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Pd^{II} Complexes of Tridentate PCP N-Heterocyclic Carbene Ligands: Structural Aspects and Application in Asymmetric Hydroamination of Cyano Olefins

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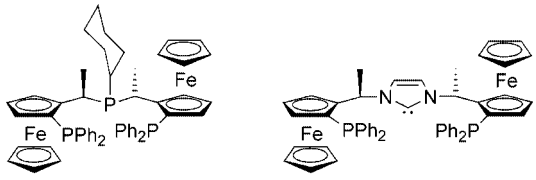
The synthesis of the ligand precursor 1,3-bis{(*R*)-1-[(*S*)-2-(diphenylphosphanyl)ferrocenyl]ethyl}imidazolium iodide ([PCPH]I, **1**) was extended to the electronically and sterically modified ligand precursors 1,3-bis{(*R*)-1-[(*S*)-2-{[3,5-bis(trifluoromethyl)phenyl]phosphanyl}ferrocenyl]ethyl}imidazolium iodide ([3,5-CF_3-PCPH]I, **6**), and 1,3-bis[(*R*)-1-{(*S*)-2-[bis(3,5-dimethylphenyl)phosphanyl]ferrocenyl}ethyl]imidazolium iodide ([3,5-Me-PCPH]I, **7**). Palladium complexes were prepared starting from $[Pd(OAc)_2]_3$ in THF to afford [PdI(PCP)]OAc (**8**), [Pd(OAc)(3,5-CF_3-PCP)]I (**9**), and [PdI(3,5-Me-PCP)]OAc (**10**), in excellent yields. The crystal structures of the ligand precursor [3,5-CF_3-PCPH]I (**6**), the complex [PdI(3,5-CF_3-PCP)]PF_6 (**14**), as well as the dicationic complex [Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**), were determined by X-ray diffraction. Complex **11** and its derivative [Pd($NCCH_3$)-(3,5-Me-PCP)]$(PF_6)_2$ (**13**) have been tested as catalysts in the asymmetric addition of, for example, thiomorpholine to methacrylonitrile giving selectivities up to 63 and 75% *ee*, respectively, at –80 °C.

Introduction

N-Heterocyclic carbenes (NHCs), their corresponding metal complexes, and their applications in catalysis have become a well-established area of research in organometallic chemistry.[1–5] An important step in the development of carbene ligands is their chiral modification and many chiral NHCs acting as monodentate[6–10] as well as bidentate ligands[11–15] in asymmetric reactions have been reported.[5]

Our interest in tridentate ligands based on the ferrocene scaffold derives from the successful application of the triphosphane Pigiphos (see Scheme 1)[16] in, for instance, Ni-catalyzed hydroamination and hydrophosphanation of cyano olefins.[17,18] The replacement of the central PCy unit of Pigiphos by an NHC fragment generates a C_2-symmetric ligand. We speculated that this should lead, in the case of square-planar complexes, to a chiral environment that is better defined than in Pigiphos. We previously reported the synthesis of the PCP ligand precursor **1** as well as its complexation with ruthenium and palladium.[19] In this work we address the modification of the ligand, the complexation with palladium, and the formation of dicationic complexes. The X-ray crystal structures of the activated palladium complex **11**, the CF_3-modified ligand precursor **6** and the palladium complex of this ligand (**14**) are presented, along with the application of these NHC complexes in the catalytic hydroamination reaction of cyano olefins.



(*R*)-(*S*)-Pigiphos (*R*)-(*S*)-PCP

Scheme 1. The C_1-symmetric triphosphane Pigiphos and a structurally related C_2-symmetric PCP ligand.

Results and Discussion

Ligand Synthesis

The introduction of substituents at the 3- and 5-positions of the phenyl groups in diphenylphosphanyl derivatives is a common approach in view of modifying both the steric and electronic properties of such ligands. Modifications of this kind, as applied to carbene precursor **1** ([PCPH]I), should lead to altered catalytic properties of the corresponding Pd complexes. The synthesis of the ligand precursors—via the amines **2** and **3**, as well as the acetates **4** and **5**, i.e. the (diarylphosphanyl)ferrocene derivatives bearing either a dimethylamino group or an acetate at the stereogenic center—containing methyl and trifluoromethyl substituents,

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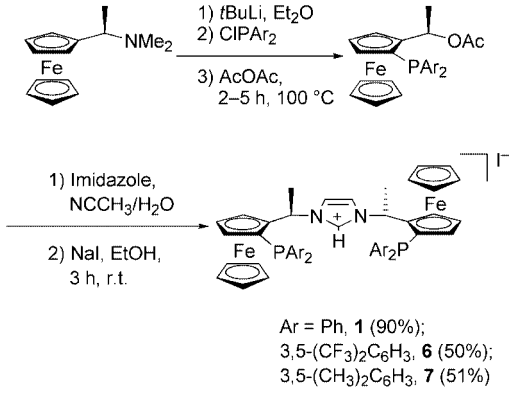
respectively, has been accomplished analogously to the one of the unsubstituted derivative **1**. The preparation of [3,5-CF_3-PCPH]I (**6**) and [3,5-Me-PCPH]I (**7**) from the corresponding acetate derivatives **4** and **5**, respectively, and imidazole was carried out in a mixture of acetonitrile and water in a ratio of 4:1 for **6** and 2:1 for **7**. However, for reactions at room temperature as described for **1**, no substitution of the acetate by imidazole was observed. Heating of the reaction mixture at 60 °C followed by ion exchange with NaI in ethanol yielded **6** in 50% yield after 24 h and **7** in 51% yield after 32 h, respectively (Scheme 2). The yields are lower than the one obtained for **1** and could not be improved by longer reaction times or by using different reaction conditions (temperature, acetonitrile/water mixture).



Scheme 2. Synthesis of the ligand precursors **1**, **6**, and **7**.

Treatment of **1**, **6**, and **7** with NaO*t*Bu in THF resulted in the deprotonation of the imidazolium salts. However, the attempted isolation of the free carbenes was not successful. For ^{13}C NMR spectroscopic reasons, these imidazolium salts were also prepared in the form containing a ^{13}C label at position 2 of the imidazole.[20] The deprotonation of the labeled **1**, **6**, and **7** using an excess of NaO*t*Bu in THF allowed us to observe broad ^{13}C NMR signals of the free carbenes at room temperature (Table 1). While the NMR spectroscopic data of the free carbenes confirm the clean generation of these reactive species, the significant line widths account for the difficulties in observing the same signals for the nonlabeled compounds. Furthermore, solutions of these species in C_6D_6 showed the formation of the imidazolium ion within minutes, indicating that the acidic sites of the NMR tube glass are sufficient to protonate the carbenes. The C(2)–H coupling constants (J_{CH}) of the imidazolium salts of 218.7, 222.6, and 218.8 Hz for **1**, **6**, and **7**, respectively, could be estimated with the help of 2D one-bond HMQC experiments. Interestingly, the coupling constant for the more electron-deficient compound **6**, containing the CF_3 substituents, is larger than for **1** and **7**.

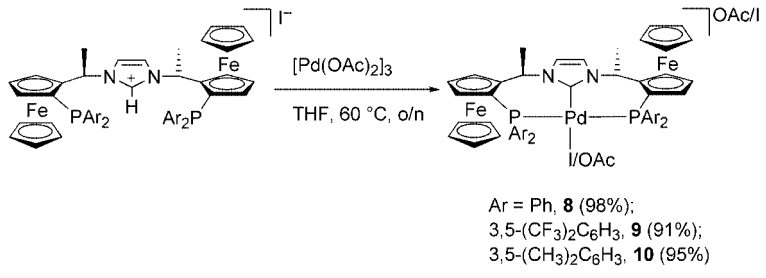
Table 1. ^{13}C NMR chemical shifts of the free carbenes derived from **1**, **6**, and **7**.

Free carbene of	δ [ppm]	Line width [Hz]	J_{CP} [Hz]
1	209.0	36	–
6	209.8	–	13.3 (t)
7	209.5	25	–

Synthesis of Palladium Complexes

As already shown for the ligand precursor **1**, the method of choice for the complexation of these carbene ligands to Pd^{II} is to start from $[Pd(OAc)_2]_3$ {see the synthesis of [PdI(PCP)]OAc (**8**), giving 98% yield}.[19] Analogously, the reaction of (3,5-CF_3-PCPH)I (**6**) and (3,5-Me-PCPH)I (**7**) with $[Pd(OAc)_2]_3$ generates the complexes [Pd(OAc)(3,5-CF_3-PCP)]I (**9**) and [PdI(3,5-Me-PCP)]OAc (**10**) in 91% and 95% yield, respectively (Scheme 3).

In order to isolate the complexes containing iodide as a ligand and acetate as the counterion, an ionic ligand exchange reaction is necessary. This ion exchange was studied by NMR on samples of the ^{13}C-labeled complexes (Table 2). It is reasonable to expect that iodide and acetate will exert a different influence on the chemical shift of the carbene carbon atom in the *trans* position. Addition of NaI to a dichloromethane solution of the palladium complexes **8**, **9**, and **10** shifts the ion exchange equilibrium towards the iodo complex (Table 2, Entries 1, 3, and 5). Abstraction of the counterion and the fourth ligand with Et_3OPF_6 (vide infra), followed by the addition of Bu_4NOAc leads to the formation of the complexes having acetate as a ligand (Table 2, Entries 2, 4, and 6). These experiments show a slight downfield shift of the ^{13}C carbene signal in going from coordinated acetate to coordinated iodide, this effect being more pronounced for [Pd(OAc)(3,5-CF_3-PCP)]I (**9**). We also observed a larger coupling constant J_{CP} between the carbene carbon atom and the P atoms for the iodo complexes. Comparing the chemical shifts and the coupling constants observed for compounds **8**, **9**, and **10** we concluded that there is an ion exchange for [PdI(PCP)]OAc (**8**)



Scheme 3. Synthesis of the palladium complexes **8**, **9**, and **10**.

Table 2. ^{13}C NMR spectroscopic data for labeled carbene derivatives.

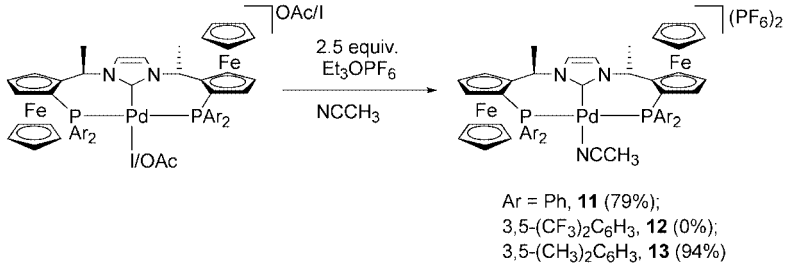
Entry	Complex	Ligand	δ [ppm] (by ion exchange)	J_{CP} [Hz]	δ [ppm] (by synthesis)	J_{CP} [Hz]
1	[PdI(PCP)]OAc (**8**)	I^-	152.3 (t)	12.0	151.4 (t)	13.2
2	[Pd(OAc)(PCP)]PF_6	^-OAc	149.8 (t)	14.6		
3	[PdI(3,5-CF_3-PCP)]OAc	I^-	151.5 (br)	–		
4	[Pd(OAc)(3,5-CF_3-PCP)]I (**9**)	^-OAc	145.7 (t)	13.5	146.8 (t)	13.3
5	[PdI(3,5-Me-PCP)]OAc (**10**)	I^-	152.5 (t)	12.4	151.8 (t)	12.4
6	[Pd(OAc)(3,5-Me-PCP)]PF_6	^-OAc	149.9 (t)	13.6		

and [PdI(3,5-Me-PCP)]OAc (**10**), resulting in products with iodide as the ligand, instead of acetate. This exchange is quite slow and takes approximately 1 d to reach completeness in dichloromethane. Therefore, for further synthesis the equilibrium mixture was used. However, the clean product [PdI(3,5-Me-PCP)]OAc (**10**) could only be obtained by flash chromatography (silica, dichloromethane + 4% methanol). For the electron-poorer complex [Pd(OAc)(3,5-CF_3-PCP)]I (**9**), ion exchange seems to be absent, resulting in a complex with acetate as the fourth ligand. Only the addition of an excess of NaI to **9** allowed us to observe the iodo complex characterized by a rather broad ^{13}C NMR signal (Table 2, Entry 3).

In order to obtain catalytically active species acting as chiral Lewis acids, complexes **8** and **10** were converted into the dicationic derivatives [Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**) and [Pd($NCCH_3$)(3,5-Me-PCP)]$(PF_6)_2$ (**13**) in 79% and 94% yield, respectively, using Et_3OPF_6 in acetonitrile (Scheme 4). The acetonitrile complexes **11** and **13** are characterized by higher ^{31}P chemical shifts and significantly lower ^{13}C carbene chemical shifts with respect to their corresponding precursors, as summarized in Table 3. Somewhat surprisingly, the activation of **9** with Et_3OPF_6 was not selective and led to product mixtures from which the dicationic species could not be identified. It is important to note that all complexes described in this section give NMR spectra consistent with C_2-symmetric structures in solution.

Crystal Structures

Crystals of imidazolium salt **6** suitable for X-ray analysis could be obtained from a dichloromethane solution overlayered with hexane. An ORTEP representation of the structure is shown in Figure 1 and selected bond lengths and angles are listed in Table 4. The overall structure is only approximately C_2-symmetric, i.e., the two ferrocenyl units are not symmetry-related. Three CF_3 groups with the atoms C(6), C(12), and C(15) are disordered over two positions, a phenomenon which can be observed very often for crystal structures containing CF_3 substituents. Iodide was also found to be disordered over two positions with an occupational ratio of 93:7. One of the most specific structural features of this compound is that the molecule backbone, i.e., the chain joining the two phosphorus atoms, displays helical chirality with (*P*) configuration. This chain approximately describes a full screw turn in going from one P atom to the other. The distance between the two P atoms is 7.353 Å and can be viewed as the screw pitch, the backbone being the screw thread. The three donor atoms are already positioned in such a way that the coordination to a metal center only requires a relatively minor conformational change that can be best viewed as a compression of the screw pitch of the ligand backbone (vide infra). Two of the aryl groups, one of each of the phosphane units, are placed on each side of the imidazole plane indicating a possible



Scheme 4. Synthesis of the dicationic complexes **11** and **13**.

Table 3. ^{31}P and ^{13}C NMR chemical shifts of **8**, **10**, and the dicationic complexes **11** and **13**.

Complex	^{31}P δ [ppm] (J_{CP} [Hz])	^{13}C δ [ppm] (J_{CP} [Hz])
[PdI(PCP)]OAc (**8**)	–1.46 (d, J_{CP} = 12.0)	152.7 (t, J_{CP} = 12.0)
[Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**)	1.81 (d, J_{CP} = 11.7)	144.8 (t, J_{CP} = 11.7)
[PdI(3,5-Me-PCP)]OAc (**10**)	–2.11 (d, J_{CP} = 12.4)	152.5 (t, J_{CP} = 12.4)
[Pd($NCCH_3$)(3,5-Me-PCP)]$(PF_6)_2$ (**13**)	0.93 (d, J_{CP} = 11.6)	144.5 (t, J_{CP} = 11.6)

weak π-stacking interaction of the aryl groups and the imidazole ring (the average distance between the aromatic rings is 4.02 Å and the interplanar angles are 23.7 and 31.4°). The orientation of the ferrocenyl moieties can be described as pseudo-equatorial with respect to the imidazole plane.

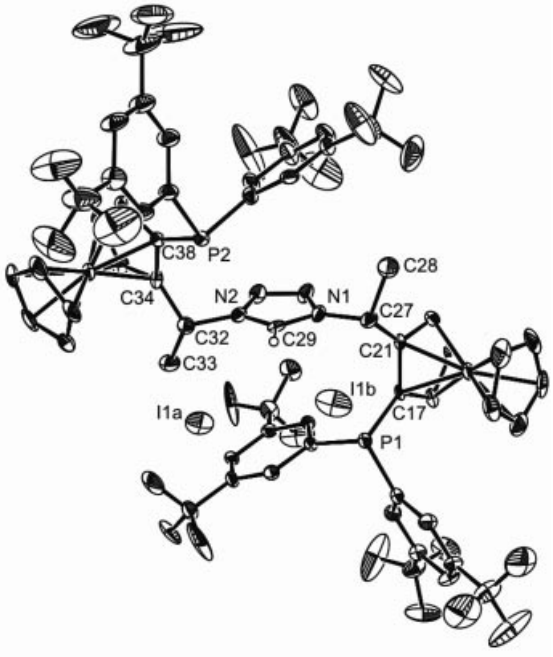


Figure 1. ORTEP representation of (3,5-CF_3-PCPH)I (**6**). Hydrogen atoms and the CF_3 disorder are omitted for clarity. Thermal ellipsoids are set to 30% probability.

The N(1)–C(29)–N(2) angle is with 109.3(5)° at the upper limit of the range found for derivatives of this kind (usually 107.6–109.7°[21–24]). It is also larger than the values measured in the complexes [PdCl(PCP)]PF_6 [106.2(7)°], [Pd($NCCH_3$)(PCP)]$(PF_6)_2$ [106.2(7)]°, [PdI(3,5-CF_3-PCP)]-PF_6 [108.4(10)°], and [RuClI(PCP)] [103.7(19), 104(2)°].

Although it was not possible to isolate the complex [PdI(3,5-CF_3-PCP)]PF_6 (**14**) on a preparative scale, we obtained crystals suitable for X-ray analysis from a chloroform solution of the mixture obtained from the activation of [Pd(OAc)(3,5-CF_3-PCP)]I (**9**) with Et_3OPF_6. The structure is represented in Figure 2 and selected bond lengths and angles are listed in Table 4.

The geometry around the Pd atom is almost square-planar with a slight tetrahedral distortion, as indicated for instance by the C(29)–Pd(1)–I(1) angle of 165.7(4)°. The Pd(1)–C(29) bond of 2.040(12) Å is longer than the reported Pd^{II}–carbene distances with iodide *trans* to a carbene C atom [1.984(4),[25] 1.990(3),[26] 1.990(9),[27] 2.004(3),[27] 1.991(5) Å,[28] 1.994(5),[28] 1.962(8) Å[19] are examples of previously reported distances]. The P(1)–Pd(1)–C(29) and P(2)–Pd(1)–C(29) bite angles are 83.0(4) and 86.3(4)°, which is less than the ideal value of 90°. Contrary to what is found for many (carbene)Pd^{II} complexes, the imidazole plane is not orthogonal to the coordination plane, as illustrated by the torsion angle P(2)–Pd(1)–C(29)–N(2) of –68.2(12)° and the angle between the least-squares planes

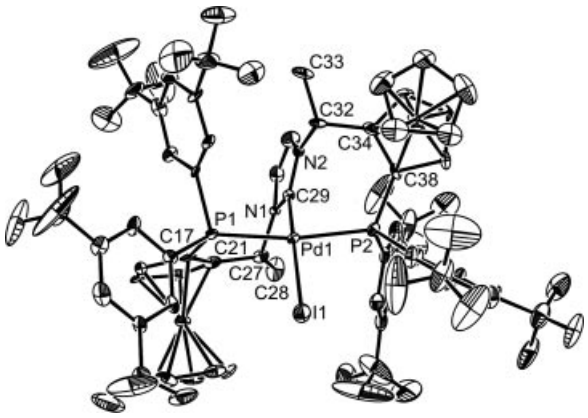


Figure 2. ORTEP representation of the cation in [PdI(3,5-CF_3-PCP)]PF_6 (**14**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 30% probability.

containing C(29), N(1), C(30), C(31), N(2) and Pd(1), I(1), P(1), P(2), C(29), respectively, which is 70.8°. This deviation from the perpendicular situation of the two planes is inherently due to the helical conformation of the ligand backbone. It has also been found in the previously reported structure of the complex [PdCl(PCP)]PF_6 (**15**), with the corresponding torsion angle of –75.6(7)° and the angle between the coordination plane and the imidazole plane of 72.9°. As opposed to the case of [PdCl(PCP)]PF_6 (**15**), the solid-state structure of **14** is almost, but not perfectly C_2-symmetric. Therefore, the aryl groups on each side of the ligand have very similar orientations. One aryl group at each phosphorus atom is lying roughly in the coordination plane defined by Pd(1), P(1), P(2) and C(29) pushing the iodo ligand out of this plane by 0.7468 Å. The other two aryl groups assume a pseudo-axial orientation.

As was the case for the precursor **6**, the ligand backbone of **14** displays helical chirality with (*P*) configuration. From a topological point of view, the essential difference between the two compounds is the compression of the screw pitch on going from **6** to **14**. In fact, the distance between the two P atoms decreases from 7.353 Å to 4.601 Å, as a consequence of a conformational change. There are only two pairs of equivalent single bonds potentially susceptible to significant conformational changes, i.e., the linkages joining the stereogenic centers to the respective Cp and N atom. An inspection of the torsion angles provided in Table 4 reveals that a counterclockwise rotation around the two N–C bonds by ca. 35 and 47°, respectively, mainly accounts for the observed change of conformation. Indeed, rotation around the crucial pair of single C–C bonds occurs in a clockwise manner, but only to an extent of ca. 19 and 3°, respectively, in going from **6** to **14**.

It was also possible to obtain X-ray quality crystals of the moisture-sensitive complex [Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**) by slow diffusion of diethyl ether into an acetonitrile solution at –20 °C. The structure is represented in Figure 3 and selected bond lengths and angles are collected in Table 4. This complex shows in the solid state an almost square-planar geometry. The overall structure is approxi-

Table 4. Selected bond lengths [Å] angles [°], and torsion angles [°] of the ligand precursor (3,5-CF_3-PCPH)I (**6**) and the complexes [PdI(3,5-CF_3-PCP)]PF_6 (**14**) and [Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**).

(3,5-CF_3-PCPH)I (**6**)			
C(29)–N(1)	1.336(8)	C(29)–N(1)–C(27)	125.1(5)
C(29)–N(2)	1.325(7)	C(29)–N(1)–C(30)	107.4(5)
N(1)–C(30)	1.394(8)	C(30)–N(1)–C(27)	127.5(5)
N(2)–C(31)	1.391(7)	C(29)–N(2)–C(32)	125.4(5)
C(30)–C(31)	1.330(9)	C(29)–N(2)–C(31)	108.2(5)
N(1)–C(27)	1.481(8)	C(31)–N(2)–C(32)	126.3(5)
N(2)–C(32)	1.486(8)		
C(29)–N(1)–C(27)–C(21)	133.9(6)	C(29)–N(2)–C(32)–C(34)	120.7(6)
C(17)–C(21)–C(27)–N(1)	–78.7(7)	N(2)–C(32)–C(34)–C(38)	–69.9(7)
C(17)–C(21)–C(27)–C(28)	161.2(6)	C(33)–C(32)–C(34)–C(38)	167.8(6)
[PdI(3,5-CF_3-PCP)]PF_6 (**14**)			
Pd(1)–C(29)	2.040(12)	Pd(1)–P(2)	2.299(4)
Pd(1)–P(1)	2.324(4)	Pd(1)–I(1)	2.6142(15)
P(1)–Pd(1)–C(29)	83.0(4)	P(2)–Pd(1)–C(29)	86.3(4)
I(1)–Pd(1)–C(29)	165.7(4)	P(1)–Pd(1)–P(2)	168.76(13)
I(1)–Pd(1)–P(1)	98.62(10)	I(1)–Pd(1)–P(2)	92.59(10)
P(1)–Pd(1)–C(29)–N(1)	–72.8(11)	P(1)–Pd(1)–C(29)–N(2)	108.2(13)
I(1)–Pd(1)–C(29)–N(1)	25(2)	I(1)–Pd(1)–C(29)–N(2)	–154.3(9)
P(2)–Pd(1)–C(29)–N(1)	110.9(11)	P(2)–Pd(1)–C(29)–N(2)	–68.2(12)
C(29)–N(1)–C(27)–C(21)	87.1(16)	C(29)–N(2)–C(32)–C(34)	85.7(15)
C(17)–C(21)–C(27)–N(1)	-60.0(17)	N(2)–C(32)–C(34)–C(38)	–67.2(18)
C(17)–C(21)–C(27)–C(28)	173.2(14)	C(33)–C(32)–C(34)–C(38)	172.0(14)
[Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**)			
Pd(1)–C(25)	1.993(9)	Pd(1)–P(2)	2.334(3)
Pd(1)–P(1)	2.351(3)	Pd(1)–N(3)	2.037(8)
N(3)–C(52)	1.126(10)		
P(1)–Pd(1)–C(25)	87.3(2)	P(2)–Pd(1)–C(25)	83.7(2)
N(3)–Pd(1)–C(25)	177.9(4)	P(1)–Pd(1)–P(2)	170.56(8)
N(3)–Pd(1)–P(1)	92.7(2)	N(3)–Pd(1)–P(2)	96.5(2)
P(1)–Pd(1)–C(25)–N(1)	–71.7(7)	P(1)–Pd(1)–C(25)–N(2)	107.0(7)
N(3)–Pd(1)–C(25)–N(1)	16(11)	N(3)–Pd(1)–C(25)–N(2)	–165(10)
P(2)–Pd(1)–C(25)–N(1)	111.0(7)	P(2)–Pd(1)–C(25)–N(2)	–70.3(7)
C(25)–N(1)–C(23)–C(14)	84.8(8)	C(25)–N(2)–C(28)–C(30)	86.1(9)
C(13)–C(14)–C(23)–N(1)	–71.1(9)	N(2)–C(28)–C(30)–C(31)	–63.8(9)
C(13)–C(14)–C(23)–C(24)	165.9(7)	C(29)–C(28)–C(30)–C(31)	170.7(7)

mately C_2-symmetric with one pair of phenyl rings located very close to the coordination plane and the second pair, together with the ferrocenyl units, in a pseudo-axial position. The C(25)–Pd(1)–N(3) angle of 177.9(4)° is much closer to the ideal value of 180° than the corresponding angles of the previously discussed complexes [PdI(3,5-CF_3-PCP)]PF_6 (**14**), with 165.7(4)°, and [PdCl(PCP)]PF_6 (**15**), containing the unsubstituted PCP ligand, with 164.3(3)°.[19] The Pd(1)–C(25) bond length for **11** is 1.993(9) Å which is longer than that observed in [PdCl(PCP)]PF_6 (**15**), with a value of 1.962(8) Å. Lee recently reported crystal structures of a cationic $[PdCl(PCP)]^+$ complex, as well as of the corresponding dicationic counterpart $[Pd(NCCH_3)(PCP)]^{2+}$, containing the tridentate NHC ligand PCP = PPh_2–$(CH_2)_2$–NHC–$(CH_2)_2$–PPh_2, i.e., compounds structurally related to ours.[29] However, in contrast to our results, Lee found that the Pd–C distance is longer in the chloro complex than in the dicationic acetonitrile derivative [1.983(7) vs. 1.961(4) Å]. The bite angles P(1)–Pd(1)–C(25) of 87.3(2)° and P(2)–Pd(1)–C(25) of 83.7(2)° are slightly larger than the corresponding values for [PdCl(PCP)]PF_6 (**15**) [86.6(3)

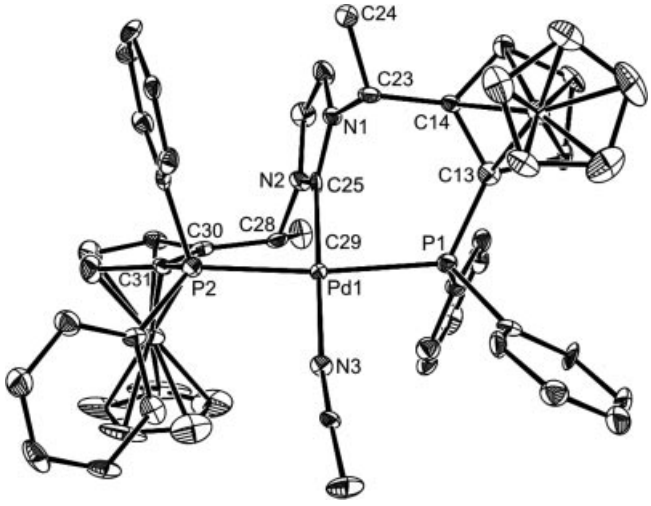
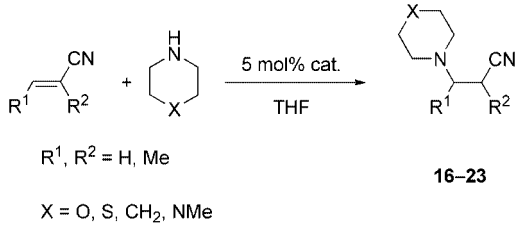


Figure 3. ORTEP representation of the dication in [Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 30% probability.

and 82.2(3)°]. The imidazole plane is again tilted away from the orientation perpendicular to the coordination plane. The torsion angle P(1)–Pd(1)–C(25)–N(1) has a value of –71.7(7)° and the angle between the least-squares planes containing C(25), N(1), C(26), C(27), N(2) and Pd(1), P(1), P(2), N(3), C(25), respectively, is 70.9°. The N(3)–C(52) bond length in the acetonitrile ligand is 1.126(10) Å which lies within the range of N–C distances found for palladium complexes containing phosphanes (1.114–1.144 Å),[30–34] or pincer-type carbene ligands (1.124–1.135 Å)[35–38] *trans* to the acetonitrile.

Catalysis

The acetonitrile ligand in the complexes $[Pd(NCCH_3)(PCP)](PF_6)_2$ (**11**) and $[Pd(NCCH_3)(3,5\text{-Me-PCP})](PF_6)_2$ (**13**) can be readily replaced by a substrate containing a functional group. This allows an activation of such substrates with the complex acting as a Lewis acid. Encouraged by the results achieved in our group[17,18] with $[Ni(PPP)(THF)](ClO_4)_2$ (PPP = Pigiphos, Scheme 1) as a Lewis acidic catalyst, we also tested our complexes in the asymmetric hydroamination of cyano olefins (Scheme 5).



Scheme 5. Hydroamination of cyano olefines.

In most experiments we used 5 mol-% of catalyst and the typical reaction time was 24 h at room temperature. The amines tested for this reaction were morpholine, thiomorpholine, piperidine, *N*-methylpiperazine, and aniline affording always the isolated product of the *anti*-Markovnikoff addition. The first experiments were carried out with the complex $[Pd(NCCH_3)(PCP)](PF_6)_2$ (**11**) using methyl methacrylate as the activated olefin; however, no activity was found. The test runs with crotonitrile as the amine acceptor afforded good to excellent yields (76–98%) but low enantioselectivities (up to 6% *ee*) in the case of aliphatic amines, whereas aniline showed no activity at all. We reasoned that aniline is poisoning the catalyst by coordination to the active site, but we never succeeded in isolating an aniline complex. The first promising results could be obtained with methacrylonitrile, having the methyl group in the α-position with respect to the electron-withdrawing group. The results involving methacrylonitrile as the substrate are summarized in Table 5. While aniline still showed no activity, the products derived from the aliphatic olefins were isolated in good to excellent yields, but the enantioselectivities were still low (up to 36% *ee* for *N*-methylpiperazine). No improvement was found by using acetone (no activity), or 1,2-dichloroethane as solvents. In this latter solvent, thiomorpholine could be added to methacrylonitrile affording 78% yield and 27% *ee*. Lowering of the reaction temperature from room temperature to –20 °C resulted, as expected, in lower isolated yields after a reaction time of 24 h (Table 5, Entries 5–8). The enantioselectivity could be somewhat improved for morpholine (38% *ee*) and thiomorpholine (44% *ee*). Surprisingly, for piperidine (23% *ee*) and *N*-methylpiperazine (33% *ee*) the enantioselectivity was reproducibly lower at –20 °C than at room temperature. Lowering of the temperature to –80 °C while using longer reaction times (3 d) in order to reach complete conversion, resulted in an improvement of the selectivity (except for piperidine) up to 63% *ee* (Table 5, Entries 9–12).

In view of a possible improvement of the enantioselectivity, the ligands bearing 3,5-disubstituted phenyl rings were tested. As mentioned earlier, the activation of the complex [Pd(OAc)(3,5-CF_3-PCP)]I (**9**) with Et_3OPF_6 re-

Table 5. Asymmetric addition of aliphatic amines to methacrylonitrile (see Scheme 5).

Entry	X	Catalyst [Ar]	*T* [°C]	*t*	Yield [%]	*ee* [%]
1	O	**11** [Ph]	20	24 h	96	32
2	S	**11** [Ph]	20	24 h	99	33
3	CH_2	**11** [Ph]	20	24 h	60	26
4	NMe	**11** [Ph]	20	24 h	84	36
5	O	**11** [Ph]	–20	24 h	82	38
6	S	**11** [Ph]	–20	24 h	83	44
7	CH_2	**11** [Ph]	–20	24 h	67	23
8	NMe	**11** [Ph]	–20	24 h	73	33
9	O	**11** [Ph]	–80	3 d	94	47
10	S	**11** [Ph]	–80	3 d	91	63
11	CH_2	**11** [Ph]	–80	3 d	94	22
12	NMe	**11** [Ph]	–80	3 d	98	46
13	O	**13** [3,5-$(CH_3)_2C_6H_3$]	20	24 h	99	54
14	S	**13** [3,5-$(CH_3)_2C_6H_3$]	20	24 h	96	61
15	CH_2	**13** [3,5-$(CH_3)_2C_6H_3$]	20	24 h	99	54
16	NMe	**13** [3,5-$(CH_3)_2C_6H_3$]	20	24 h	99	51
17	O	**13** [3,5-$(CH_3)_2C_6H_3$]	–80	3 d	91	71
18	S	**13** [3,5-$(CH_3)_2C_6H_3$]	–80	3 d	83	75
19	CH_2	**13** [3,5-$(CH_3)_2C_6H_3$]	–80	3 d	93	56
20	NMe	**13** [3,5-$(CH_3)_2C_6H_3$]	–80	3 d	92	73

sulted in a mixture from which the active species could not be identified. Using this mixture as the catalyst did not result in any activity even after heating the reaction mixture at 60 °C. Therefore, the less electron-deficient complex $[Pd(NCCH_3)(3,5\text{-Me-PCP})](PF_6)_2$ (**13**) was tested for the methacrylonitrile system. The activity at room temperature (Table 5, Entries 13–16) as well as at –80 °C (Table 5, Entries 17–20) was found to be in the same range as when using the unsubstituted ligand. The enantioselectivities, however, were improved up to 61% *ee* (thiomorpholine) at room temperature and finally up to 75% *ee* (thiomorpholine) at –80 °C. Interestingly, the lowering of the reaction temperature again had no significant influence on the selectivity for piperidine. This indicates that in this system the additional heteroatom (O, S, NMe) has an influence on the stereodifferentiating step during the catalysis.

Conclusions

The three-step synthesis of the ligand precursor [PCPH]-I (**1**) was extended to the synthesis of the electronically and sterically modified ligand precursors (3,5-CF_3-PCPH)I (**6**) and (3,5-Me-PCPH)I (**7**), bearing substituents at the 3- and 5-positions of the aryl groups. The reaction of the imidazolium salts **1**, **6**, and **7** with $[Pd(OAc)_2]_3$ in THF is the most efficient route to Pd^{II} complexes of the corresponding carbene ligands affording [PdI(PCP)]OAc (**8**), [Pd(OAc)(3,5-CF_3-PCP)]I (**9**), and [PdI(3,5-Me-PCP)]OAc (**10**) in excellent yields. These complexes displayed a different behavior concerning the exchange of the anions acetate and iodide as addressed by NMR studies. Reaction of these complexes with Et_3OPF_6 in acetonitrile afforded the dicationic species $[Pd(NCCH_3)(PCP)](PF_6)_2$ (**11**) and $[Pd(NCCH_3)(3,5\text{-Me-PCP})](PF_6)_2$ (**13**) in good to excellent yields. However, a similar activation of [Pd(OAc)(3,5-CF_3-PCP)]I (**9**) failed and resulted in a product mixture that was catalytically not active.

The solid-state structures of the ligand precursor (3,5-CF_3-PCPH)I (**6**) and its corresponding complex [PdI(3,5-CF_3-PCP)]PF_6 (**14**) show that their common molecule backbone assumes a helical conformation and that the most relevant conformational difference between the two compounds is accounted for mainly by a different torsion around the two N–C single bonds.

The dicationic complexes $[Pd(NCCH_3)(PCP)](PF_6)_2$ (**11**) and $[Pd(NCCH_3)(3,5\text{-Me-PCP})](PF_6)_2$ (**13**) are active catalysts for the addition of cyclic aliphatic secondary amines to cyano olefins. The additions to methacrylonitrile catalyzed by $[Pd(NCCH_3)(PCP)](PF_6)_2$ (**11**) showed moderate enantioselectivities which increased at low temperatures. The sterically modified complex $[Pd(NCCH_3)(3,5\text{-Me-PCP})](PF_6)_2$ (**13**) showed higher enantioselectivities at room temperature (up to 61% *ee*) as well as at –80 °C (up to 75% *ee*). Comparing Pd(PCP) and Ni(Pigiphos) catalysts having the same absolute configuration of the ferrocenyl units, it is interesting to note that products of opposite absolute configuration are obtained. Somewhat surprisingly and disappointingly, it appears that the C_2-symmetric PCP ligands described here do not offer any significant advantage when compared to the asymmetric ligand Pigiphos in the Ni/Pd-catalyzed addition of amines to methacrylonitrile.

Experimental Section

General Methods: (*R*)-*N*,*N*-Dimethyl-1-ferrocenylethylamine was generously provided by Solvias AG (Basel) and was recrystallized as tartrate salt according to the reported procedure.[39] The chlorophosphanes $[3,5\text{-}(CF_3)_2C_6H_3]_2PCl$ and $[3,5\text{-}(CH_3)_2C_6H_3]_2PCl$ were prepared as described.[40] Derivatives **2**–**5** have been prepared before in our laboratory.[41] All reactions were performed under an inert gas and air-sensitive substances were handled in a glove box. NMR: The routine ^1H, ^{13}C, and ^{31}P NMR spectra were measured in the given solvent with either a Bruker DPX250 or Bruker DPX300 instrument. The 2D experiments were generally carried out with a Bruker DPX500 instrument. EI-MS, FAB-MS, MALDI-MS: Measurements were performed by the MS service of the "Laboratorium für Organische Chemie der ETHZ". The signals are given as *m*/*z*. Elemental analyses were performed by the micro elemental analysis service of the "Laboratorium für Organische Chemie der ETHZ". Crystallography: X-ray structural measurements were carried out with a Bruker CCD diffractometer (Bruker SMART PLATFORM, with a CCD detector, graphite monochromator, and Mo-K_α radiation). The program SMART served for data collection. Integration was performed with SAINT. The structure solution (direct methods) and refinement on F^2 were accomplished with SHELXTL-97. Model plots were made with ORTEP32. For the structures of **6**, **14** (with exceptions), and **11** all non-hydrogen atoms were refined freely with anisotropic refinement parameters. For **6** a CH_2Cl_2 molecule was found to be disordered over two sites. The C–Cl bond lengths were restrained to standard values. Iodide and some of the CF_3 groups are disordered over two sites. The C–F distances were restrained by the use of a variable and the F···F distances were equalized with the SADI instruction. In the structure of **14** there are three $CHCl_3$ molecules present. The carbon atom in one of the $CHCl_3$ molecules is disordered over two positions. The C–Cl bond lengths were restrained to standard values. For the disordered CF_3 groups of C(6) and C(45) the same procedure was adopted as for **6**. Due to the low data-to-parameter ratio, the atoms C(1), C(10), C(62), C(29), and N(2) were refined anisotropically in combination with the ISOR instruction. In the structure of **11** one ethanol and one diethyl ether molecule are present. C(55) of the ether molecule and C(58) of ethanol is disordered over two positions. Hydrogen atoms were refined at calculated positions riding on their carrier atoms. Weights were optimized in the final refinement cycles. Crystallographic data are given in Table 6. CCDC-240665 (**6**), -240662 (**14**), and -240664 (**11**) contain 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.

1,3-Bis{(*R*)-1-[(*S*)-2-{[3,5-bis(trifluoromethyl)phenyl]phosphanyl}-ferrocenyl]ethyl}imidazolium Iodide (6): A suspension of **4** (1.51 g, 2.07 mmol) and imidazole (77.5 mg, 1.14 mmol, 0.55 equiv.) in a mixture of acetonitrile (14 mL) and water (3.5 mL) was heated at 60 °C for 24 h. After addition of benzene (9 mL), the organic phase was separated and concentrated in vacuo. The residue was dissolved together with NaI (683 mg, 4.55 mmol, 2 equiv.) in ethanol (15 mL) and stirred for 3 h. After evaporation of the solvent in vacuo, the crude product was filtered through silica (CH_2Cl_2, then

Table 6. Crystallographic data for (3,5-CF_3-PCPH)I (**6**), [PdI(3,5-CF_3-PCP)]PF_6 (**14**), and [Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**).

	(3,5-CF_3-PCPH)I (**6**)	[PdI(3,5-CF_3-PCP)]PF_6 (**14**)	[Pd($NCCH_3$)(PCP)]$(PF_6)_2$ (**11**)
Color, shape	yellow cube	red cube	yellow needle
Empirical formula	$C_{59}H_{39}F_{24}Fe_2N_2P_2$, I, CH_2Cl_2	$C_{59}H_{38}F_{24}Fe_2IN_2P_2Pd$, PF_6, 3($CHCl_3$)	$C_{53}H_{49}Fe_2N_3P_2Pd$, 2(PF_6), C_2H_6O, $C_4H_{10}O$
Formula mass	1615.37	2053.28	1401.99
Temperature [K]	200	200	150
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1$	$P2_1$	$P\bar{1}$
Unit cell dimensions [Å; °]	a = 8.3762(4); α = 90 b = 33.4516(16); β = 109.0080(10) c = 12.4853(6); γ = 90	a = 10.781(3); α = 90 b = 28.236(8); β = 114.11 c = 13.194(4); γ = 90	a = 10.645(9); α = 94.368(17) b = 11.133(9); β = 107.592(19) c = 13.707(11); γ = 109.542(18)
Volume [Å^3]	3307.6(3)	3665.9(17)	1431(2)
Z	2	2	1
Calcd. density [g cm^{-3}]	1.622	1.860	1.627
Absorption coeff. [mm^{-1}]	1.141	1.486	1.009
Crystal size [mm]	0.94 × 0.42 × 0.36	0.32 × 0.23 × 0.16	0.24 × 0.07 × 0.04
Reflns. collected, unique	18999, 10593	21112, 9648	9837, 7953
R_{int}	0.0352	0.1028	0.0287
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data, restraints, params.	10593, 29, 958	9648, 48, 1008	7953, 3, 766
Goodness of fit	1.094	1.021	1.000
R, R_w	0.0581, 0.1304	0.0811, 0.1655	0.0525, 0.0892
Abs. structure parameter	0.006(16)	0.06(4)	0.02(2)
Min./max. resd. [e·Å^{-3}]	1.108/–0.369	1.211/–0.941	1.028/–0.753

CH_2Cl_2 + 4% MeOH) and chromatographed (silica, hexane/ethyl acetate, 1:1 + 2% acetic acid). Yield: 793 mg (0.52 mmol, 50%), orange crystals. TLC (hexane/ethyl acetate, 1:1): R_f = 0.64. $C_{59}H_{39}F_{24}Fe_2IN_2P_2$ (1532.46): calcd. C 46.24, H 2.57, N 1.83; found C 45.95, H 2.83, N 1.97. MS-MALDI: m/z = 669 [Ar_2PFcEt^+]. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.21 (d, J_{CHMe} = 6.9 Hz, 6 H, CH*Me*), 3.91 (t, J_{CHCH} = 1.2 Hz, 2 H, Cp), 4.08 (s, 10 H, Cp′), 4.69 (t, J_{CHCH} = 2.6 Hz, 2 H, Cp), 4.79 (m, 2 H, Cp), 6.44 (dq, J_{CHMe} = 6.9 Hz, J_{PH} = 3.0 Hz, 2 H, C*H*Me), 6.50 (d, J_{CHCH} = 1.2 Hz, 2 H, HC=CH Im), 7.24 (s, 2 H, P*Ar*$_2$), 7.26 (s, 2 H, P*Ar*$_2$), 7.79 (s, 2 H, P*Ar*$_2$), 8.06 (s, 4 H, P*Ar*$_2$), 8.09 (s, 2 H, P*Ar*$_2$), 10.65 (s, 1 H, $^+$CH, Im) ppm. ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 20.6 (CH_3, CH*Me*), 55.1 (d, J_{CP} = 9.8 Hz, CH, *C*HMe), 70.4 (d, J_{CP} = 4.5 Hz, CH, Cp), 70.7 (CH, Cp′), 72.3 (d, J_{CP} = 4.7 Hz, CH, Cp), 72.5 (CH, Cp), 90.3 (d, J_{CP} = 29.7 Hz, C, Cp), 118.1 (CH, HC=CH Im), 122.5 (CH, P*Ar*$_2$), 123.0, (dq, J_{CP} = 7.8 Hz, J_{CF} = 273.2 Hz, C, CF_3), 124.2 (CH, P*Ar*$_2$), 131.1 (d, J_{CP} = 16.5 Hz, CH, P*Ar*$_2$), 131.3 (dq, J_{CP} = 4.2 Hz, C, *C*CF_3), 131.8 (dq, J_{CP} = 8.2 Hz, J_{CF} = 33.5 Hz, C, *C*CF_3), 134.3 ($^+$CH, Im), 135.1 (d, J_{CP} = 4.2 Hz, C, P*Ar*$_2$), (d, J_{CP} = 22.9 Hz, CH, P*Ar*$_2$), 138.8 (d, J_{CP} = 14.3 Hz, C, P*Ar*$_2$), 142.4 (d, J_{CP} = 17.2 Hz, C, P*Ar*$_2$) ppm. ^{31}P NMR (300 MHz, CD_2Cl_2): δ = –25.32 (*P*Ar$_2$) ppm.

1,3-Bis[(*R*)-1-{(*S*)-2-[(3,5-Dimethylphenyl)phosphanyl]ferrocenyl}-ethyl]imidazolium Iodide (7): A suspension of **5** (300 mg, 0.59 mmol) and imidazole (20.3 mg, 0.30 mmol, 0.51 equiv.) in a mixture of acetonitrile (8 mL) and water (4 mL) was heated at 60 °C for 32 h. After addition of benzene (5 mL), the organic phase was separated and concentrated in vacuo. The residue was dissolved together with NaI (193 mg, 1.29 mmol, 2 equiv.) in ethanol (10 mL) and stirred for 3 h. After evaporation of the solvent in vacuo, the crude product was filtered through silica (CH_2Cl_2, then CH_2Cl_2 + 4% MeOH) and chromatographed (silica, ethyl acetate, then ethyl acetate + 2% MeOH). Yield: 163.3 mg (0.15 mmol, 51%), orange crystals. $C_{59}H_{63}Fe_2IN_2P_2$ (1100.69): calcd. C 64.38, H 5.77, N 2.55; found C 64.45, H 5.87, N 2.41. MS-MALDI: m/z = 973 [3,5-Me-PCPH$^+$], 453 [Ar_2PFcEt^+]. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.58 (d, J_{CHMe} = 6.9 Hz, 6 H, CH*Me*), 2.37 (s, 6 H, Ar-*Me*), 2.42 (s, 6 H, Ar-*Me*), 4.10 (s, 10 H, Cp′), 4.14 (s, 2 H, Cp), 4.58 (t, J_{CHCH} = 2.4 Hz, 2 H, Cp), 4.89 (m, 2 H, Cp), 5.38 (q, J_{CHMe} = 6.9 Hz, 2 H, C*H*Me), 6.66 (s, 2 H, P*Ar*$_2$), 6.68 (s, 2 H, P*Ar*$_2$), 7.04 (s, 2 H, P*Ar*$_2$), 7.17 (s, 2 H, P*Ar*$_2$), 7.18 (s, J_{CHCH} = 1.5 Hz, 2 H, HC=CH Im), 7.26 (s, 2 H, P*Ar*$_2$), 7.29 (s, 2 H, P*Ar*$_2$), 8.08 (t, J_{CHCH} = 1.6 Hz, 1 H, $^+$CH, Im) ppm. ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 20.4 (CH_3, CH*Me*), 21.2 (CH, Ar*Me*), 21.4 (CH, Ar*Me*), 55.4 (d, J_{CP} = 9.8 Hz, CH, *C*HMe), 69.7 (CH, Cp), 70.3 (CH, Cp′), 71.0 (CH, Cp), 73.1 (CH, Cp), 75.8 (d, J_{CP} = 9.1 Hz, C, Cp), 90.6 (d, J_{CP} = 25.4 Hz, C, Cp), 119.4 (CH, HC=CH Im), 129.7 (d, J_{CP} = 17.8 Hz, CH, P*Ar*$_2$), 130.3 (CH, P*Ar*$_2$), 131.5 (CH, P*Ar*$_2$), 132.5 ($^+$CH, Im), 132.8 (d, J_{CP} = 20.8 Hz, CH, P*Ar*$_2$), 135.4 (C, P*Ar*$_2$), 137.9 (C, P*Ar*$_2$), 138.0 (C, P*Ar*$_2$), 138.9 (d, J_{CP} = 4.5 Hz, C, P*Ar*$_2$) ppm. ^{31}P NMR (300 MHz, CD_2Cl_2): δ = –28.36 (*P*Ar$_2$) ppm.

(SP-4)-(1,3-Bis{(*R*)-1-[(*S*)-2-{[3,5-bis(trifluoromethyl)phenyl]phosphanyl-κ*P*}ferrocenyl]ethyl}imidazol-2-ylidene)(iodo)palladium(II) Acetate, [Pd(OAc)(3,5-CF_3-PCP)]I (9): [$Pd(OAc)_2$]$_3$ (44 mg, 0.065 mmol) and **6** (300 mg, 0.196 mmol) were dissolved in THF (6 mL) and heated at 60 °C for 12 h. After evaporation of the solvent in vacuo, the residue was dissolved in CH_2Cl_2 and the product precipitated with hexane, filtered off, washed three times with hexane and dried in vacuo. Yield: 313.6 mg (0.272 mmol, 91%), deep red crystals. ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 1.16 (d, 6 H, J_{CHMe} = 7.0 Hz, CH*Me*), 2.85 (br., 3 H, OAc), 4.08 (m, 2 H, Cp), 4.35 (s, 10 H, Cp′), 4.66 (t, J_{CHCH} = 2.5 Hz, 2 H, Cp), 4.98 (m, 2 H, Cp), 6.30 (q, J_{CHMe} = 7.0 Hz, 2 H, C*H*Me), 7.53 (s, 2 H, HC=CH Im), 7.83 (t, J_{CHCH} = 4.5 Hz, 4 H, P*Ar*$_2$), 8.19 (br., 2 H, P*Ar*$_2$), 8.35 (br., 2 H, P*Ar*$_2$), 9.41 (t, J_{CHCH} = 5.3 Hz, 4 H, P*Ar*$_2$) ppm. ^{13}C NMR (250 MHz, [D$_6$]acetone): δ = 14.0 (CH_3, CH*Me*), 52.8 (CH, *C*HMe), 53.7, 54.14 (CH_3, O*Ac*), 70.0 (CH, Cp), 71.0 (CH, Cp), 71.3 (CH, Cp), 71.7 (CH, Cp′), 73.7 (C, Cp), 93.1 (C, Cp), 121.3 (CH, HC=CH Im), 120.9, 124.3, 125.2, 125.6, 130.3, 130.7, 131.3, 131.9, 136.2, 136.9 (CH, C, P*Ar*$_2$), 146.8 (br., CPd, Im) ppm. ^{31}P NMR (250 MHz, [D$_6$]acetone): δ = 1.79 (*P*Ar$_2$) ppm.

(SP-4)-(1,3-Bis{(*R*)-1-{(*S*)-2-[(3,5-dimethylphenyl)phosphanyl-κ*P*]-ferrocenyl}ethyl}imidazol-2-ylidene)(iodo)palladium(II) Acetate, [PdI(3,5-Me-PCP)]OAc (10): [$Pd(OAc)_2$]$_3$ (165.4 mg, 0.25 mmol)

and **7** (811 mg, 0.74 mmol) were dissolved in THF (20 mL) and heated at 60 °C for 12 h. After evaporation of the solvent in vacuo, the residue was dissolved in CH_2Cl_2 and the product precipitated with hexane, filtered off, washed three times with hexane, and dried in vacuo. Yield: 883.6 mg (0.70 mmol; 95%), brown solid. $C_{61}H_{65}Fe_2IN_2O_2P_2Pd$ (1265.14): calcd. C 53.16, H 4.69; found: C 52.00, H 5.30. MS-MALDI: *m*/*z* = 1205 [PdI(3,5-Me-PCP)$^+$], 1077 [Pd(3,5-Me-PCP)$^+$]. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 1.27 (d, J_{CHMe} = 7.0 Hz, 6 H, CH*Me*), 2.04 (s, 3 H, OAc), 2.30 (s, 6 H, Ar*Me*), 2.40 (s, 6 H, Ar*Me*), 3.65 (m, J_{CHCH} = 1.3 Hz, 2 H, Cp), 4.28 (s, 10 H, Cp′), 4.51 (t, J_{CHCH} = 2.6 Hz, 2 H, Cp), 4.87 (m, 2 H, Cp), 5.56 (q, J_{CHCH} = 7.2 Hz, 2 H, C*H*Me), 6.54 (t, J_{CHCH} = 5.5 Hz, 4 H, P*Ar*$_2$), 6.90 (s, 2 H, HC=CH Im), 7.16 (br., 2 H, P*Ar*$_2$), 7.22 (br., 2 H, P*Ar*$_2$), 7.50 (t, J_{CHCH} = 5.8 Hz, 4 H, P*Ar*$_2$) ppm. ^{13}C NMR (250 MHz, CD_2Cl_2): δ = 15.6 (CH_3, CH*Me*), 21.2 (CH, Ar*Me*), 53.9 (CH, *C*HMe), 70.5 (t, J_{CP} = 3.5 Hz, CH, Cp), 71.8 (t, J_{CP} = 2.8 Hz, CH, Cp), 71.2 (CH, Cp′), 71.7 (t, C, Cp), 76.0 (t, J_{CP} = 2.8 Hz, CH, Cp), 90.2 (t, J_{CP} = 6.6 Hz, C, Cp), 118.7 (CH, HC=CH Im), 128.2 (t, J_{CP} = 27.9 Hz, C, P*Ar*$_2$), 128.4 (t, J_{CP} = 6.0 Hz, CH, P*Ar*$_2$), 132.5 (CH, P*Ar*$_2$), 133.0 (CH, P*Ar*$_2$), 133.6 (t, J_{CP} = 24.7 Hz, C, P*Ar*$_2$), 134.1 (t, J_{CP} = 5.5 Hz, CH, P*Ar*$_2$), 136.8 (t, J_{CP} = 5.9 Hz, C–Me, P*Ar*$_2$), 138.8 (t, J_{CP} = 5.3 Hz, CMe, P*Ar*$_2$), 152.7 (t, J_{CP} = 12.4 Hz, CPd, Im) ppm. ^{31}P NMR (250 MHz, CD_2Cl_2): δ = –2.11 (P*Ar*$_2$) ppm.

(SP-4)-(Acetonitrilo)(1,3-bis{(*R*)-1-[(*S*)-2-(Diphenylphosphanyl-κ*P*)-ferrocenyl]ethyl}imidazol-2-ylidene)palladium(II) Bis(hexafluorophosphate), [PdPCP(NCCH$_3$)](PF$_6$)$_2$ (11): A solution of **8** (253 mg, 0.22 mmol) and Et_3OPF_6 (136 mg, 0.55 mmol, 2.5 equiv.) in acetonitrile (10 mL) was stirred at room temperature for 10 h. The mixture was concentrated to an amount of 2 mL and the product was precipitated with diethyl ether, filtered off, washed two times with diethyl ether and dried in vacuo. Yield: 225 mg (0.17 mmol, 79%), brown solid. ^{1}H NMR (300 MHz, $NCCD_3$): δ = 1.27 (d, J_{CHMe} = 7.2 Hz, 6 H, CH*Me*), 2.25 (br., 3 H, $NCCH_3$), 3.93 (m, J_{CHCH} = 1.2 Hz, 2 H, Cp), 4.25 (s, 10 H, Cp′), 4.65 (t, J_{CHCH} = 2.6 Hz, 2 H, Cp), 4.89 (d, J_{CHCH} = 1.2 Hz, 2 H, Cp), 5.47 (q, J_{CHCH} = 6.9 Hz, 2 H, C*H*Me), 6.90 (s, 2 H, HC=CH Im), 7.10 (q, J_{CHCH} = 6.9 Hz, 4 H, P*Ph*$_2$), 7.53 (t, J_{CHCH} = 7.5 Hz, 4 H, P*Ph*$_2$), 7.61–7.84 (m, 12 H, P*Ph*$_2$) ppm. ^{13}C NMR (300 MHz, $NCCD_3$): δ = 0.4 (NC*C*H$_3$), 15.1 (CH_3, CH*Me*), 55.0 (CH, *C*HMe), 68.6 (t, J_{CP} = 29.4 Hz, C, Cp), 70.9 (t, J_{CP} = 3.4 Hz, CH, Cp), 71.5 (t, J_{CP} = 4.2 Hz, CH, Cp), 71.6 (CH, Cp′), 75.1 (t, J_{CP} = 3.1 Hz, CH, Cp), 90.6 (t, J_{CP} = 6.9 Hz, C, Cp), 117.7 (N*C*CH$_3$), 120.1 (CH, HC=CH Im), 126.9 (t, J_{CP} = 27.7 Hz, CH, P*Ph*$_2$), 128.9 (t, J_{CP} = 5.6 Hz, CH, P*Ph*$_2$), 129.7 (t, J_{CP} = 5.3 Hz, CH, P*Ph*$_2$), 130.8 (t, J_{CP} = 27.2 Hz, CH, P*Ph*$_2$), 131.3 (t, J_{CP} = 6.3 Hz, CH, P*Ph*$_2$), 131.8 (CH, P*Ph*$_2$), 132.5 (CH, P*Ph*$_2$), 134.2 (t, J_{CP} = 6.5 Hz, CH, P*Ph*$_2$), 144.5 (t, J_{CP} = 11.6 Hz, CPd, Im) ppm. ^{31}P NMR (300 MHz, $NCCD_3$): δ = –144.45 (sept, J_{PF} = 706.8, PF_6), 1.57 (*P*Ph$_2$) ppm.

(SP-4)-(Acetonitrilo)(1,3-bis[(*R*)-1-{(*S*)-2-[(3,5-dimethylphenyl)phosphanyl-κ*P*]ferrocenyl}ethyl]imidazol-2-ylidene)palladium(II) Bis(hexafluorophosphate), [Pd(3,5-Me-PCP)(NCCH$_3$)](PF$_6$)$_2$ (13): A solution of **10** (81.9 mg, 0.065 mmol) and Et_3OPF_6 (40.3 mg, 0.16 mmol, 2.5 equiv.) in acetonitrile (4 mL) was stirred at room temperature for 10 h. The mixture was concentrated to an amount of 2 mL and the product was precipitated with diethyl ether, filtered off, washed two times with diethyl ether and dried in vacuo. Yield: 86.2 mg (0.06 mmol, 94%), brown solid. ^{1}H NMR (300 MHz, $NCCD_3$): δ = 1.26 (d, J_{CHMe} = 7.2 Hz, 6 H, CH*Me*), 1.99 (s, 3 H, $NCCH_3$), 2.31 (s, 6 H, Ar*Me*), 2.45 (s, 6 H, Ar*Me*), 3.92 (m, J_{CHCH} = 1.8 Hz, 2 H, Cp), 4.23 (s, 10 H, Cp′), 4.63 (t, J_{CHCH} = 2.4 Hz, 2 H, Cp), 4.86 (m, 2 H, Cp), 5.39 (q, J_{CHCH} = 6.9 Hz, 2 H, C*H*Me), 6.62 (t, J_{CHCH} = 6.3 Hz, 4 H, P*Ar*$_2$), 6.93 (s, 2 H, HC=CH Im), 7.27 (br., J_{CHCH} = 7.5 Hz, 2 H, P*Ar*$_2$), 7.40 (m, 6 H, P*Ar*$_2$) ppm. ^{13}C NMR (300 MHz, $NCCD_3$): δ = 0.3 (NC*C*H$_3$), 14.7 (CH_3, CH*Me*), 20.4 (CH, Ar*Me*), 20.5 (CH, Ar*Me*), 54.8 (CH, *C*HMe), 69.3 (t, J_{CP} = 29.1 Hz, C, Cp), 70.6 (t, J_{CP} = 3.0 Hz, CH, Cp), 71.3 (m, CH, Cp), 71.4 (CH, Cp′), 75.3 (t, J_{CP} = 2.8 Hz, CH, Cp), 90.4 (t, J_{CP} = 6.8 Hz, C, Cp), 118.1 (N*C*CH$_3$), 119.9 (CH, HC=CH Im), 126.7 (t, J_{CP} = 27.2 Hz, C, P*Ar*$_2$), 128.6 (t, J_{CP} = 6.2 Hz, CH, P*Ar*$_2$), 130.8 (t, J_{CP} = 27.0 Hz, C, P*Ar*$_2$), 131.8 (t, J_{CP} = 6.4 Hz, CH, P*Ar*$_2$), 133.2 (CH, P*Ar*$_2$), 134.0 (CH, P*Ar*$_2$), 138.7 (t, J_{CP} = 5.8 Hz, CMe, P*Ar*$_2$), 139.5 (t, J_{CP} = 5.5 Hz, CMe, P*Ar*$_2$), 144.5 (t, J_{CP} = 11.6 Hz, CPd, Im) ppm. ^{31}P NMR (300 MHz, $NCCD_3$): δ = –144.47 (sept, J_{PF} = 706.6, PF_6), 1.01 (*P*Ph$_2$) ppm.

General Procedure for the Pd-Catalyzed Hydroamination of Cyano Olefins: A solution of palladium complex (0.025 mmol; 5 mol-%) and olefin (1 mmol; 2 equiv.) in THF (3 mL) was stirred at room temperature for 5 min. The amine (0.5 mmol) was then added and the reaction mixture was stirred at the required temperature for the corresponding time. The reaction was stopped by the addition of hexane. Filtration and evaporation of the solvent yielded the hydroamination product. If necessary, the product was purified by chromatography (silica, hexane/ethyl acetate, 1:1 + 5% NEt_3). Enantioselectivities were determined by GC or HPLC analysis.

3-(Morpholino)butanenitrile (16): TLC (hexane/ethyl acetate, 1:1 + 5% NEt_3): R_f = 0.47. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (d, J = 6.8 Hz, 3 H, CHC*H*$_3$), 2.38 (dd, J = 7.3 Hz, J = 16.8 Hz, 1 H, C*H*H′CN), 2.52 (t, J = 4.8 Hz, 4 H, C*H*$_2$N), 2.52 (dd, J = 6.5 Hz, J = 16.8 Hz, 1 H, CH*H*′CN), 2.94 (m, J = 6.0 Hz, 1 H, NC*H*CH$_3$), 3.70 (t, J = 4.6 Hz, 4 H, C*H*$_2$O) ppm. ^{13}C(DEPT) NMR (250 MHz, $CDCl_3$): δ = 15.2 (CH*C*H$_3$), 21.3 (*C*HH′CN), 48.8 (*C*H$_2$N), 56.3 (N*C*HCH$_3$), 67.1 (*C*H$_2$O) ppm. GC (β-dex, 90 °C iso): t_r = 267.50, 267.64 min.

3-(Thiomorpholino)butanenitrile (17): TLC (hexane/ethyl acetate, 1:1 + 5% NEt_3): R_f = 0.60. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14 (d, J = 6.8 Hz, 3 H, CHC*H*$_3$), 2.32 (dd, J = 7.3 Hz, J = 16.8 Hz, 1 H, C*H*H′CN), 2.48 (dd, J = 6.5 Hz, J = 16.8 Hz, 1 H, CH*H*′CN), 2.63 (m, 4 H, C*H*$_2$N), 2.77 (m, 4 H, C*H*$_2$S), 2.99 (m, J = 7.0 Hz, 1 H, NC*H*CH$_3$) ppm. ^{13}C(DEPT) NMR (250 MHz, $CDCl_3$): δ = 15.1 (CH*C*H$_3$), 21.1 (*C*HH′CN), 28.3 (*C*H$_2$N), 50.8 (*C*H$_2$S), 57.7 (N*C*HCH$_3$) ppm. HPLC (OJ, hexane/*i*PrOH, 95:5, 0.5 mL/ min, 25 °C, DAD 210 nm): t_r = 38.12, 41.18 min.

3-(Piperidin-1-yl)butanenitrile (18): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.19 (d, J = 6.8 Hz, 3 H, CHC*H*$_3$), 1.42 (m, 2 H, CH$_2$), 1.56 (m, J = 5.4 Hz, 4 H, CH$_2$), 2.32 (dd, J = 8.0 Hz, J = 16.8 Hz, 1 H, C*H*H′CN), 2.47 (m, 4 H, C*H*$_2$N), 2.51 (dd, J = 5.5 Hz, J = 16.8 Hz, 1 H, CH*H*′CN), 2.99 (m, 1 H, NC*H*CH$_3$) ppm. ^{13}C(DEPT) NMR (250 MHz, $CDCl_3$): δ = 15.5 (CH*C*H$_3$), 20.6 (*C*HH′CN), 24.6 (CH$_2$), 26.2 [(CH$_2$)$_2$], 49.4 (*C*H$_2$N), 56.8 (N*C*HCH$_3$) ppm. GC (β-dex, 80 °C iso): t_r = 324.7, 325.2 min.

3-(4-Methylpiperazin-1-yl)butanenitrile (19): ^{1}H NMR ($CDCl_3$): δ = 1.16 (d, J = 6.8 Hz, 3 H, CHC*H*$_3$), 2.24 (s, 3 H, NCH$_3$), 2.32 (dd, J = 7.5 Hz, J = 16.8 Hz, 1 H, C*H*H′CN), 2.40 (br. s, 4 H, C*H*$_2$N), 2.49 (dd, J = 5.5 Hz, J = 16.8 Hz, 1 H, CH*H*′CN), 2.52 (br. m, 4 H, C*H*$_2$NCH$_3$), 2.96 (m, 1 H, NC*H*CH$_3$) ppm. ^{13}C(DEPT) NMR ($CDCl_3$): δ = 15.4 (CH*C*H$_3$), 21.1 (*C*HH′CN), 45.9 (NCH$_3$), 48.1 (*C*H$_2$N), 55.2 (*C*H$_2$NCH$_3$), 56.8 (N*C*HCH$_3$) ppm. GC (β-dex, 90 °C iso): t_r = 352.4, 360.1 min.

2-Methyl-3-(morpholino)propionitrile (20): TLC (hexane/ethyl acetate, 1:1 + 5% NEt_3): R_f = 0.55. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 (d, J = 7.0 Hz, 3 H, CHC*H*$_3$), 2.37 (dd, J = 6.3 Hz, J = 12.5 Hz, 1 H, C*H*H′), 2.47 (t, J = 4.6 Hz, 4 H, C*H*$_2$N), 2.57 (dd, J = 8.3 Hz, J = 12.5 Hz, 1 H, CH*H*′), 2.75 (m, 1 H, C*H*CH$_3$), 3.67

(t, J = 4.6 Hz, 4 H, CH_2O) ppm. ^{13}C(DEPT) NMR (250 MHz, $CDCl_3$): δ = 15.9 (CHCH$_3$), 24.1 (CHCH$_3$), 53.6 (CH$_2$N), 61.3 (CHH′), 66.8 (CH$_2$O) ppm. GC (β-dex, 92 °C iso): t_r = 128.1 (R), 130.3 (S) min.

2-Methyl-3-(thiomorpholino)propionitrile (21): TLC (hexane/ethyl acetate, 1:1 + 5% NEt_3): R_f = 0.58. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26 (d, J = 7.0 Hz, 3 H, CHCH_3), 2.42 (dd, J = 6.3 Hz, J = 12.8 Hz, 1 H, CHH′), 2.59 (dd, J = 8.3 Hz, J = 12.8 Hz, 1 H, CHH′), 2.65 (m, 4 H, CH_2N), 2.75 (m, 1 H, CHCH$_3$, 4 H, CH_2S) ppm. ^{13}C(DEPT) NMR (250 MHz, $CDCl_3$): δ = 15.9 (CHCH$_3$), 24.5 (CHCH$_3$), 27.9 (CH$_2$N), 55.2 (CH$_2$S), 61.7 (CHH′) ppm. HPLC (OJ, hexane/*i*PrOH, 95:5, 0.5 mL/ min, 25 °C, DAD 230 nm): t_r = 25.52, 28.06 min.

2-Methyl-3-(piperidin-1-yl)propionitrile (22): TLC (hexane/ethyl acetate, 1:1 + 5% NEt_3): R_f = 0.8. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31 (d, J = 7.0 Hz, 3 H, CHCH_3), 1.43 (m, 2 H, CH_2), 1.58 (m, J = 5.3 Hz, 4 H, CH_2), 2.37 (dd, J = 6.5 Hz, J = 12.5 Hz, 1 H, CHH′), 2.44 (t, J = 5.5 Hz, 4 H, CH_2N), 2.59 (dd, J = 8.0 Hz, J = 12.5 Hz, 1 H, CHH′), 2.76 (m, 1 H, CHCH$_3$) ppm. ^{13}C(DEPT) NMR (250 MHz, $CDCl_3$): δ = 16.2 (CHCH$_3$), 24.2 (CH_2), 24.3 (CHCH$_3$), 25.9 [$(CH_2)_2$], 54.7 (CH$_2$N), 61.8 (CHH′) ppm. GC (α-dex, 50 °C iso): t_r = 566, 578 min.

2-Methyl-3-(4-methylpiperazin-1-yl)propionitrile (23): TLC (hexane/ethyl acetate, 1:1 + 5% NEt_3): R_f = 0.1. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (d, J = 7.0 Hz, 3 H, CHCH_3), 2.22 (s, 3 H, NCH_3), 2.36 (dd, J = 6.3 Hz, J = 2.5 Hz, 1 H, CHH′), 2.37 (s br, 4 H, CH_2N), 2.49 (s br, 4 H, CH_2NCH$_3$), 2.57 (dd, J = 8.5 Hz, J = 12.5 Hz, 1 H, CHH′), 2.72 (m, 1 H, CHCH$_3$) ppm. ^{13}C(DEPT) NMR (250 MHz, $CDCl_3$): δ = 16.0 (CHCH$_3$), 24.3 (CHCH$_3$), 45.9 (NCH_3), 53.2 (CH$_2$N), 54.9 (CH$_2$NCH$_3$), 60.9 (CHH′) ppm. GC (α-dex, 80 °C iso): t_r = 223, 228 min.

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