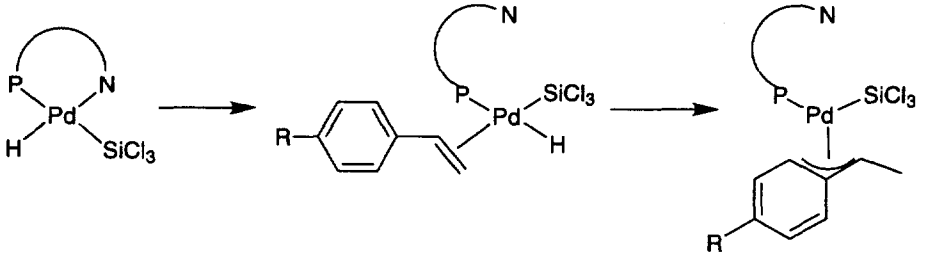


Figure 1. Hammett plots for the hydrosilylation of *para*-substituted styrenes. Data for *para*-(trifluoromethyl)styrene have been omitted (see text)

opening of the chelate ring, with the pyrazole nitrogen dissociating, could fulfill such a condition. The above observation that ligands containing bulky pyrazole substituents give rise to more active catalysts is consistent with this interpretation, i.e., they probably tend to dissociate more readily. A comparable mechanistic description, involving olefin hydride insertion and a low coordinated metal center, based on a theoretical study, has recently been reported for the analogous Pt-catalyzed hydrosilylation by Sakaki and co-workers.[22]



Scheme 3. The styrene insertion step forming an η^3-coordinated benzylic intermediate

3. Conclusion

We have shown that ferrocene-based P,N-ligands are suited chiral auxiliaries for the Pd-catalyzed hydrosilylation of selected olefins with trichlorosilane. A fine-tuning of these ligands, both in terms of steric and electronic properties is readily achieved. Thus, a ligand with optimal properties, leading to a very high enantioselectivity, could be found for the hydrosilylation of norbornene (>99.5% ee). Furthermore, very pronounced substrate electronic effects on stereoselectivity were found for a series of

para-substituted styrenes. Such effects have fundamental implications for a reaction that is not very well known from a mechanistic point of view. We are currently extending the use of our catalyst system to further olefins, as well as studying the mechanism in more detail. We shall report on this in due course.

4. Experimental

All reactions were carried out in an atmosphere of argon using standard Schlenk techniques. Benzene and diethyl ether were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Acetic acid was degassed prior to use. All other chemicals were used without prior purification. TLC was performed on Merck plates coated with silica gel 60 F254 (0.2 mm). Chromatography was performed with Fluka silica gel 60 (230–400 mesh). Melting points are uncorrected. Optical rotations were determined on a Perkin–Elmer 341 polarimeter (10 cm cell, $CHCl_3$ at 23°C, *c* in g/100 mL). Chemical shifts are reported in ppm relative to TMS (^1H, ^{13}C), to 85% H_3PO_4 (^{31}P) and to $CFCl_3$ (^{19}F): δ 0.00 as the internal standard. NMR data were recorded on Bruker DPX-250, Bruker DPX-300, or Bruker DRX-400 spectrometers. HPLC analyses were performed on a Hewlett–Packard series 1050 instrument with UV detector (254 nm); the chiral columns used are Daicel Chiracel OJ (4.6×250 mm, 5 μm mesh), Chiracel OD-H (4.6×250 mm, 5 μm mesh), Chiracel OB-H (4.6×250 mm, 5 μm mesh). GC analyses were performed on a Fisons GC 8000 Series instrument; the chiral columns used are Supelco α-DEX (0.25 mm×30 m, 0.25 μm film), β-DEX (0.25 mm×30 m, 0.25 μm film), γ-DEX (0.25 mm×30 m, 0.25 μm film). $Pd(COD)Cl_2$ was prepared following a reported procedure.[23]

4.1. A general procedure for the hydrosilylation of norbornene 1

$Pd(COD)Cl_2$ (6.05 mg, 0.021 mmol), ligand (0.025 mmol), norbornene (2 g, 21 mmol), and benzene (8 mL) were stirred for 30 min until the solid $Pd(COD)Cl_2$ dissolved and the solution turned from yellow to red. By the addition of $HSiCl_3$ (2.8 mL, 28 mmol) the reaction was started. After complete conversion, the product was carefully poured into a suspension of KF (20 g, 0.34 mol) in methanol (150 mL) and stirred for 30 minutes. The solvent was removed in vacuo, dimethylformamide (150 mL) and H_2O_2 (30% water solution, 20 mL) were added and the suspension heated for 1 hour at 70°C. Product **3** was then isolated by aqueous workup, extraction and sublimation. The yields given in Table 1 refer to sublimed product.

4.2. A general procedure for the hydrosilylation of vinylarenes 17–22

Complex **10** (13 mg, 0.017 mmol) and the vinylarene (8.5 mmol) were mixed in 4 mL of benzene. The addition of trichlorosilane (1.1 mL, 11 mmol) started the reaction. The mixture was stirred until disappereance of the NMR signals of the vinylarene. The crude product was carefully poured into a suspension of KF (10 g, 0.17 mol) in 80 mL of methanol, and stirred for 30 minutes. The solvent was removed in vacuo. The resulting solid was suspended in 100 mL of DMF, H_2O_2 (30% water solution, 10 mL) was added and the mixture heated for 1 hour at 60–70°C. The products **17–22** were isolated by aqueous workup, extraction and distillation. In the case of product **20**, column chromatography (silica, hexane:ethyl acetate=2:1+1% of NEt_3) was preferred to distillation because of its thermal sensitivity. The yields given in Table 2 refer to purified products.

4.3. 1-{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]ethyl}-3-(2,4,6-trimethoxyphenyl)-1H-pyrazole 7

(*R*)-(*S*)-PPFA (1 g, 2.26 mmol) and 3-(2′,4′,6′-trimethoxyphenyl)pyrazole (690 mg, 2.94 mmol) were dissolved in 8 mL of degassed AcOH and stirred for 3 hours at 80°C. The solvent was then removed in vacuo. The product was isolated as a yellow foam by chromatography on silica (hexane:ethyl acetate=2:1+1% of NEt_3). Yield: 427 mg, 30%. R_f (silica, hexane:ethyl acetate=2:1+1% of NEt_3): 0.18. ^1H NMR (250 MHz, $CDCl_3$, 20°C): δ 7.70–7.58 (m, 2H, Ph–*H*), 7.45–7.35 (m, 3H, Ph–*H*), 7.10–6.90 (m, 4H, Ph–*H*, Py–*H*), 6.85–6.75 (m, 2H, Ph–*H*), 6.17 (s, 2H, trimethoxyphenyl–*H*), 5.78 (m, 1H, Py–*H*), 5.74 (dq, 1H, C*H*Me, ^3J(HH)=7, ^4J(HP)=3), 4.78 (m, 1H, C_5H_3), 4.38 (m, 1H, C_5H_3), 4.01 (s, 5H, C_5H_5), 3.94 (m, 1H, C_5H_3), 3.82 (s, 3H, OCH_3), 3.67 (s, 6H, OCH_3), 2.15 (d, 3H, CH*Me*, ^3J(HH)=7). $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 20°C): δ −23.8. $^{13}C\{^1H\}$ NMR (62.89 MHz, $CDCl_3$, 20°C): δ 161–126 (Ph–*C*, Py–*C*, trimethoxyphenyl–*C*), 106.7 (Py–*C*), 94.8 (d, C_5H_3, J(CP)=26), 91.4 (trimethoxyphenyl–*C*), 75.5 (d, C_5H_3, J(CP)=11), 71.6 (d, C_5H_3, J(CP)=5), 70.1 (d, C_5H_3, J(CP)=4), 69.8 (CP–*C*), 69.7 (d, C_5H_3, J(CP)=5), 56.1 (OCH_3), 55.6 (*C*HMe), 55.3 (OCH_3), 21.8 (CH*Me*). MS (EI) m/z 630 (M^+, 40%), 564 ($M^+-C_5H_5$, 100%), 396 (M^+−3-(2,4,6-trimethoxyphenyl)-1*H*-pyrazole, 87.3%). $[\alpha]_D^{20}$ −277 (*c* 1.18). Anal. calcd for $C_{36}H_{35}FeN_2O_3P$: C, 68.58; H, 5.59; N, 4.44. Found: C, 68.36; H, 5.68; N, 4.30.

4.4. 1-{(R)-1-[(S)-2-(Diphenylphosphino)ferrocenyl]ethyl}-3-(2,4,6-trimethylphenyl)-1H-pyrazole 8

From (*R*)-(*S*)-PPFA (2 g, 4.53 mmol) and 3-(2,4,6-trimethylphenyl)-1*H*-pyrazole (1.01 g, 5.44 mmol), analogously to **7** (80°C, 2 hours). Chromatography (silica, hexane:ethyl acetate=10:1+1% of NEt_3): yield 1.572 g (60%). R_f (silica, hexane:ethyl acetate=4:1+1% of NEt_3): 0.51. ^1H NMR (250 MHz, $CDCl_3$, 20°C): δ 7.66–7.58 (m, 2H, Ph–*H*), 7.45–7.35 (m, 3H, Ph–*H*), 7.05–6.95 (m, 4H, Ph–*H*), 6.92–6.80 (m, 4H, Ph–*H*, Mes–*H*, Py–*H*), 6.87 (dq, 1H, C*H*Me, ^3J(HH)=7, ^4J(HP)=2), 5.65 (d, 1H, Py–*H*, ^3J(HH)=2), 4.82 (m, 1H, C_5H_3), 4.45 (m, 1H, C_5H_3), 4.04 (s, 5H, C_5H_5), 4.01 (m, 1H, C_5H_3), 2.29 (s, 3H, Mes–CH_3), 2.01 (d, 3H, CH*Me*), 1.96 (s, 6H, Mes–CH_3). $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 20°C): δ −25.6. $^{13}C\{^1H\}$ NMR (62.89 MHz, $CDCl_3$, 20°C): δ 149.6–127.4 (Ph–*C*, Mes–*C*, Py–*C*), 105.1 (Py–*C*), 94.1 (d, C_5H_3, J(CP)=25), 75.6 (d, C_5H_3, J(CP)=10), 70.1 (C_5H_3), 69.9 (C_5H_5, C_5H_3), 55.5 (d, *C*HMe, J(CP)=11), 21.8 (Mes–CH_3), 21.1 (CH*Me*), 20.6 (Mes–CH_3). MS (EI) m/z 582 (M^+, 65%), 396 (M^+−3-(2,4,6-trimethylphenyl)-1*H*-pyrazole, 100%). $[\alpha]_D^{20}$ −299.9 (*c* 1.13). Anal. calcd for $C_{36}H_{35}FeN_2P$: C, 74.23; H, 6.06; N, 4.81. Found: C, 74.07; H, 6.01; N, 4.75.

4.5. 1-{(R)-1-[(S)-2-Bis(3,5-bis(trifluoromethyl)phenyl)phosphino)ferrocenyl]ethyl}-3-(2,4,6-trimethylphenyl)-1H-pyrazole 9

From dimethyl-{(*R*)-1-[(*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)phosphino)-ferrocenyl]ethyl}-amine (835 mg, 1.17 mmol) and 3-(2,4,6-trimethylphenyl)-1*H*-pyrazole (435 mg, 2.34 mmol), analogous to **7** (90°C, 15 hours). Chromatography (silica, hexane:diethyl ether=10:1+2% of NEt_3): yield 893 mg (89%). R_f (silica, hexane:diethyl ether=3:1): 0.34. ^1H NMR (400 MHz, $CDCl_3$, 20°C): δ 7.99 (s, 1H, Ph–*H*), 7.94 (d, 2H, Ph–*H*, ^3J(HP)=7), 7.65 (s, 1H, Ph–*H*), 7.28 (d, 2H, Ph–*H*, ^3J(HP)=7), 7.06 (d, 1H, Py–*H*, ^3J(HH)=2), 6.80 (s, 2H, Mes–*H*), 5.91 (m, 1H, C*H*Me), 5.76 (d, 1H, Py–*H*, ^3J(HH)=2), 4.94 (m, 1H, C_5H_3), 4.67 (m, 1H, C_5H_3), 4.05 (s, 5H, C_5H_5), 3.86 (m, 1H, C_5H_3), 2.25 (s, 3H, Mes–CH_3), 1.90 (d, 3H, CH*Me*, ^3J(HH)=7), 1.69 (s, 3H, Mes–CH_3). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 20°C): δ −21.7. $^{13}C\{^1H\}$ NMR (62.89 MHz, $CDCl_3$, 20°C): δ 151.3–119.2 (Ph–*C*, Py–*C*, Mes–*C*), 106.8 (Py–*C*), 94.3 (d, C_5H_3, J(CP)=71), 72.7 (d, C_5H_3, J(CP)=10), 72.0 (C_5H_3), 71.8 (d, C_5H_3, J(CP)=5), 71.2

(d, C_5H_3, J(CP)=5), 70.6 (C_5H_5), 56.4 (d, *C*HMe, 3J(CP)=11), 22.3 (Mes–CH_3), 21.4 (*C*HMe), 20.4 (Mes–CH_3). $^{19}F\{^1H\}$ NMR (376.46 MHz, $CDCl_3$, 20°C): δ −63.3 (CF_3), −63.4 (CF_3). MS (EI) m/z 854 (M^+, 100%), 789 ($M^+-C_5H_5$, 44.9%). $[\alpha]_D^{20}$ −190.4 (*c* 0.57). Anal. calcd for $C_{40}H_{31}F_{12}FeN_2P$: C, 56.22; H, 3.66; N, 3.28. Found: C, 56.30; H, 3.74; N, 3.28.

4.6. *(8)*$PdCl_2$ *10*

$Pd(COD)Cl_2$ (82 mg, 0.286 mmol) and **8** (160 mg, 0.289 mmol) were stirred for 15 min in 4 mL of CH_2Cl_2 under argon. Et_2O (5 mL) was added, and the complex precipitated. The red solid was filtered off, washed twice with 5 mL of Et_2O and dried in vacuo. Yield 162 mg (75%). ^1H NMR (250 MHz, CD_2Cl_2, 20°C): δ 8.11–7.93 (m, 4H, Ph–*H*), 7.81 (d, 1H, Py–*H*, ^3J(HH)=3), 7.75–7.65 (m, 1H, Ph–*H*), 7.62–7.48 (m, 5H, Ph–*H*), 7.05–6.82 (m, 2H, Mes–*H*, C*H*Me), 6.78 (s, 1H, Mes–*H*), 6.21 (d, 1H, Py–*H*, ^3J(HH)=3), 4.42 (m, 1H, C_5H_3), 4.33 (m, 1H, C_5H_3), 4.29 (m, 1H, C_5H_3), 3.90 (s, 5H, C_5H_5), 2.37 (s, 3H, Mes–CH_3), 2.33 (d, 3H, CH*Me*, 3J(HH)=7), 2.25 (s, 3H, Mes–CH_3), 1.09 (s, 3H, Mes–CH_3). $^{31}P\{^1H\}$ NMR (101.26 MHz, CD_2Cl_2, 20°C): δ 11.2. $^{13}C\{^1H\}$ NMR (62.89 MHz, CD_2Cl_2, 20°C): δ 156.4–125.5 (Ph–*C*, Mes–*C*, Py–*C*), 110.8 (Py–*C*), 91.7 (d, C_5H_3, J(CP)=21), 74.4 (d, C_5H_3, J(CP)=3), 73.4 (d, C_5H_3, J(CP)=55), 70.9 (C_5H_5), 69.8 (d, C_5H_3, J(CP)=7), 66.2 (d, C_5H_3, J(CP)=7), 57.9 (*C*HMe), 21.6 (Mes–CH_3), 21.0 (Mes–CH_3), 20.7 (Mes–CH_3), 17.1 (CH*Me*). MS (FAB^+) m/z 725 (M^+-Cl, 100%), 723 (M^+-Cl, 98%). Mp >186°C (dec.). Anal. calcd for $C_{36}H_{35}Cl_2FeN_2PPd$: C, 56.91; H, 4.64; N, 3.69. Found: C, 56.63, H, 4.69, N, 3.52.

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